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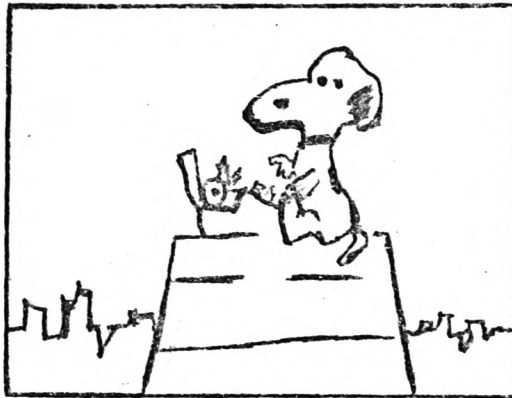
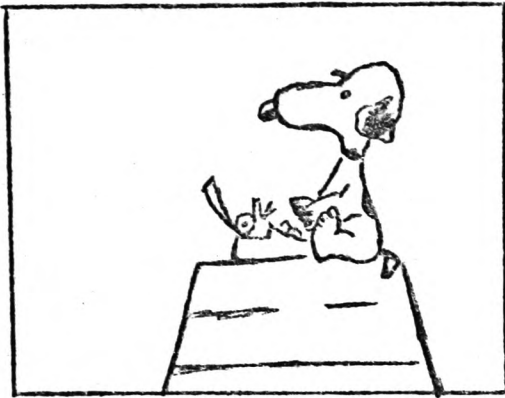
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LIGHT SCATTERING IN FERROELECTRIC CRYSTALS

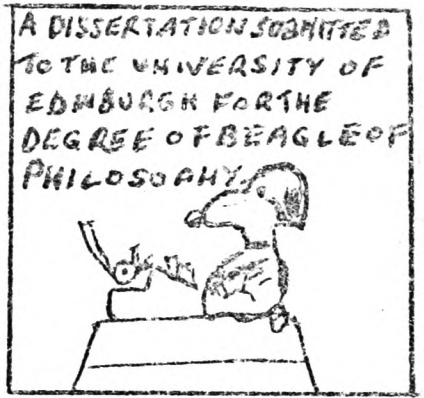
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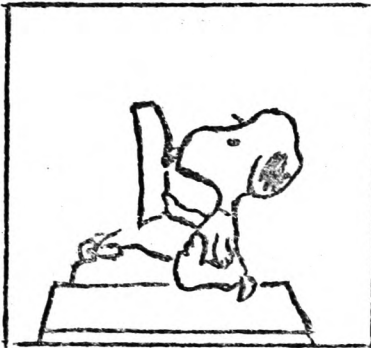


LIGHT SCATTERING
IN FERROELECTRIC
CRYSTALS



A DISSERTATION SUBMITTED
TO THE UNIVERSITY OF
EDINBURGH FOR THE
DEGREE OF BEAGLE OF
PHILOSOPHY.

DEPT. OF PHYSICS
OCTOBER 1972



THAT'S ENOUGH FOR
THIS WEEK----



BACK TO BED!

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ABSTRACT

The ferroelectric phase transitions in the hydrogen-bonded phosphates and arsenates isomorphous to KH_2PO_4 have been studied using inelastic light scattering. Earlier measurements on KH_2PO_4 (KDP) and KD_2PO_4 (KD*P) have been extended to include KH_2AsO_4 (KDA), CsH_2AsO_4 (CsDA) and CsD_2AsO_4 (CsD*A). The spectrum from 0 - 3000 cm^{-1} has been recorded and is compared with the results of a group theoretical analysis. In each case the low frequency Raman spectrum is characterised by a broad wing on the Rayleigh line which narrows and increases in intensity as the transition is approached. A strong anharmonic interaction between this ferroelectric mode and an optical mode of B_2 symmetry is observed; the spectra fit well to a spectral distribution function obtained from a Green's function calculation, yielding the temperature dependence of the characteristic frequency and damping constant of the modes. There is no unique solution for the coupling due to the arbitrary phase of the modes, and so three models are considered:-

(i) The mode coupling here does not correspond closely to the Kobayashi scheme in which the overdamped ferroelectric mode is regarded as collective proton-tunneling with zero dipole moment. The overdamped mode must possess a large non-zero polarisability and further, the far infra-red reflectivity spectrum of CsDA indicates that the mode must be assigned a large dipole moment. The second collective proton mode predicted to appear in

the Raman spectrum is not observed.

(ii) In considering real coupling it is found that the Debye relaxation time of the ferroelectric mode diverges at a temperature T_0 which is lower than the actual transition temperature T_c . This effect may arise simply from the mode coupling.

(iii) With imaginary coupling it is found that $T_0 < T_c$. This result is interpreted in terms of a theory due to Cowley and Coombs in which dielectric fluctuations couple to changes in local thermodynamic equilibrium so that there may be an additional response at low frequency.

The ammonium salts $(\text{NH}_4)\text{H}_2\text{PO}_4$ (ADP) and $(\text{ND}_4)\text{D}_2\text{PO}_4$ (AD*P) undergo transitions to an antiferroelectric phase at low temperature. Whereas the transition is due to a zone boundary instability at T_A , zone centre soft modes are observed which would become unstable at some lower temperature.

A soft mode has also been observed in the Raman spectrum of the recently discovered ferroelectric $5\text{PbO} \cdot 3\text{GeO}_2$. Near 270K there is a coupling with another lattice mode which results in a characteristic level repulsion and intensity transfer. The damping constant of the ferroelectric mode is found to diverge at $T_c = 451\text{K}$ and a high resolution study of the low frequency spectrum has revealed the presence of quasi-elastic scattering. The temperature dependence of this additional response is well described by the theory of Cowley and Coombs.

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CHAPTER 1

Ferroelectric Transition in KDP

In this chapter we review the various features of the ferroelectric transition in KDP and its isomorphous salts. Thermodynamical and electrical properties and the observed structural changes are presented firstly, and then compared with the predictions of proposed model theories. The shortcomings of these theories are indicated and finally the purpose of this research is outlined.

1.1 Properties of KDP-type ferroelectrics

Ferroelectricity is a combination of phenomena associated with the occurrence in some materials of a spontaneous electric polarisation which may be reversed by the application of an external electric field. This spontaneous polarisation disappears at the Curie temperature T_c where the crystal undergoes a phase transition to a non-polar phase. Large anomalies are observed in the dielectric and thermodynamic properties which has led to the discovery of most known ferroelectrics. The tetragonal phosphates and arsenates were shown to be ferroelectric following the discovery in 1935 by Busch and Scherrer [1] that KDP has a dielectric anomaly at 122°K and a large reversible spontaneous polarisation at

lower temperatures.

The temperature dependence of some of these properties is shown in figure 1.1. Below T_c the polarisation increases rapidly and quickly saturates; the onset is continuous, however, and the transition appears to be second order [2]. The saturation value, P_s , is approximately 0.05 coulombs m^{-2} in the normal isomorphs; there is some disagreement about the effect of deuteration, but the most recent results by Azoulay et al. [3] give $P_s(KD^*P)/P_s(KDP) = 1.2$. A large entropy change accompanies the transition, and the specific heat has a λ -type anomaly at T_c [4], corresponding to the energy required to destroy the spontaneous polarisation. Reese [5a] has since shown that the heat capacity in fact exhibits a logarithmic dependence on $(T - T_c)$. While the transition entropies of the KDP isomorphs do not differ substantially, there are large differences in transition temperatures, as shown in Table 1.1, which is most evident for normal and deuterated crystals, e.g. $T_c(KD^*P)/T_c(KDP) = 1.73$. This effect, and the large entropy change, suggest that the transition is of the order-disorder type. The measurements of Reese [5b] indicate a discontinuous entropy change and so a first order transition, but the discontinuity is extremely small.

At 300 K the dielectric constants ϵ_{11} and ϵ_{33} are both about 10^2 . On cooling, ϵ_{33} increases hyperbolically to near 10^5 at T_c , while on further cooling it drops rapidly, corresponding to the large increase in the spontaneous polarisation. An anomaly also occurs in ϵ_{11} at T_c

but it is much less pronounced. Mason [6] observes ϵ_{33} to obey a Curie-Weiss law above T_c :-

$$\epsilon_{33} = A + \frac{C}{T - T_c} \quad (1.1)$$

with $A = 4.5$, $T_c = 122$ K, and the Curie constant $C = 3122$ K.

KD*P behaves similarly with $C = 4050$ K [7]. More accurate experiments by Tsunekawa and Takagi [8] verify Reese's conclusions that the transition in KDP is of first order. Results quoted here have been obtained at frequencies of 10^3 Hz and the crystal can be considered "free"; at much higher frequencies, e.g. 10^7 Hz, which is well above piezo-electric dispersion, the crystal is inertia "clamped".

The Curie-Weiss temperature, T'_c , of the clamped crystal is lower than that of the free crystal; for KDP $(T_c - T'_c) \simeq 4^\circ$ K [9]. A study of the elastic properties shows that C_{66}^E falls to zero at T_c in the Curie-Weiss fashion [6,10], whereas C_{66}^D exhibits a normal temperature dependence.

These observations are consistent with the crystal symmetry and thermodynamical predictions; Cady [11] has shown that the free and clamped dielectric constants, ϵ_{33}^X and ϵ_{33}^x , are related to the insulated and shorted elastic constants, C_{66}^D and C_{66}^E ,

$$\frac{C_{66}^D}{C_{66}^E} = \frac{\epsilon_{33}^X}{\epsilon_{33}^x} \quad (1.2)$$

The zero of C_{66}^E at T_c corresponds to the singularity in ϵ_{33}^X . The lower Curie-Weiss temperature of ϵ_{33}^x indicates that the clamped crystal should undergo a transition at T'_c , but as inertia clamping cannot prevent spontaneous strain accompanying the spontaneous polarisation at T_c ,

the transition occurs at the Curie point of the free crystal.

The isomorphous ammonium salts behave quite differently. Both ϵ_{11} and ϵ_{33} in ADP rise only slightly with decreasing temperature [6,12], as shown in figure 1.2, and drop abruptly at the transition. Moreover, ϵ_{11} rises more rapidly than ϵ_{33} , indicating larger polarisation fluctuations in the xy-plane. AD*P behaves similarly [13]. At the transition, the crystals shatter - undergoing a first-order change - and fail to show ferroelectric properties. The specific heat shows a pronounced endothermic anomaly, the shape of which indicates a latent heat and large transition entropy consistent with order-disorder transitions [14]. These properties are characteristic of antiferroelectrics in which a spontaneous anti-polarisation occurs with dipole moments oppositely directed in neighbouring unit cells, making the crystal macroscopically unpolarised.

1.2 Symmetry and structure

At different temperatures, ferroelectrics as a rule have different crystallographic modifications, the symmetry of the high temperature phase being higher than that of the low temperature phase. A simple application of Curie's principle of superposition of symmetries tells us that the symmetry of the ferroelectric phase will be the highest common subgroup of the paraelectric symmetry group and the spontaneous polarisation. For a first-order

transition to occur there are no symmetry requirements; for a second-order transition, the gradual change in properties near the transition leads to certain symmetry conditions being imposed. The Landau theory [15] emphasises these conditions which lead to a discontinuity of symmetry at T_c but with no discontinuity of state. The general result is obtained that the electric dipole order set up transforms as a single irreducible representation of the space group of the paraelectric crystal. The symmetry elements leaving this dipole moment invariant form a subgroup of the paraelectric space group. Recently, Cochran [16] has discussed the Landau theory from a lattice dynamical viewpoint, showing that the soft mode theory (which is discussed in 1.3.4) may be regarded as an extension of the Landau theory, and that the pattern of atomic displacements below T_c corresponds to the eigenvectors of a highly temperature dependent normal mode of vibration above T_c .

The first detailed X-ray study of the paraelectric phase of KDP was carried out by West [17]; Frazer and Pepinsky [18] later refined this structure and also that of the ferroelectric phase. The Bravais lattice above T_c is body-centred tetragonal with cell dimensions,

$$a = b = 7.43\text{\AA}; \quad c = 6.94\text{\AA}$$

and has point group symmetry $D_{2d}(\bar{4} 2 m)$. The contents of the unit cell are shown in figure 1.3. Each phosphorous atom is surrounded by a nearly regular oxygen tetrahedron, and the PO_4 and K build up the structure so

that they alternate by a distance $c/2$ along the Z-axis. Each PO_4 group is linked to four neighbouring PO_4 groups by a network of hydrogen bonds which lie almost in the xy-plane. The neutron diffraction structure determination of Bacon and Pease [14] located the hydrogen atoms in the O.H...O bonds, but the Fourier projections show an elongated peak along the bond indicating that the proton is either statistically distributed between two equilibrium positions (separated by 0.35Å), or is situated at the middle and undergoes large thermal motion. A refinement of their data shows that the proton motion is $\approx 6^\circ$ out of the xy-plane (R.J. Nelmes, private communication), and this is verified by the recent neutron scattering experiment of Plessner and Stiller [20].

The low temperature form is orthorhombic, with point group $C_{2v}(mm2)$, and the x and y axes are at 45° to the original axes of the tetragonal form. The oxygen framework is little changed but the K and P atoms move relative to each other. The H atoms are displaced by 0.2Å from the centre of the O-O line, moving towards the oxygen from which the P atom has moved away. The protons therefore become ordered in such a way that in a single domain crystal they are either all near "upper" or "lower" oxygens, depending on the direction of the spontaneous polarisation. Reversal of the polarisation drives the hydrogens along the O.H...O bond from one equilibrium position to the other and reverses the displacements of the K and P atoms with respect to the O atoms. The atomic displacements below T_c are

shown in figure 1.4.

The symmetry of the isomorphous crystals has been verified but in many cases the detailed structure has not been investigated. The most notable of these is the low temperature phase of KD^*P . It is well known that the highly deuterated salts crystallise in a monoclinic form and there is also now much documented evidence of a high temperature monoclinic phase of KDP and RbDP, but it is not known if the structures are the same. It is also of interest that CsDP and NaDP are unstable in the tetragonal form and are monoclinic at room temperature. The structure of monoclinic KD^*P has recently been reported by Nelmes [21] but otherwise this variation has very surprisingly been little studied.

The low temperature structure of the ammonium salts differs quite drastically from that of ferroelectrics. Since they shatter at T_c , only X-ray structural determination is possible. Wood et al. [22] have shown that ADP is orthorhombic below T_c but with axes along the sides of the tetragonal cell; the point group is then $D_2(2\ 2\ 2)$. Although the hydrogen atoms have not been located, Nagamiya [23] has proposed that the essential difference is due to the protons ordering at one upper and one lower corner of the PO_4 tetrahedron. As a result the crystal does not possess a spontaneous polarisation. The ordering of protons in the ferroelectric and anti-ferroelectric phases and the resulting dipole arrangements are shown in figure 1.5. Although there is no

direct evidence for the antiferroelectric ordering, Weiner et al. [24] have shown the infra-red absorption spectra of ADP and AD*P to be consistent with this proposal; the splitting of spectral lines due to a relaxation of selection rules in the low temperature phase indicates that the site symmetry of the PO_4 group is $\text{C}_1(1)$.

1.3 Mechanism of the phase transition

1.3.1 Introduction

Although several models have been proposed to explain the mechanism of the phase transition in KDP type ferroelectrics, there is as yet insufficient evidence which would lead us to a definite choice. Since we prefer a microscopic model, the phenomenological theories of Landau [15] and Devonshire [25] will not be discussed, but it is of interest that Cochran [16] has made contact with them through a consideration of the lattice dynamical aspects of structural phase transitions.

Historically, the first molecular model was proposed by Slater [26]; the mechanism was considered to be order-disorder and a statistical mechanical analysis predicted a first-order phase transition. Further developments of these ideas followed but the isotope effects described above could not be explained. Later, the presence of a highly temperature dependent lattice vibration was predicted by Cochran [27]. The "freezing" of this mode at T_c explained the atomic displacements and the spontaneous polarisation, and could account qualitatively for the antiferroelectric phase transition in ADP. However,

the large isotope effect on T_c indicates an important role for the protons in the transition mechanism, but there is no provision for this in the model.

Consequently, others have been led to concentrate on the motion of the protons. Blinc [28] adopted the idea of the proton in a double minimum potential well, where it could tunnel between the two equilibrium positions, and was able to account for the isotope effect on T_c . Collective proton motions were later considered and shown to have a temperature dependence similar to that of the "soft" lattice mode. Kobayashi [29] has extended this treatment to include coupling of the lattice-collective proton motions.

1.3.2 Order-disorder model

Different possible arrangements of the hydrogens result in different orientations of the $(\text{H}_2\text{PO}_4)^-$ dipoles, and it is the alignment of these dipoles below T_c which produces the spontaneous polarisation. Slater [26] considered the situation where there are only two hydrogens near any one PO_4 group and assumed that other configurations, e.g. (H_3PO_4) or $(\text{HPO}_4)^{2-}$, are so unlikely to occur that they can be neglected entirely. When the two hydrogens are nearest the two "upper" oxygens the resulting dipole is considered pointing in the negative c direction; when they are nearest the two lower "oxygens" the dipole is in the positive c direction. Other arrangements produce dipoles perpendicular to the c axis.

The six possible configurations are not equivalent. When the dipole is parallel to c , Slater assigned an energy

for the system which is normalised to zero; he assumed the four remaining configurations to be energetically equivalent with energy e_0 . The internal energy of the crystal is then obtained by summing over all possible allowed configurations, and a first-order phase transition is predicted at T_c , given by

$$k_B T_c = e_0 / \ln 2 \quad (1.3)$$

Evidence in support of this order-disorder mechanism may be taken from the neutron diffraction work of Bacon and Pease [19], but as indicated above, this data is also consistent with large amplitude dynamical behaviour of the protons. The model does not explain the gradual increase in spontaneous polarisation, however, and since the interaction parameter e_0 is little affected by deuteration, the isotope effect on T_c is not predicted.

Takagi [30], Tokunaga and Matsubara [31] have extended the model to include other proton configurations. The order-disorder Hamiltonian may be written in terms of the Ising operators $\{ Z_i = \pm \frac{1}{2} \}$, the two values of which denote the two proton equilibrium positions:-

$$H = -\frac{1}{2} \sum_{ij} J_{ij} Z_i Z_j \quad (1.4)$$

J_{ij} is the effective interaction between the i th and j th protons. Slater considered only nearest neighbour interactions, but these authors have included higher order terms: the resulting energy levels for the system are shown in figure 1.7. However, this model is insufficient in describing the transition in KDP and it is found that

dynamical behaviour of the protons must be included in the Hamiltonian.

1.3.3 Tunneling model

This static effective interaction constrains the proton to remain at one equilibrium site; tunneling motion causes a transfer to the other site. The transition point corresponds to the balance of these effects. As the temperature is decreased, interactions with other protons cause the proton to spend more of its time at one site and hence we have the onset of an ordered phase. The existence of a double minimum potential well along the O.H...O bond has been discussed by Ubbelohde [32] as a special case of the theory of acids and bases, applied to the dissociation equilibrium within the crystal. When the bond is "short" there may be two alternative basic sites, normally with different proton affinities; if there is overlap of the two potential energy curves describing the sites, then there exists the possibility of quantum mechanical tunneling. The case of the symmetric double minimum is discussed here.

The discrete simple harmonic oscillator energy levels become split when the barrier between the wells is lowered. The form of the potential is shown in figure 1.6. V_a and V_b are the simple harmonic oscillator potential functions and ϕ^a , ϕ^b are their corresponding wave functions. The double minimum comes from the overlap ($V_a + V_b$), and the new wave functions $\{\psi_i\}$ obtained from the set $\{\phi^a, \phi^b\}$. However, ϕ^a and ϕ^b are not completely orthogonal in the new system and so we have here an essential approximation.

The two levels of the split ground state are the symmetric state $\psi_S = \phi^a + \phi^b$ and the antisymmetric state $\psi_A = \phi^a - \phi^b$. In the notation of second quantisation operators $\hat{a}$ and $\hat{b}$ annihilate fermions in states ϕ^a and ϕ^b respectively, and so the Hamiltonian for the proton in the double minimum potential can be written:-

$$H = H_{aa} \hat{a}^\dagger \hat{a} + H_{bb} \hat{b}^\dagger \hat{b} + H_{ab} \hat{a}^\dagger \hat{b} + H_{ba} \hat{b}^\dagger \hat{a} \quad (1.5)$$

$H_{aa} = H_{bb} = E_0 + V_0$; E_0 is the ground state of the single harmonic oscillator, and $V_0 = \langle \phi^a | V_b | \phi^a \rangle = \langle \phi^b | V_a | \phi^b \rangle$. Also, the $H_{ba} = H_{ab} = -\Omega = \langle \phi^a | V_a | \phi^b \rangle$, 2Ω corresponds to the ground state splitting as shown in figure 1.6.

We now define spin operators:-

$$\begin{aligned} X &= \frac{1}{2}(\hat{a}^\dagger \hat{b} + \hat{b}^\dagger \hat{a}) \\ Y &= \frac{1}{2i}(\hat{a}^\dagger \hat{b} - \hat{b}^\dagger \hat{a}) \\ Z &= \frac{1}{2}(\hat{a}^\dagger \hat{a} - \hat{b}^\dagger \hat{b}) \end{aligned} \quad (1.6)$$

whose matrix representations are the familiar Pauli matrices. The single particle Hamiltonian then becomes

$$H_1 = -2\Omega X \quad (1.7)$$

Consideration of interactions between protons which leads to collective motion gives

$$H_p = - (2\Omega) \sum_i X_i - \frac{1}{2} \sum_{i,j} J_{ij} Z_i Z_j \quad (1.8)$$

The first term represents the kinetic energy of a system of isolated protons, $\frac{2\Omega}{\hbar}$ being the tunneling frequency, and the second includes interactions between pairs of spins, and is of the same form as the Ising Hamiltonian in (1.4).

To obtain a measure of the ordering of the protons we

determine the thermodynamic average $\langle Z_i \rangle$. In the mean field approximation this quantity is independent of site and so we may write:-

$$H_p = -\underline{H} \cdot \sum_i \underline{S}_i \quad (1.8)$$

where $\underline{H} = [2\Omega, 0, J\langle Z \rangle]$ is the mean field acting on the spin system $\underline{S}_i = [X_i, Y_i, Z_i]$, having written $\langle Z \rangle = \langle Z_i \rangle$ and $J = \sum_j J_{ij}$. Using the definition $\langle A \rangle = \text{Tr}[e^{-\beta H_p} A] / \text{Tr}[e^{-\beta H_p}]$ ($\beta = 1/k_B T$) we obtain:-

$$\begin{aligned} \langle X \rangle &= \frac{2\Omega}{H} \cdot \frac{1}{2} \tanh \frac{H}{2k_B T} \\ \langle Y \rangle &= 0 \\ \langle Z \rangle &= \frac{J\langle Z \rangle}{H} \cdot \frac{1}{2} \tanh \frac{H}{2k_B T} \end{aligned} \quad (1.9)$$

This self-consistency relation for $\langle Z \rangle$ yields for T_c

$$\tanh \frac{\Omega}{k_B T_c} = \frac{4\Omega}{J} \quad (1.10)$$

When $J \gg \Omega$ we have $k_B T_c = J/4$.

Defining now the Fourier components of these quantities

$$\begin{aligned} J(\underline{q}) &= \sum_{ij} J_{ij} \exp i(\underline{q} \cdot (\underline{R}_i - \underline{R}_j)) \\ X(\underline{q}) &= N^{-\frac{1}{2}} \sum_i X_i \exp i(\underline{q} \cdot \underline{R}_i) \\ Z(\underline{q}) &= N^{-\frac{1}{2}} \sum_i Z_i \exp i(\underline{q} \cdot \underline{R}_i) \end{aligned} \quad (1.11)$$

we can rewrite the Hamiltonian:-

$$H_p = -2\Omega N^{\frac{1}{2}} X(0) - \frac{1}{2} \sum_{\underline{q}} J(\underline{q}) Z(\underline{q}) Z(-\underline{q}) \quad (1.12)$$

To determine the eigenvalues we use the equation of motion $\hbar \dot{A} = -i[H, A]$ and linearise within the random phase approximation. This is equivalent to ignoring

torques acting on the spin components, due to fluctuations in the Z-component, which would give rise to finite lifetimes for the excitations. The dispersion relation for a single collective mode is :-

$$(\hbar \Omega(\underline{q}))^2 = 2\Omega(2\Omega - \langle X \rangle J(\underline{q})) + J^2 \langle Z \rangle^2 \quad (1.13)$$

so that above the transition

$$(\hbar \Omega(\underline{q}))^2 = 2\Omega(2\Omega - J(\underline{q}) \langle X \rangle) \quad (1.14)$$

If J_{ij} represents long range interactions so that $J(\underline{q})$ is large near $\underline{q} = 0$, then we obtain, putting $\langle X \rangle \approx \Omega/2k_B T$ in the limit $\Omega \ll k_B T$,

$$(\hbar \Omega(0))^2 = (2\Omega)^2 \left(\frac{T - T_c}{T} \right) \quad (1.15)$$

In the tunneling model the isotope effect in T_c results from the decrease in the tunneling frequency, Ω , with increasing mass of the particle, and is due to reduction in overlap of the wave-functions. From (1.15) we see that the collective mode frequency is also isotope dependent. Since the spontaneous polarisation is given by :-

$$P = 2\mu N \langle Z \rangle \quad (1.16)$$

where μ is the dipole moment of the $K-PO_4$ complex and N is the number of unit cells, this model also predicts an isotope effect here which is not observed [3].

The dielectric susceptibility may be obtained by including in the Hamiltonian an additional term describing coupling of the spin system to an applied electric field. By analogy with equation A2.6, the susceptibility may be written :-

$$\chi_{\alpha\beta}(\omega, \underline{q}) = \beta |m_\alpha m_\beta| G(\underline{q}, \omega) \quad (1.17)$$

where G is the spin-spin correlation function and $\underline{m}$ is the dipole arising from proton displacement. This is given by Cochran [34] :-

$$G(\underline{q}, \Omega) = \frac{4 \Omega \tanh \beta \Omega}{\hbar \Omega(\underline{q})} (n(\underline{q}) + \frac{1}{2}) \quad (1.18)$$

where $n(\underline{q})$ is the Bose-Einstein population factor. Using the high temperature approximations of $n(\underline{q})$ and $\tanh \beta \Omega$, and the form of $\Omega(\underline{q})$ in (1.14), we obtain a Curie-Weiss law for χ . However, $\underline{m}$ occurs in the xy-plane, not parallel to the Z-axis as observed. We must therefore include ionic displacements in the theory.

In KDP the primitive cell contains four non-equivalent protons, which when taken into consideration [32] give rise to four quasi-spin modes. $\Omega_1(\underline{q})$ has the lowest frequency and belongs to the irreducible representation Γ_4 of $D_{2d}(\bar{4} 2 m)$. This corresponds to the mode discussed above. $\Omega_2(\underline{q})$ and $\Omega_3(\underline{q})$ are degenerate, belonging to Γ_5 , and $\Omega_4(\underline{q})$ belongs to Γ_2 . It is found that while $\Omega_1(\underline{q})$ behaves as described above, the other modes do not reveal any anomaly at T_c . Paul and Montgomery [42] have discussed the possible $\underline{q}$ -dependence of these modes, and a model which describes the behaviour qualitatively is illustrated in figure 1.8. The zone-centre Γ_2 (A_2) mode and the zone-boundary M_5 mode are expected to have high frequency since they correspond to modes in which all four protons approach the PO_4 group simultaneously. $\Omega_4(B_2)$ and $\Omega_5(E)$, being infra-red active, will be affected by the Coulomb field in the crystal. If Γ_4 is approached along Λ_1 then the

polarisation produced by the mode is parallel to $\underline{q}$, and so as $\underline{q} \rightarrow 0$, the frequency is raised by the depolarising field. If Γ_4 is approached along Σ_2 , the polarisation is perpendicular to $\underline{q}$ and there is no interaction. Similar effects occur with the Γ_5 mode. Now, if $J(\underline{q})$ has a maximum at $\underline{q} = 0$ at the limit of the $\Sigma_2 \rightarrow \Gamma_4$ branch such that $\Omega(0)^2 \rightarrow 0$ as the temperature is lowered, then the crystal becomes unstable against this mode and the transition occurs. The protons then become ordered according to Γ_4 in figure 1.8.

However, if $J(\underline{q})$ has a maximum at M_{34} then the transition results from an instability against the zone-boundary M_{34} modes. The material then undergoes an antiferroelectric phase transition e.g. ADP. The hydrogens then become ordered according to the M_{34} mode, shown also in figure 1.8, which agrees with the scheme proposed by Nagamiya, figure 1.5(b).

1.3.4 Lattice dynamical model

This model has proved very successful in providing a microscopic theory of ferroelectricity in certain materials e.g. BaTiO_3 . If a crystal is wholly or partly ionic, lattice vibrations are accompanied by polarisation fluctuations of equal frequency which create a local field interacting with ions through long range Coulomb forces. If these balance the short range restoring forces for one particular normal mode, the crystal becomes unstable. Above the Curie temperature, anharmonic interactions stabilise the system, and the observable quasi-

harmonic frequency is therefore temperature dependent. At T_c this soft mode condenses leading to a structural phase transition.

In the Harmonic Approximation the Hamiltonian for lattice vibrations is:-

$$H_L = \frac{1}{2} \sum_{\ell, \kappa} m_{\kappa} u^2(\ell_{\kappa}) + \frac{1}{2} \sum_{\substack{\ell, \kappa \\ \ell', \kappa'}} \Phi(\ell\ell', \kappa\kappa') u_{\alpha}(\ell_{\kappa}) u_{\beta}(\ell'_{\kappa'}) \quad (1.19)$$

where $u(\ell_{\kappa})$ is the displacement from equilibrium of the κ^{th} ion in the ℓ^{th} unit cell and m_{κ} is its mass. In terms of phonon coordinates the displacement may be expressed

$$\underline{u}(\ell_{\kappa}) = (Nm_{\kappa})^{-\frac{1}{2}} \sum_{\underline{qj}} \underline{e}(\kappa, \underline{qj}) Q(\underline{qj}) \exp i(\underline{q} \cdot \underline{r}(\ell, \kappa)) \quad (1.20)$$

and the Hamiltonian becomes

$$H_L = \frac{1}{2} \sum_{\underline{qj}} P(\underline{qj}) P(-\underline{qj}) + \omega^2(\underline{qj}) Q(\underline{qj}) Q(-\underline{qj}) \quad (1.21)$$

where $P(\underline{qj})$ is the momentum conjugate to the phonon coordinate $Q(\underline{qj})$, $\underline{e}(\kappa, \underline{qj})$ is the eigenvector of the mode and $\omega(\underline{qj})$ its frequency. In general, it has been shown [35] that the Hamiltonian must include terms quadratic in ionic displacements and dipole moments to take into account the polarisability of the ions and the fact that the short range forces depend on the state of polarisation.

Cochran [27] has solved the equations of motion for a diatomic cubic crystal and obtains for the frequency of a $\underline{q} = 0$ transverse optical (TO) mode and longitudinal optical (LO) mode :-

$$m \omega(0, TO)^2 = R'_0 - \frac{4\pi(\epsilon(\infty) + 2)Z'}{9v}$$

$$m \omega(0, LO)^2 = R'_0 + \frac{8\pi(\epsilon(\infty) + 2)Z'}{9v \epsilon(\infty)} \quad (1.22)$$

where R'_0 is the effective short range force constant, m is the reduced mass, v the unit cell volume and Z' the effective charge of the ions. The two frequencies differ because there is a macroscopic field which tends to resist the deformation in the LO wave. A relation between $\omega(0, LO)$ and $\omega(0, TO)$, and the dielectric constants, $\epsilon(0)$ and $\epsilon(\infty)$, was first derived by Lyddane et al. [35]; it is

$$\frac{\omega^2(0, LO)}{\omega^2(0, TO)} = \frac{\epsilon(0)}{\epsilon(\infty)} \quad (1.23)$$

Thus, $\epsilon(0) \rightarrow \infty$ if $\omega(0, TO) \rightarrow 0$, i.e. if

$$R'_0 = \frac{4\pi(\epsilon(\infty) + 2)Z'}{9v}$$

The susceptibility of the crystal is related to statistical fluctuations in the dipole moments as discussed in App. I, II. It may be expressed in terms of the one-phonon response function $G(Ojj, \omega)$ of the soft mode, since this mode dominates the dielectric behaviour.

From A2.6:-

$$\chi(\omega) = \beta |M(Ojj)|^2 G(Ojj, \omega) \quad (1.24)$$

where $M(Ojj, \omega)$ is the dipole moment of the mode and

$$G(Ojj, \omega) = \frac{1}{\beta} [\omega(Oj)^2 - \omega^2 + 2\omega(Oj) \{ \Delta(\omega, T) + i \Gamma(\omega, T) \}]^{-1} \quad (1.25)$$

The frequency shift and width, Δ and Γ , are shown in A1.20, 1.21 to be temperature dependent, and in the high temperature limit may be written:-

$$2\omega(0j) \Delta(\omega, T) = aT; \quad 2\omega(0j) \Gamma(\omega, T) = b\omega T$$

To obtain the Curie-Weiss law for $\chi(0)$ we then require $T'_C = -\omega^2(0j)/a$ and $\omega^2(0j) < 0$. At low temperatures therefore, the optical mode is unstable and is only stabilised at high temperatures by the anharmonicity.

The model may be extended to the case of the zinc-blende structure (Cochran [27]), and exhibits properties typical of the paraelectric phase of piezoelectric crystals. The elastic constants can be derived by considering the ratio ω/q ($q \rightarrow 0$) for acoustic modes propagating in special symmetry directions. The mode corresponding to C_{44}^E produces a polarisation which is transverse to q , and so is a TA mode, whereas the mode corresponding to C_{44}^D produces a longitudinal polarisation and is therefore LA. As C_{44}^E vanishes at T_C , the crystal becomes unstable against a TA mode before the optic mode instability occurs. This occurs in tetragonal KDP except that the important elastic constants are C_{66}^D and C_{66}^E .

Since the material is piezoelectric, the TO and TA modes are coupled even in the harmonic approximation. The lower frequency component, whose character is predominantly "pure" acoustic, is the mode responsible for the phase transition. However, the eigenvectors of this mode include also a contribution from the "pure" optic mode. At T_C the mode "condenses" and the difference between the high and low temperature structures is interpreted as the atomic displacements in the mode. The spontaneous strain arises from the acoustic part and the relative motion of K and P

along the z axis, which gives rise to the spontaneous polarisation, is due to the optic mode part. There has been no direct confirmation of this in KDP, but Skalyo et al. [37] have obtained a good correspondence for the soft mode eigenvectors in KD*P. However, they also find a considerable distortion of the oxygen tetrahedron to occur and a large movement of the deuteron out of the xy plane. Unfortunately, the low temperature structure of KD*P is not known sufficiently accurately to enable us to make a firm conclusion on the validity of this interpretation.

The antiferroelectric behaviour of the ammonium isomorphs can be explained by the presence of a soft zone boundary mode at the M pt. $(0,0, \frac{2\pi}{c})$. This mode frequency is lower than both the TO and TA zone centre modes and condenses at a higher temperature, giving rise to a spontaneous anti-polarisation.

1.3.5 Spin-phonon interaction

The obvious extension of these theories is to incorporate both mechanisms in the same model. The main features of the phase transition were shown by Kobayashi [29] to be explained quite readily by assuming a dynamical coupling between the proton tunneling mode and the lattice optical mode. The structure becomes unstable against one of the mixed modes whose character is predominantly that of the collective proton mode but which also acts to trigger a displacement of the K, P and O ions, giving rise to the spontaneous polarisation. The coupling is limited to modes of the same symmetry; the proton

however, can respond to other lattice modes but merely follows adiabatically,

The simplest form of the interaction may be written

$$H_{PL} = -2 \sum_{\underline{qj}} V(\underline{qj}) Q(\underline{qj}) Z(-\underline{q}) \quad (1.26)$$

and the total Hamiltonian is then $H = H_P + H_L + H_{PL}$.

We define spin-spin correlation functions:-

$$G^z(\underline{q}, \underline{q}') = -i \theta(t - t') \langle [Z(\underline{q}, t), Z(\underline{q}', t)] \rangle$$

(c.f. equation A1.1a) and similarly for G^x and G^y . The equations of motion are once again obtained from the general relation $i\hbar \frac{\partial A}{\partial t} = [A, H]$, and linearised in the random phase approximation. The correlation functions are then obtained from the set of simultaneous differential equations, and the dispersion relation from the pole of the function. The result is:-

$$\omega^2(\underline{q}) = \Omega^2(\underline{q}) + \frac{8 \Omega}{\hbar^2} x \sum_j \frac{|V(\underline{qj})|^2}{\omega^2(\underline{q}) - \omega^2(\underline{qj})} \quad (1.27)$$

Kobayashi has considered only one term in this series corresponding to the lattice optical mode, and obtains for the two coupled modes:-

$$\omega^2(\underline{q}) = \frac{1}{2} \left\{ [\omega^2(\underline{qj}) + \Omega^2(\underline{q})] \pm [\omega^2(\underline{qj}) - \Omega^2(\underline{q})] x \left[1 + \frac{32 \Omega |V(\underline{q})|^2}{\hbar^2 (\omega^2(\underline{qj}) - \Omega^2(\underline{q}))^2} x \right]^{\frac{1}{2}} \right\} \quad (1.28)$$

In the case of weak coupling the two solutions are

$$\begin{aligned} \omega_+^2(\underline{q}) &= \omega^2(\underline{qj}) + \frac{8 \Omega |V(\underline{q})|^2}{\hbar^2 (\omega^2(\underline{qj}) - \Omega^2(\underline{q}))} x \\ \omega_-^2(\underline{q}) &= \Omega^2(\underline{q}) - \frac{8 \Omega |V(\underline{q})|^2}{\hbar^2 (\omega^2(\underline{qj}) - \Omega^2(\underline{q}))} x \end{aligned} \quad (1.29)$$

However, $\Omega^2(\underline{q}) \longrightarrow 0$ as $T \longrightarrow T_c$ and so we may take $\omega^2(\underline{qj}) \gg \Omega^2(\underline{q})$. Therefore,

$$\begin{aligned} \omega_+^2(\underline{q}) &\approx \omega^2(\underline{qj}) \\ \omega_-^2(\underline{q}) &\approx \frac{2\Omega}{\hbar^2} [2\Omega - \langle X \rangle (J(\underline{q}) + \frac{4|V(\underline{q})|^2}{\omega^2(\underline{qj})})] \end{aligned} \quad (1.30)$$

The transition will now occur when $\omega_-(\underline{q}) = 0$. Using the same approximation as before, and assuming the mode involved has $\underline{q} = 0$, we obtain:-

$$T_c = \frac{1}{4k_B} [J(0) + \frac{4|V(0)|^2}{\omega^2(0j)}] \quad (1.31)$$

Therefore, the effect of the spin-lattice interaction is to increase the spin-spin coupling by $4|V(0)|^2/\omega^2(0j)$ and thereby raise the transition temperature.

The ferroelectric mode, $\omega_-(0)$, has the atomic displacements originally proposed by Cochran, but it must be emphasised that while in Cochran's theory the lattice instability arises from the cancellation of short-range and long-range forces, the instability here arises from the ordering of the proton system. The mode $\omega_+(0)$ corresponds closely to the lattice vibration but has displacements of K and P opposite to those shown in figure 1.4; in this case the Coulomb repulsion between the K, P ionic system and the proton system cause the frequency to be higher.

The isotope effect on T_c is explained as before by $J(0)$ being dependent on the particle mass. Also, the shift in T_c due to substitution of Rb or Cs for K, and As for P, may arise from the term $(V(0))^2/\omega^2(0j)$. However, the spontaneous polarisation predicted by this model

depends on the finite displacements $\langle Q \rangle$ of the lattice parallel to the z-axis, which cannot be determined within the linear approximation used. We cannot therefore discuss the effect of deuteration on the spontaneous polarisation. Finally, the Curie constant C obtained from the static susceptibility shows no great isotope effect, in accordance with observation [7].

1.4 Discussion

The mixed mode theory of Kobayashi would therefore appear to be the most satisfactory presented so far. One very unsatisfactory feature, however, is the prediction of a well defined frequency with no damping. The Raman spectrum of KDP obtained by Kaminow and Damen [38] shows that the ferroelectric mode is in fact overdamped at all temperatures. The susceptibility was shown to be of the form:-

$$\chi(\omega) = \frac{\chi(0) \omega_0^2}{\omega_0^2 - \omega^2 + i\gamma\omega}$$

with the damping constant γ being temperature independent while $\omega_0^2 \propto (T - T_c)/T$. A phenomenological Bloch-type damping has been considered by Silverman [39] but no comparison is made with experiment.

It has been pointed out by Elliott [40] that the expression (1.27) obtained by Kobayashi overestimates the additional spin-spin coupling via the phonon mechanism. The predictions of the model must therefore be reconsidered in the light of this correction.

Finally, it must be mentioned that Kobayashi's theory deals with a clamped crystal in the sense that acoustic modes are not taken into account. Dvorak [41] extended

the calculation to include coupling with the acoustic mode and has shown that while C_{66}^E follows the observed behaviour, C_{66}^D should also in principle be anomalous, but the effect remains hidden as it would occur at a temperature lower than the free crystal transition temperature.

The purpose of this research is therefore to study the Raman spectrum of KDP and the isomorphous phosphates and arsenates in order to check the conclusions of Kaminow and Damen and extend the analysis to investigate the coupling scheme proposed by Kobayashi. The isotope effect on the frequency and damping of the ferroelectric mode is also investigated. The presence of the temperature independent collective modes is also sought; this requires a classification of the bands observed in the Raman spectrum and a careful comparison with group theoretical predictions.

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Table 1.1

	$T_c(H)$ (K)	$T_c(D)$ (K)	$T_c(D) / T_c(H)$
KH_2PO_4	122	213	1.74
KH_2AsO_4	92	162	1.69
RbH_2PO_4	146	218	1.49
RbH_2AsO_4	110	178	1.62
CsH_2AsO_4	143	212	1.48
$NH_4H_2PO_4$	147	240	1.63

Figure 1.1

Temperature dependence of the spontaneous polarisation, specific heat, dielectric and elastic constants of KDP. [1, 4, 6, 10].

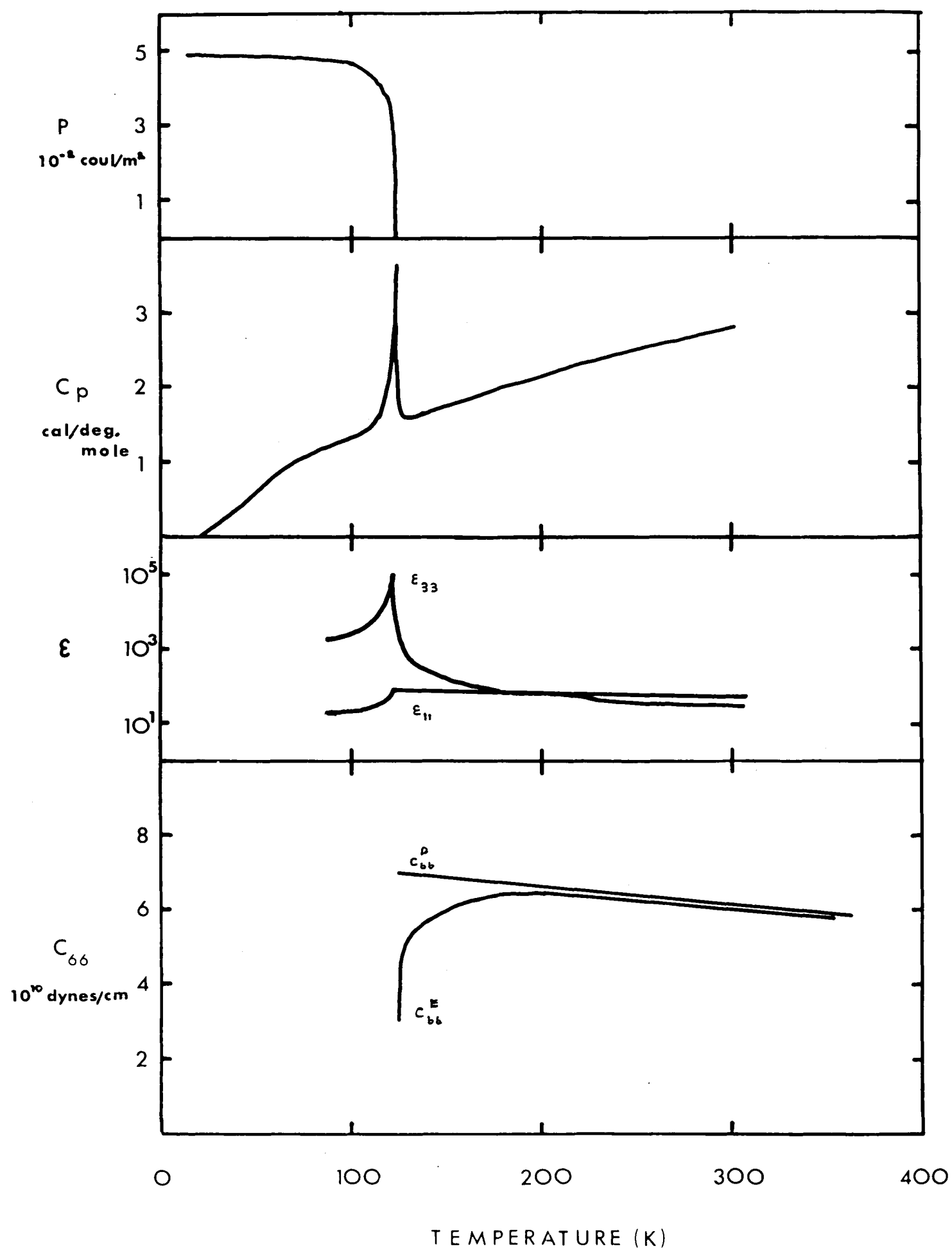


Figure 1.2

Dielectric constants of ADP and AD*P [6,13]

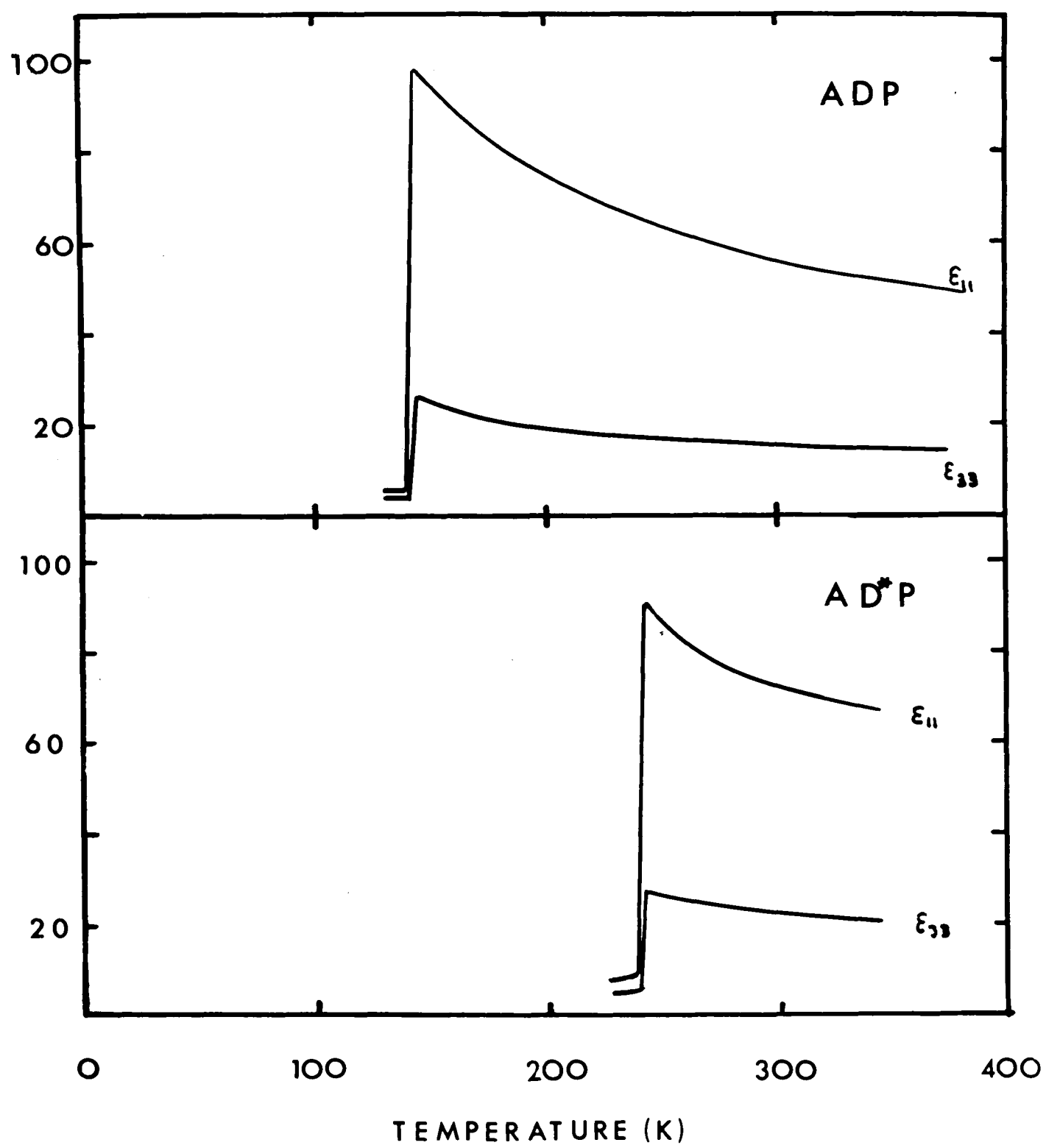


Figure 1.3

Contents of the unit cell of KDP [17]

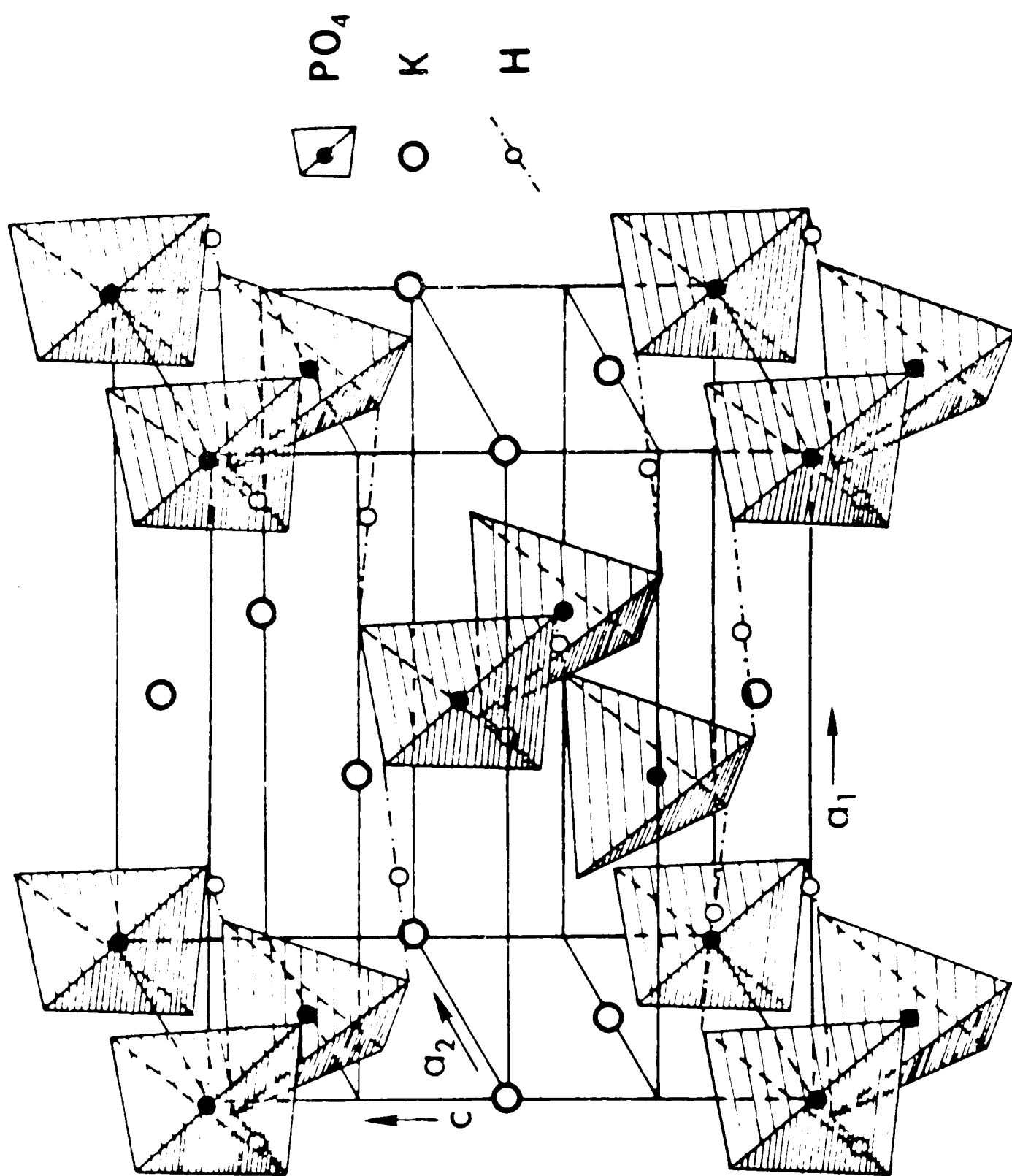


Figure 1.4

Ferroelectric mode motion as depicted by
Cochran [27] based on structural studies
by Bacon and Pease [19].

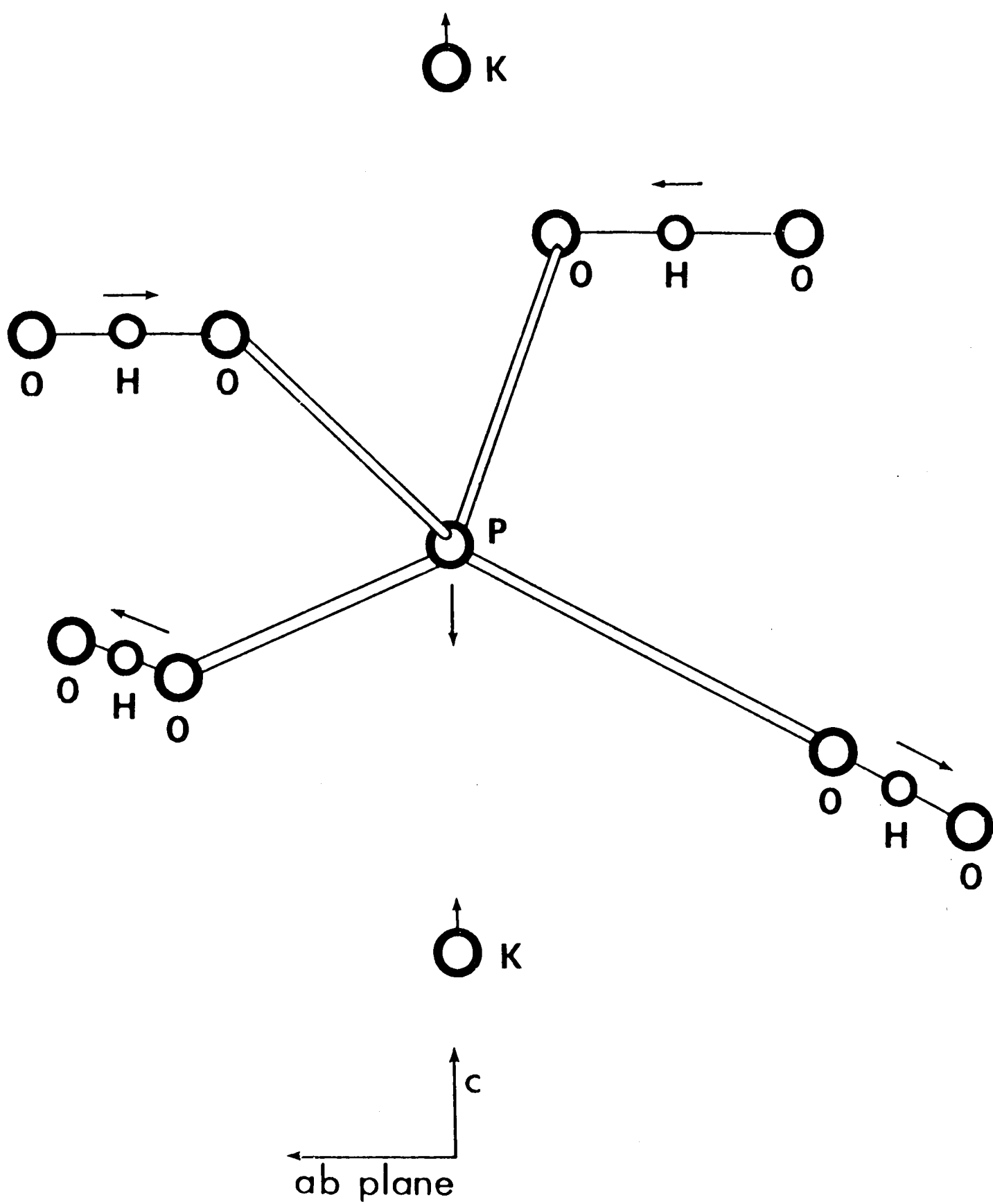
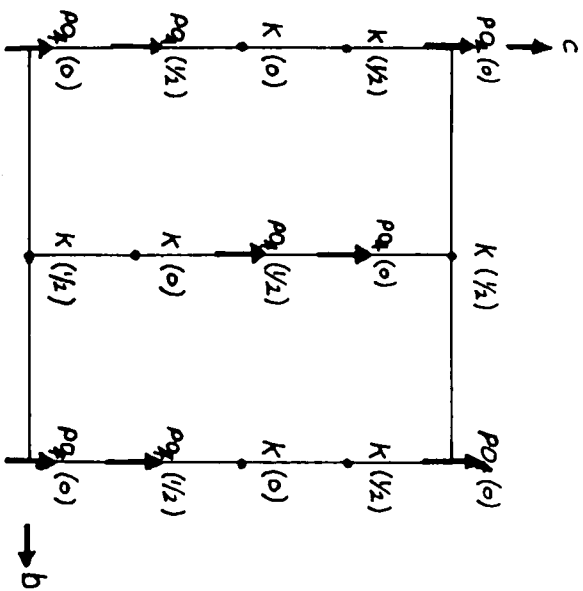
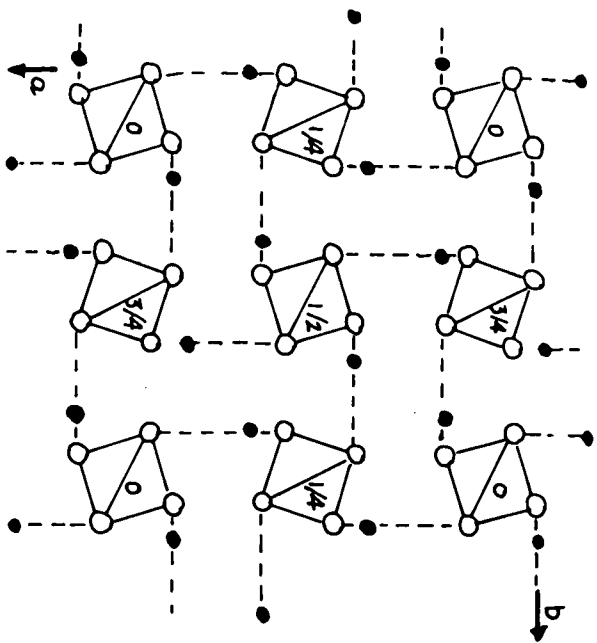


Figure 1.5

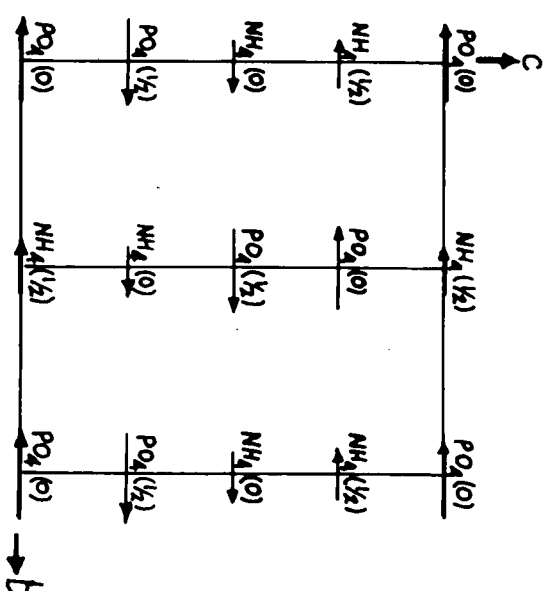
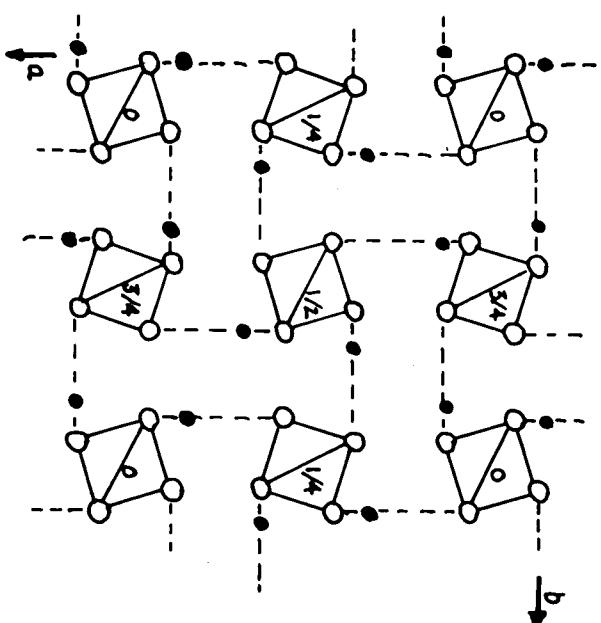
Proton ordering in

(a) the ferroelectric

(b) antiferroelectric phase [27]



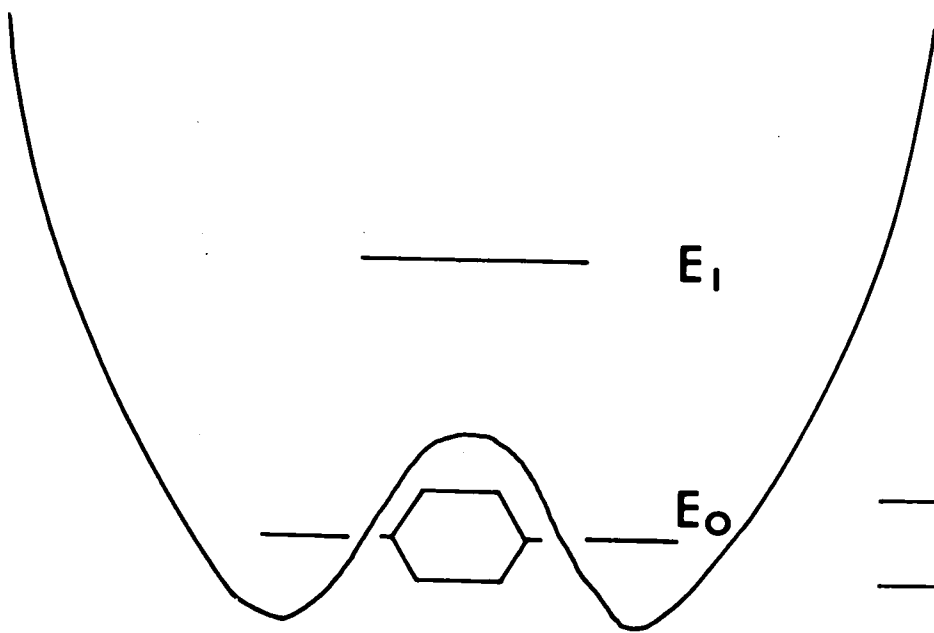
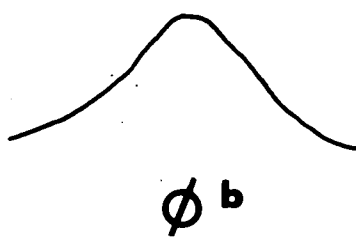
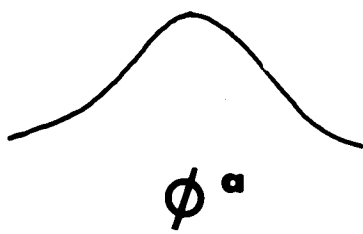
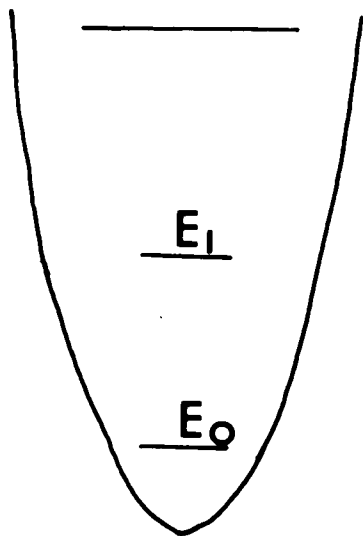
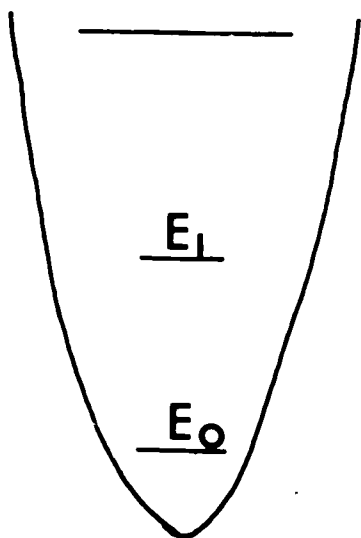
(a)



(b)

Figure 1.6

Double minimum potential well produced by
the overlap of the two simple harmonic
oscillator potentials

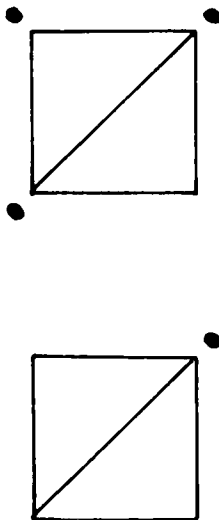
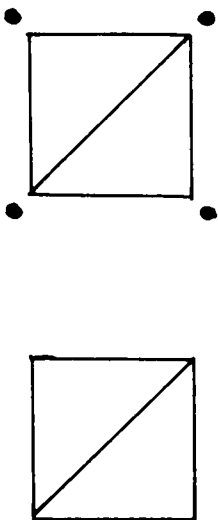


$$\begin{array}{l} \downarrow \\ \hline 2\Omega \\ \hline \uparrow \end{array} \begin{array}{l} \psi_A \\ \psi_S \end{array} = \begin{array}{l} \phi^a - \phi^b \\ \phi^a + \phi^b \end{array}$$

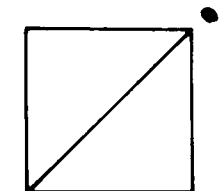
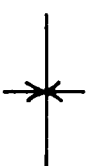
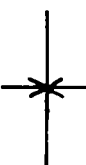
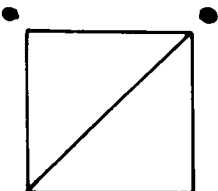
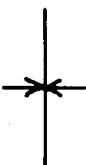
Figure 1.7

Energy levels of PO_4 for the various extensions of the order-disorder model

- (1) Slater model [26]
- (2) Takagi [30]
- (3) Tokunaga and Matsubara [31]



∞



(1)

(2)

(3)

e_o

e_o

e_o

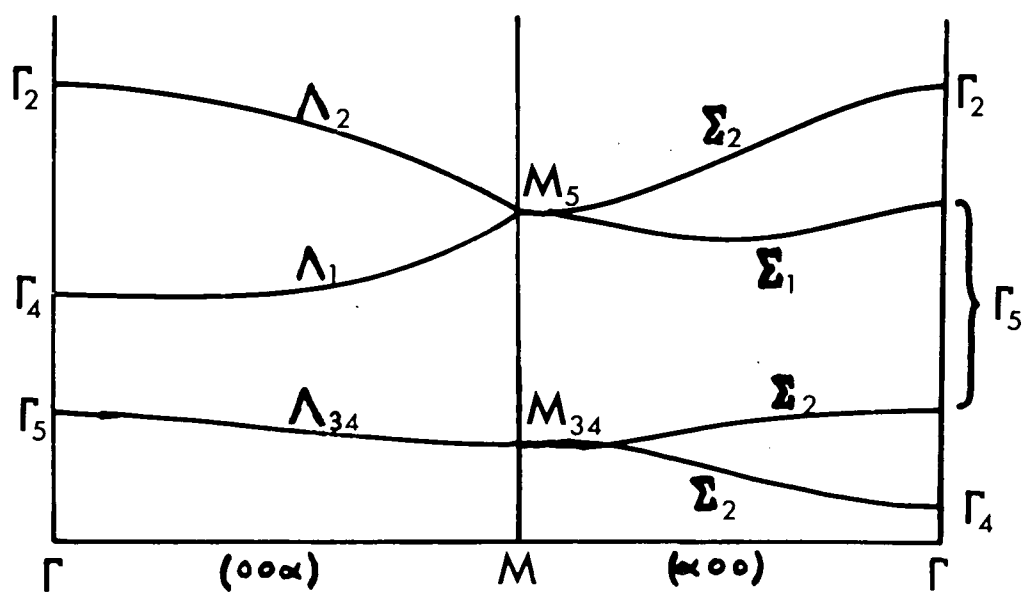
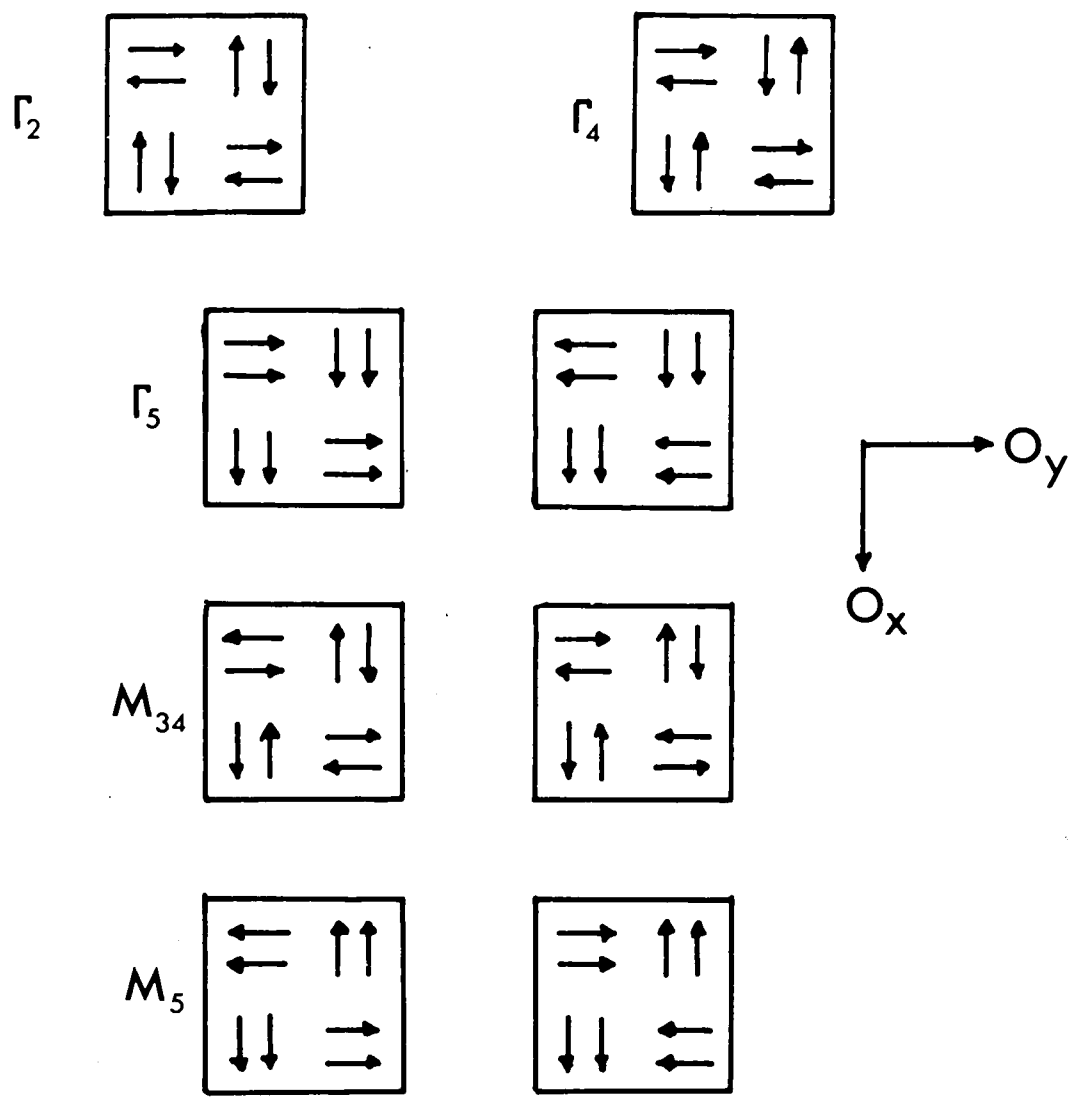
e_i

e_i

e_o+3e_i

Figure 1.8

Possible q -dependence of the proton collective modes (after Paul and Montgomery [42]).



CHAPTER 2

Raman Scattering Theory

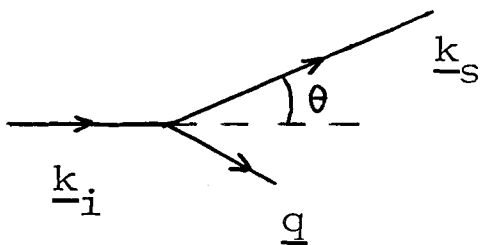
Raman scattering in a crystal is the inelastic scattering of light by the lattice vibrations of the crystal, or by some other excitation e.g. plasmons, spin-waves etc. For a Raman active mode the thermal vibrations of the lattice at a frequency ω disturb the electronic polarisability, P , causing scattering of the incident light and shifting its frequency by $\pm\omega$, corresponding to Anti-Stokes and Stokes scattering respectively. Although spontaneous scattering has been observed with ordinary light sources for nearly forty years, the advent of the c.w. laser has totally transformed the field. The availability of an intense, well-collimated and virtually monochromatic light source - together with the vast improvement in detection systems, spectrometers and phototubes - has made it possible to study phenomena which have in the past been undetectable or unresolvable.

The first quantum-mechanical treatment of the scattering process was presented by Placzek in 1934 [1] and a review of the early experimental work is given by Menzies [2]. An excellent review has been given by Loudon [3] immediately prior to the development of laser

sources. The progress in this field can be measured from the large number of experiments reported in the literature, especially at the two recent international conferences in 1968 and 1971 [4,5].

2.1 Theory of the scattering process

In a typical experimental arrangement, monochromatic collinear light of frequency ω_i and wave vector $\underline{k}_i$ from a laser source is incident on the crystal sample. We consider a scattering event in which a quantum of crystal excitation of frequency ω and wave vector $\underline{q}$ is created. The scattered photon resulting from this event will have a frequency ω_s and wave vector $\underline{k}_s$ determined by the equations of conservation of energy and momentum



$$\omega_i = \omega + \omega_s \quad (2.1)$$

$$\underline{k}_i = \underline{q} + \underline{k}_s \quad (2.2)$$

Since the difference between ω_i and ω_s is small, $\underline{k}_i$ and $\underline{k}_s$ are not very different; this approximation leads to:-

$$|\underline{q}| = 2 |\underline{k}_i| \sin(\theta/2) \quad (2.3)$$

The most common geometry is right-angle scattering with $\theta = \pi/2$: in this situation the phonon wave vector lies very close to the centre of the Brillouin zone and thus has wavelength very long compared to the lattice constant.

The Raman shifts thus measure the phonon frequencies at $q \approx 0$. Higher-order processes, involving the creation, or destruction, of more than one phonon, are possible, but are not important to this discussion.

The Raman spectrum is therefore a measure of the response of the system to an incident light beam. The radiation interacts with the lattice vibrations indirectly through the electrons in the crystal; the initial and final crystal states correspond to the electronic ground state but intermediate virtual states involve the excitation of electron-hole pairs. Second-order perturbation theory gives for the scattering probability [6]

$$W = \left(\frac{2\pi}{\hbar}\right) g(\omega_s) \left| H(\underline{k}_i, i : \underline{k}_s, f) \right|^2 \delta(\hbar\omega_i + E_i - \hbar\omega_s - E_f) \quad (2.4)$$

where the crystal changes from the initial state $|i\rangle$ to the final state $|f\rangle$. The scattered photon density of states $g(\omega_s)$ is given by :-

$$g(\omega_s) d\omega_s d\xi = \left(\frac{1}{2\pi c}\right)^3 \frac{\omega_s^2}{\hbar} d\omega_s d\xi \quad (2.5)$$

where $d\xi$ is an element of solid angle. The photon-crystal interaction, H , is very complex, including electron-lattice, photon-lattice and electron-photon interactions in first-order, and three-phonon anharmonic and second-order photon-lattice interactions in higher order. In this scattering process, however, since molecular dimensions are much smaller than the wavelength of the radiation we can express the total interaction macroscopically in terms of the polarisability; an electric dipole is produced in the crystal by the incident light beam and the scattered light is produced by the

re-radiation of the oscillating dipole. The interaction Hamiltonian may be written

$$H = \sum_{\alpha\beta} P_{\alpha\beta} (\underline{k}_i, i : \underline{k}_s, f) E_{\alpha}(i) E_{\beta}(s) \quad (2.6)$$

where $\underline{E}(i)$ and $\underline{E}(s)$ are the electric vectors of the incident and scattered light respectively, which are expressed quantum-mechanically in terms of the photon creation and destruction operators as :-

$$\underline{E}(i) = i(2\pi\hbar \omega_i)^{\frac{1}{2}} \underline{\epsilon}(i) \{ a(\underline{k}_i) - a^{\dagger}(-\underline{k}_i) \} \quad (2.7)$$

Using these relations we obtain for the total Raman cross-section :-

$$I d\xi d\omega_s = \frac{\omega_s^4}{2\pi c^3} \sum_{\alpha\beta \gamma\delta} E_{\alpha}(i) E_{\gamma}(i) \epsilon_{\beta}(s) \epsilon_{\delta}(s) I_{\alpha\beta\gamma\delta} \quad (2.8)$$

where

$$I_{\alpha\beta\gamma\delta} = \sum_{if} \rho_i P_{\alpha\beta} (\underline{k}_i, i : \underline{k}_s, f) P_{\gamma\delta}^* (\underline{k}_i, i : \underline{k}_s, f) \times \delta (E_i + \hbar\omega_i - E_f - \hbar\omega_s) \quad (2.9)$$

where we have summed over all possible initial and final states; ρ_i is the thermodynamic probability of state $|i\rangle$, $\exp(-\beta E_i)/Z$, Z is the partition function and $\beta = 1/k_B T$. This can be re-written in terms of polarisability operators (expressed in the Heisenberg representation - see Appendix I) as :-

$$I_{\alpha\beta\gamma\delta} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \langle P_{\alpha\beta} (\underline{k}_i, \underline{k}_s, t) P_{\gamma\delta}^* (\underline{k}_i, \underline{k}_s, 0) \rangle \exp(i\omega t) dt \quad (2.10)$$

where $\omega = \omega_i - \omega_s$ is the frequency transfer. Comparison with equation A1.1 indicates that details of the scattering process may be very conveniently determined by Green's function techniques.

Since the electronic wave functions depend on the relative positions of atoms, the normal modes of vibration modulate the polarisability; if the incident photon energy is not close to any of the crystal electronic resonances, the optical frequency polarisability may be expanded in a power series of the atomic displacements

$$P_{\alpha\beta} = P_{\alpha\beta}^{(0)} + \sum_{\mu} P_{\alpha\beta,\mu} U_{\mu} + \dots \quad (2.11)$$

or quantum mechanically in a phonon series

$$P_{\alpha\beta} = P_{\alpha\beta}^{(0)} + \sum_{Oj} P_{\alpha\beta}(Oj) A(Oj) + \dots$$

where

$$U_{\ell x} = \sum_{\underline{q}j} \left(\frac{\hbar}{2\omega(\underline{q}j)NM} \right)^{\frac{1}{2}} e(\underline{x}|\underline{q}j) \exp(i\underline{q} \cdot \underline{R}(\ell x)) A(\underline{q}j) \quad (2.12)$$

in the usual notation [7]. In (2.12) we have used the result that only zone-centre phonons with $\underline{q} = 0$ are involved. The validity of this expansion depends on the Born -Oppenheimer separation of electronic and nuclear motions; for a low frequency vibration, the electronic structure follows and adjusts adiabatically to the instantaneous nuclear configuration.

Using the relations and the results of eqn. A1.26 we obtain the Raman cross-section for Stokes scattering

$$\begin{aligned} I d\omega_s d\xi &= \frac{\omega_s^4}{2\pi c^3} \sum_{\alpha\beta} E_{\alpha}(i) E_{\beta}(i) \varepsilon_{\alpha}(s) \varepsilon_{\beta}(s) \\ &\times (n(\omega) + 1) \sum_{jj'} P_{\alpha\beta}(Oj) P_{\gamma\delta}(Oj') \\ &\times \{G(Ojj', \Omega) - G^*(Ojj', \Omega)\} \end{aligned} \quad (2.13)$$

This is the result obtained by Cowley [8]. The expression

{ } becomes $\text{Im}(G(Ojj', \Omega))$, and the result is

then identical to that obtained using the fluctuation-dissipation theorem (see Barker and Loudon [9]).

The subscripts α , β , γ and δ determine the symmetry of modes giving rise to scattering. They can be chosen by selecting appropriate directions of the incident and scattered light and its polarisation. In addition to the momentum and energy conservation selection rules discussed above, the symmetry of the crystal imposes further restrictions on the phonons which can participate in Raman scattering. The polarisability is a symmetric second rank tensor, in the adiabatic approximation, which may be reduced to give the irreducible representations of the point group of the crystal. From eqn. (2.12) we have therefore that only those phonons whose irreducible representations are the same as those which occur in the reduction of the polarisability tensor will contribute to the scattering. A complete list of Raman tensors showing this reduction for all point groups is given by Loudon [3]. The group theoretical analysis for the KDP point group D_{2d} is given in Chapter 4.

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CHAPTER 3

Experimental Technique

3.1 Introduction

The equipment used in laser Raman spectroscopy has now become fairly standardised and is available "off the shelf". The principle type of instrumentation is illustrated schematically in figure 3.1. The exciting source used in these experiments is an argon laser producing approximately 50 mW at 514.5 nm and 488.0 nm. A lens system focuses a polarised beam of light in the crystal and then images the scattered light on the entrance slit of a spectrometer. The laser intensity is monitored by directing a reflected beam from the first lens surface into a photocell and recorded simultaneously with the Raman spectrum on a 2-pen chart-recorder. A lens of 20 cm. focal length focuses the beam in the crystal to a diameter of ~ 50 microns. This is positioned in the focal plane of the collection optics which is matched to the effective aperture of the spectrometer, in this case f/6.8. A double grating spectrometer is used in order to attenuate the very strong Rayleigh scattering which would otherwise swamp the weak Raman spectrum. The output of the spectrometer is focussed onto the cathode of a photomultiplier and the resulting

pulses of electrons give a direct measure of the light intensity. If this is strong, then the electrical current produced can be measured by an electrometer. On the other hand, when the signal is weak, each individual pulse of electrons must be counted.

This is very briefly the instrumentation required for Raman spectroscopy, but to illustrate the technique, further discussion of some details is necessary.

3.2 Spectrometer

The most unwanted component of the scattered light is the very strong Rayleigh line at the laser frequency. This originates mainly from imperfections in the crystal surface, inclusions in the crystal and the scattering of this radiation inside the spectrometer itself. Severe amounts of stray light and grating ghosts completely overpower the weak Raman components, particularly in the low frequency region ($0 - 100 \text{ cm.}^{-1}$). In order to suppress the Rayleigh component a double grating spectrometer must be used; the attenuation achieved is the product of that for two single gratings, e.g.

if at 50 cm.^{-1} $I \sim 10^{-5} I_0$ for single grating
then at 50 cm.^{-1} $I \sim 10^{-10} I_0$ for double grating,
and since the Raman signal $\lesssim 10^{-3} I_0$, it is obvious that the double grating instrument is required if the Raman spectrum in the region $0 - 100 \text{ cm.}^{-1}$ is to be studied. The machine used here is a Spex 1400 and is illustrated in figure 3.2; it has two 10 cm. by 10 cm. Bausch and Lomb gratings, with 1200 grooves/mm.,

located on a Czerny-Turner mount. It is in effect two monochromators running in tandem. At this point it is useful to recall the fundamental equation of the plane reflection grating spectrometer.

$$m\lambda = d(\sin \alpha + \sin \beta) \quad (3.1)$$

where :-

m = order of the spectrum

λ = wavelength

d = grating spacing

α = angle of incidence

β = angle of diffraction

The apparent disadvantage of this instrument is that the incident energy is dispersed over a large number of orders and in the case of a weak scattering process much of the signal would be lost. To overcome this problem the gratings are "blazed" at an angle which will concentrate the energy in a given direction. The blaze angle ψ is chosen such that it relates to the wavelength λ , where the maximum occurs for arbitrary incidence, by

$$2d \sin \psi = m\lambda \quad (3.2)$$

$$\therefore \psi = \frac{1}{2}(\alpha + \beta) \quad (3.3)$$

The linear dispersion D of a plane grating at normal incidence is

$$D = \frac{dx}{d\lambda} = \frac{m F}{d \cos \beta} \quad (3.4)$$

where F is the focal length of the exit mirror. The dispersion is then directly proportional to the diffraction order m . For normal incidence and small values of β , the angular position is proportional to λ . However, in a scanning device α deviates from normal and the wavelength

may not be linear with the rotation of the grating. Since the incident and scattering directions are fixed, $(\alpha + \beta)$ is unchanged, and so (3.1) becomes

$$\lambda = k \sin \frac{1}{2}(\beta - \alpha)$$

where k is a constant. If the drive is linear in $\sin \frac{1}{2}(\beta - \alpha)$ then the output is linear in wavelength; if the drive is linear in $\operatorname{cosec} \frac{1}{2}(\beta - \alpha)$, the output is linear in wave-number, $\nu = 1/\lambda$.

The fact that D may be either positive or negative, depending on the value of β , means that double dispersion can be achieved in a double grating spectrometer, so that the dispersion at the exit slit is double that at the intermediate slit. Accordingly, the passband

$$\Delta \lambda = S/D \tag{3.5}$$

where S is the slitwidth, is halved and the resolution improved.

When set for double dispersion, the transmission function with equal entrance and exit slits is the familiar triangle with halfwidth $\Delta \lambda/2$. Increasing the size of the intermediate slit beyond this value does not lead to any increase in throughput, while narrowing it leads to a decrease in flux and an increase in bandpass. However, the stability of the instrument, being dependent on such factors as temperature, barometric pressure and vibrations, can vary and measurable intensity fluctuations occur. For this reason it is advisable to retain the intermediate slit > 100 microns so that these effects are not noticeable.

Finally, there is one additional characteristic of the grating which requires mention. It is found experimentally that the grating efficiency is a function of the light polarisation. There are two possible reasons for this :-

- (a) the dielectric nature of the grating surface
- (b) the interference terms which are present in rigorous diffraction theory but not in the simple scalar theory whose results are quoted here,

but so far there has been no satisfactory explanation of this effect. If we are to be able to compare spectra, study lineshapes and make absolute cross-section measurements, then we must include a polarisation scrambler in the collection optics. This ensures a uniformly mixed polarisation input to the spectrometer.

3.3 Optimum illumination geometry

Because the scattering process is so weak, the most efficient illumination and collection optics are essential. Criteria for optimum illumination geometry have been discussed in varying degrees of complexity [1 - 3].

A focussed laser beam is essential for maximum efficiency; with a lens essentially free from aberrations, absorption and reflection losses, the full output power of the laser can be concentrated into a diffraction limited focal volume. This may be taken to be a circular cylinder of length l and diameter w

$$W = \lambda(f/a) \quad (3.6a)$$

$$l = 3\lambda(f/a)^2 \quad (3.6b)$$

where f is the focal length of the lens L_1 and a is the diameter of the incident beam. If ξ is the collection solid angle subtended by lens L_2 at the source and ξ_0 is the acceptance solid angle of the spectrometer, then

$$\xi = M^2 \xi_0 \quad (3.7)$$

where M is the magnification of L_2 and L_3 . Since the light collected is proportional to ξ , the larger the magnification the higher the efficiency. This is valid as long as the slit width $S \lesssim MW$. Also, the slit having height h , will pass a length h/M of the source: the optimum situation is when $S = MW$, so that

$$\frac{f}{a} = \frac{S}{M\lambda} \quad (3.8a)$$

$$\text{and} \quad l = \frac{h}{M} \quad (3.8b)$$

The magnification will then be

$$M = \frac{3S^2}{\lambda h} \quad (3.9)$$

Schwiesow [3] has carried a more detailed analysis using more accurate expressions for l and W , and while he obtains results that are qualitatively the same, they differ numerically by a factor of >2 . He points out that the above analysis is invalid when the slits are very narrow, and finds

$$\frac{f}{a} = \left(\frac{h}{14M\lambda} \right)^{\frac{1}{2}} \quad (3.10)$$

In general, the magnification of the collection optics should be as large as possible consistent with the solid angle considerations mentioned above. However, this must

be qualified in the important case where the direction of the scattered radiation is critical. The "direction of propagation" of phonons observed will be uncertain by an amount $d\theta$, the semi-angle of the cone of gathered light. It may therefore be necessary to reduce the aperture of the optics to meet this requirement.

The alignment procedure in our experiments is simplified by using the reverse optics technique; the entrance slit is illuminated by shining light back through the first half of the spectrometer and its image in the crystal is observed through a microscope. The laser beam, and L_1 and L_2 , are then adjusted until the slit image and focussed beam are simultaneously in focus. With the slitwidth fixed, the magnification and aperture are set to the optimum position consistent with the above considerations. In the early experiments on KDA and CsDA major precautions were essential as the laser (Laser Associates 311) was very unstable, varying by as much as 50% during a run, and produced very low power, < 30 mW. Initially, a servo-correction device was employed to correct the observed signal by an amount proportional to the source fluctuation, but the overshoot and time constant inherent in the device made it unsuitable for accurate lineshape analysis. A simpler system was adopted which involved only recording the laser and Raman intensity simultaneously, and corrections made in the analysis stage. More recently, up to date lasers (Spectra Physics 165 and Coherent Radiation 52) with high output power (~ 2 W) and excellent stability ($\sim 1\%$) have been available, making most of these precautions

redundant.

3.4 Detection system

The most widely used detector of light is the photomultiplier (PM). When a bunch of photons impinge on the photocathode, the photoelectron released is accelerated to the first dynode, positively charged to about 100 volts. Secondary electrons released are then accelerated to the next dynode, and so on. By the time this procedure is repeated a dozen times a burst of $\sim 10^6$ electrons is obtained. The pulse height will vary from one signal photon to the other and so each photon contributes differently to the signal current. Therefore, the most sensitive method of detection is "photon" counting which involves the direct recording of the digital output of the PM. Since all PM tubes are sources of noise, special attention must be given to distinguishing the genuine signal from the noise and ultimately recording the signal only.

The phototube used here is the ITT FW 130 (a special purpose 16-stage tube, having an end window type photocathode with an S-20 spectral response) which is convenient in the case where the input flux is confined to a small area of the photocathode. An electrostatically focussed electron lens system with a defining aperture in the electron image plane is incorporated between the photocathode and the first dynode. This limits the effective photocathode and so reduces the noise input by minimising the collected thermionic emission, while at the same time giving high collection efficiency in the

effective photocathode area. The remaining dark current from the PM arising from thermionic emission can be virtually eliminated by cooling to -20°C . This is achieved thermoelectrically, and the final dark counts reduced to about one per second.

When a "noise" electron originates in the dynode chain its resultant amplified pulse will be progressively smaller on average than that of a "signal" electron. For optimum signal-to-noise ratio it is therefore desirable to discriminate against these low level pulses. It is in practice difficult to determine the optimum discriminator level since the signal pulses have an approximately Poisson distribution of heights. The adjustment can be made by visually estimating the average heights of signal and noise pulses on an oscilloscope display.

The PM is first matched into $50\ \Omega$ cable by a unity gain *negative* feedback preamplifier situated in the housing, and the pulses are then amplified and shaped, becoming the standard height and length (5v and 30 ns.) which enables the counting to be more efficient. The signal may be integrated over a count period ranging from 0.3 to 100 sec. which allows the detection of very low light levels. The speed of the ratemeter is all important, and with the electronics used "pile up" begins at 10^6 pulses/sec.; the response is linear to better than 1% over the entire counting range, and produces a full scale output of 50 mv. This output then drives a stripchart recorder whose chart-speed is matched to the scanspeed and time constant.

3.5 Temperature control and measurement

Spectra were recorded at various temperatures ranging from 80°K to 500°K . Those above room temperature were obtained with the crystal mounted in an optical cell filled with spectroscopically pure silicone oil. A Harwell temperature controller was used in conjunction with a rough electrical heater which delivered most of the power. The temperature was measured by a C-A thermocouple and kept constant to better than 1°K . The temperature homogeneity in the bath was found to be about 1°K so that in the sample itself a fairly even temperature was obtained. The thermocouple was calibrated at various points between the boiling points of liquid N_2 and water, and checked with the standard tables; the uncertainty was found to be less than 1°K .

The low temperature data were obtained with the sample mounted in the specially constructed glass dewar shown in figure 3.3. A continuous flow of cold nitrogen gas, boiled off from a storage dewar, cools the copper cell containing the crystal, and the temperature measured and controlled in a fashion similar to that just described. A refractive index matching liquid (2 - methyl butane) was used at temperatures as low as 120°K in order to eliminate spurious surface scattering and increase the collection efficiency; it also improves considerably the temperature stability and homogeneity of the sample. The stability achieved is $\sim 0.2^{\circ}\text{K}$ and an overall accuracy of 1°K obtained.

3.6 Sample preparation

The samples were large oriented single crystals (~ 1 cm cubic) with optically polished faces perpendicular to the crystallographic axes. The KDP and ADP were purchased from Electro-Optic Components Ltd., AD*P and KD*P from Isomet Corp., and CsDA, CsD*A and KDA from Quantum Technology. They were received with a high quality optical polish but this disappeared rapidly due to their hygroscopic behaviour. Special storage precautions were necessary and all experiments were carried out with the crystals in a moisture free liquid. This is extremely important in the case of deuterated crystals since hydrogen substitution also occurs. Although deuteration of $\sim 100\%$ was indicated by the manufacturers, 95% is probably more reasonable, and for AD*P the level of incoherent neutron scattering indicates 92%. Periodic polishing with 0.25 micron powder was necessary.

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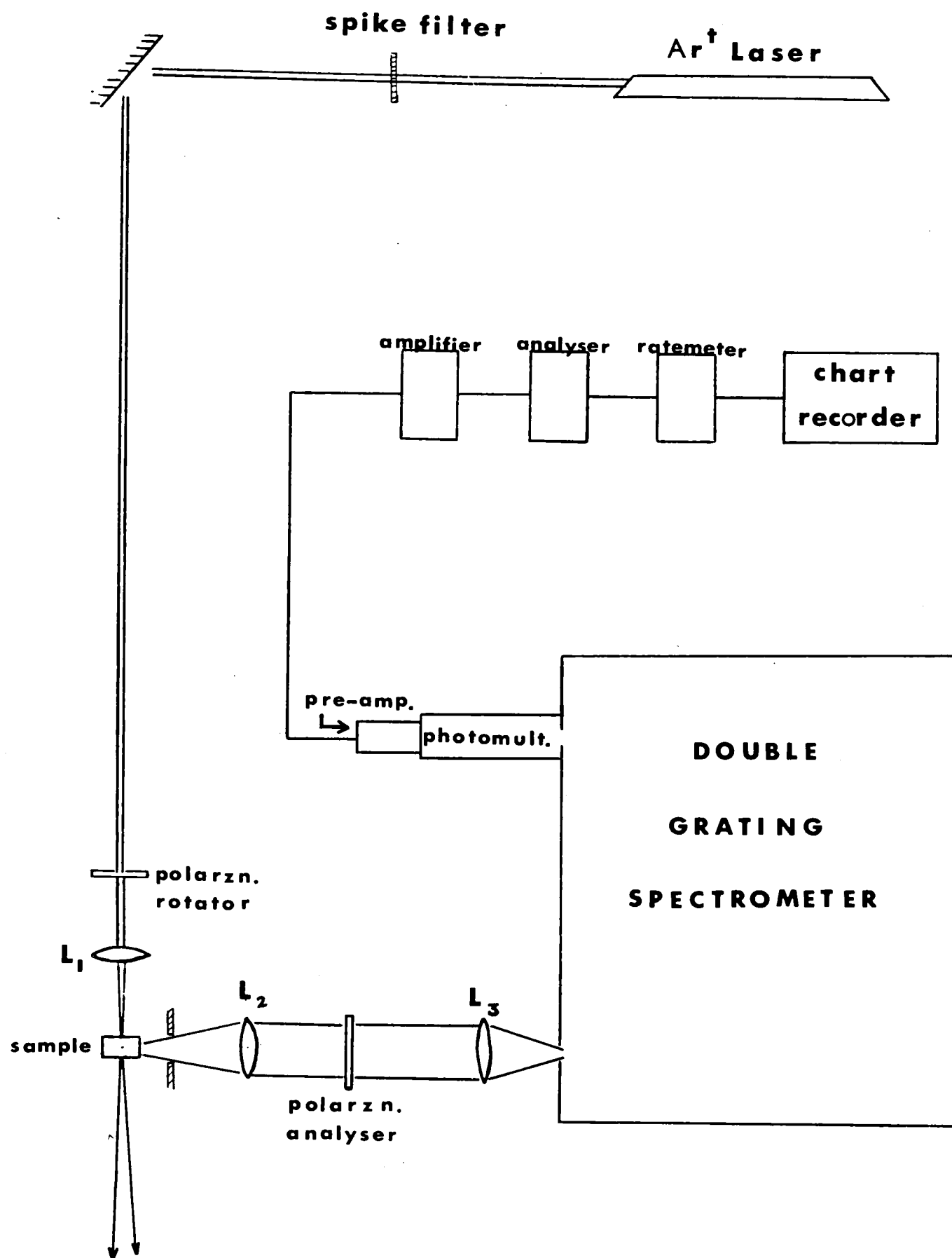


Figure 3.2

The Spex 1400 double grating spectrometer

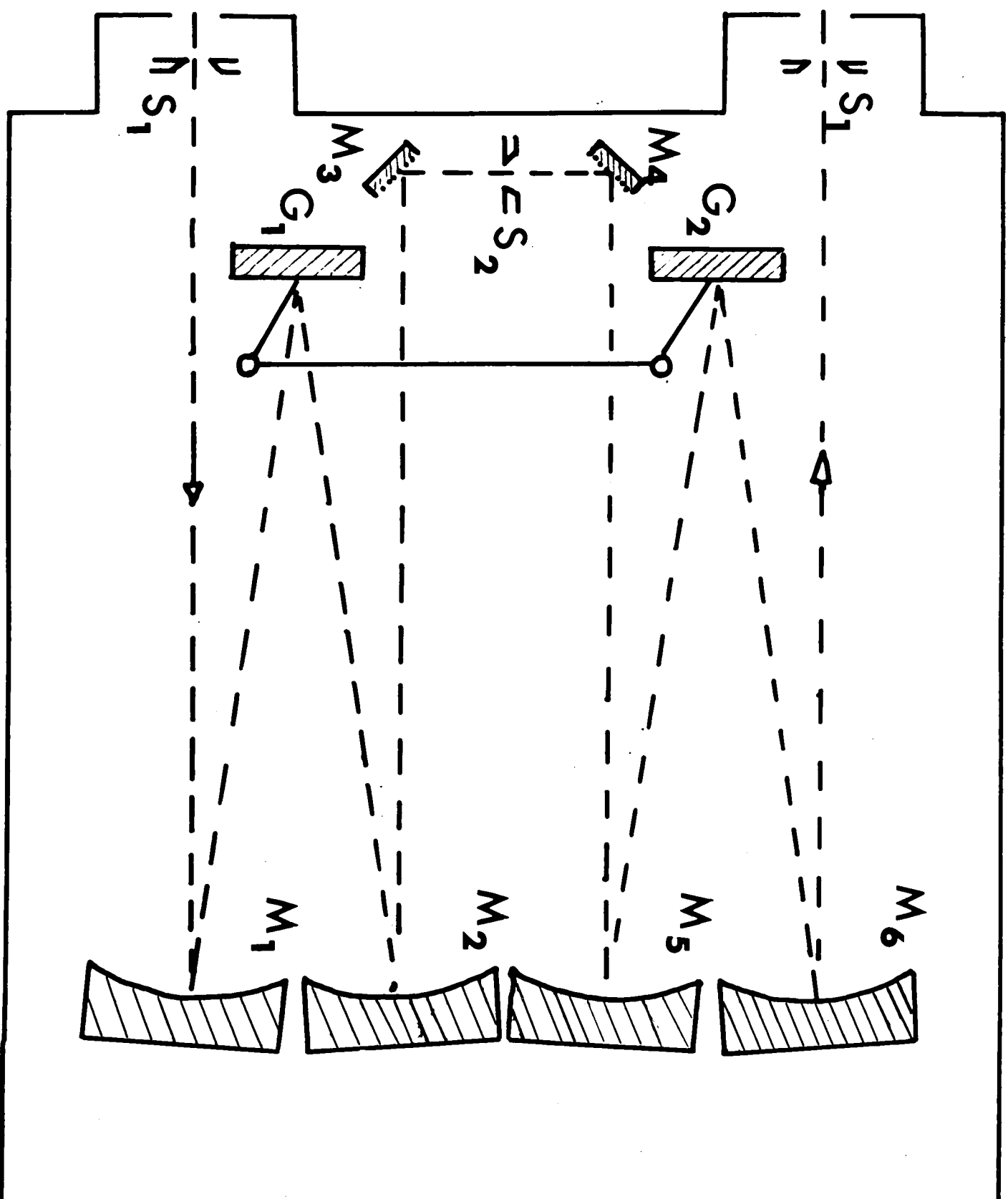
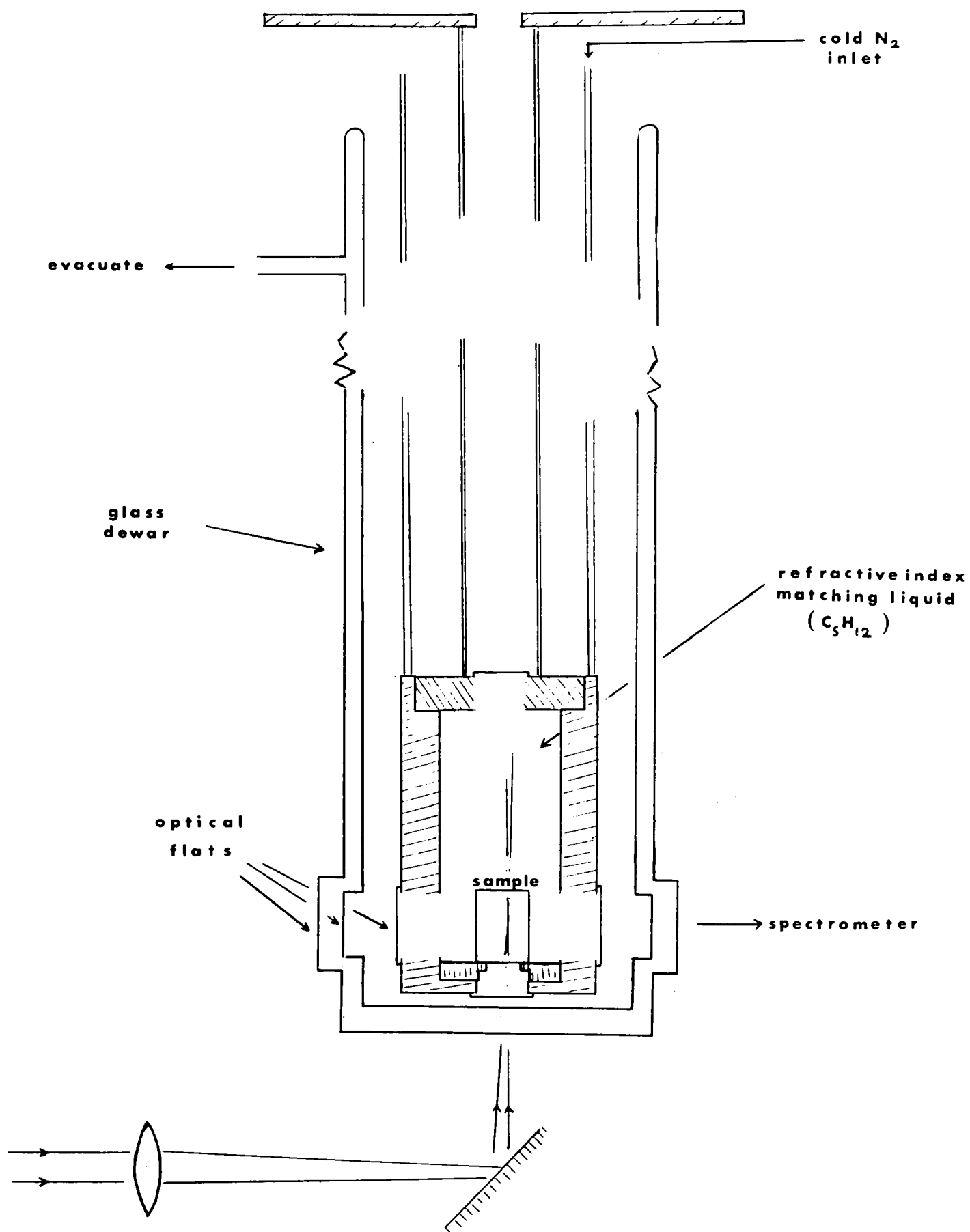


Figure 3.3

Continuous gas flow cryostat. The outer vessel is an evacuated glass dewar, and the sample is mounted in the copper cell



CHAPTER 4

Raman Scattering in CsDA and CsD*A

4.1 Introduction

The optically active vibrational modes in KDP and its isomorphous ferroelectrics and anti-ferroelectrics have been studied in detail by infra-red spectroscopy [1 - 11] and Raman scattering techniques [12 - 27], but so far the determination of theoretically allowed modes and assignment of the observed have not been fully successful. The group theoretical analysis of Shur [28] for KDP is valid for the isomorphous ferroelectrics, and that of Paul and Montgomery [29] is valid also for the antiferroelectrics. By far the major theoretical problem has been the treatment of the hydrogen atoms moving in what is well known to be a highly anharmonic potential. Shur's treatment is entirely within the harmonic approximation and his conclusions have not been fully verified experimentally. There have been several attempts, notably by Blinc [30], Novakovic [31] and more recently by Paul and Montgomery [29], to include anharmonic effects by considering the symmetry properties of the pseudospin Hamiltonian. However, the temperature independent collective modes have not yet been identified.

Marked changes occur in the infra-red and Raman spectra

of these materials on crossing the Curie temperature. This is due mainly to the change in crystallographic symmetry, which causes a relaxation in the group theoretical selection rules, but also to changes in the motion of the hydrogen atoms. X-ray and neutron diffraction structural determinations have been unable to specify the role of the hydrogen atoms in the phase transition, but a greater understanding may be gained from a study of the temperature and isotope dependence of the vibrational spectrum. The group theoretical analysis outlined in the next section enables us to predict the number of Raman active modes of each symmetry species, and a comparison with the observed spectrum should lead us to a preference for one of the proposed models. However, the assignment of observed vibrational modes is difficult and there is disagreement between various authors.

In section 4.3 we present the Raman spectra of CsDA and CsD*A in the paraelectric phase and compare them in detail with the published spectra of KDP and KD*P.

4.2 Group theoretical analysis

In the first-order Raman effect, momentum conservation restricts the range of wavevectors of phonons participating in the scattering process to near the Brillouin-zone centre. Under these conditions the wavevector can be regarded as effectively zero, and only the point group of the unit cell need be considered in deriving the symmetry species of the vibrational modes. In the paraelectric phase KDP has the point group $D_{2d}(\bar{4} 2 m)$

with two molecular units in the primitive cell. The phosphorous and potassium atoms occupy positions with site symmetry S_4 , whereas the oxygens occupy general positions; two protons lie on each of the x and y diads.

In this treatment, which follows closely that of Paul and Montgomery [29], we make use of multiplier groups (see Montgomery [32] and references therein), and regard normal modes as vectors spanning a linear space S_V . This is factorised into two simpler spaces, S_E a 3 dimensional Euclidean space and S_C a $3n$ dimensional cell space, where n is the number of atoms in the primitive unit cell. S_C is further decomposed into subspaces relating to the chemical species present. Using the direct product we have :-

$$S_V = (S_P + S_K + S_O) \times S_E \quad (4.1)$$

where we have included vibrations of heavy atoms only.

S_P and S_K are two dimensional while S_O is eight dimensional. The characters of S_P , S_K and S_O under the symmetry operations of the point group are given in table 4.1. We see that both S_P and S_K transform as $(A_1 + A_2)$ while S_O transforms as $(A_1 + A_2 + B_1 + B_2 + 2E)$. Since S_E transforms as $(B_2 + E)$, we obtain for the number of modes :-

$$\Gamma = 3A_1 + 3A_2 + 5B_1 + 5B_2 + 10E \quad (4.2)$$

This can be separated into optic and acoustic modes; the latter transform as S_E , and so :-

$$\begin{aligned} \Gamma_{\text{acoustic}} &= B_2 + E \\ \Gamma_{\text{optic}} &= 3A_1 + 3A_2 + 5B_1 + 4B_2 + 9E \end{aligned} \quad (4.3)$$

Since A_1 and A_2 occur only in $S_O \times S_E$, the K and P atoms will be at rest for A_1 and A_2 modes.

Classification of the optical modes into external and internal modes is possible (although not rigorously true) if the forces between P and O atoms are very much stronger than the bonding of the PO_4 group with the rest of the crystal. The external or lattice modes can be further subdivided into translatory and rotatory types, which in the limit of vanishing forces between the groups, correspond to pure translations and rotations respectively. The primitive cell can now be regarded as having four units, viz. 2K and $2PO_4$ groups. External vibrations are then determined by assuming PO_4 groups to be points at sites occupied by P, and the internal vibrations of PO_4 are considered separately.

For external vibrations the linear space S_V is written

$$S_V = (S_K + S_{PO_4}) \times S_E \quad (4.4)$$

S_K and S_{PO_4} transform as $(A_1 + A_2)$ and S_E is a translational space which transforms as $(B_2 + E)$. Thus,

$$\begin{aligned} \Gamma_T^{\text{ext.}} &= (2A_1 + 2A_2) \times (B_2 + E) \\ &= 2B_1 + 2B_2 + 4E \end{aligned} \quad (4.5)$$

This includes optic and acoustic modes.

In order to obtain the rotatory modes we regard S_E as a rotational space, S_R , and consider the transformation of the rotational vectors in it. Further, S_K does not contribute and so S_V may be written

$$S_V = S_{PO_4} \times S_R \quad (4.6)$$



Since $S_R \approx (A_2 + E)$ we have:-

$$\begin{aligned} \Gamma_R^{\text{ext}} &= (A_1 + A_2) \times (A_2 + E) \\ &= A_1 + A_2 + 2E \end{aligned} \quad (4.7)$$

The internal vibrations of the phosphate group are obtained by subtracting the external from the total number of vibrations:-

$$\Gamma^{\text{int}} = 2A_1 + 2A_2 + 3B_1 + 3B_2 + 4E \quad (4.8)$$

Using the site group method described by Halford [33] we may correlate directly the free molecule vibrations, whose frequencies and eigenvectors are well known, and the internal modes observed in the crystal spectra. The free AsO_4^{3-} or PO_4^{3-} ion has tetrahedral symmetry T_d ; the character table is shown in table 4.2. In the crystal, the S_4 axis coincides with the S_4 axis of the PO_4 group, and so the motions of the ion must be classified as those of a molecule with S_4 symmetry only. If the crystal field giving rise to the reduction in symmetry is weak, then the mode frequencies will be only slightly shifted, but there will be a lowering of the degeneracies. The symmetry elements of S_4 are listed in table 4.3. The free molecule modes are then distributed between the three irreducible representations of the S_4 point group, as shown in the correlation chart in table 4.4.

When we consider two formula units in the unit cell and take account of their relative phase, we obtain the additional splitting shown in the right hand column. The

result is then identical with that obtained in equation (4.8), but now we have a good knowledge of the atomic displacements.

Finally, if we include the hydrogen atoms in the discussion we should expect 48 degrees of freedom. The linear space S_V is then:-

$$S_V = (S_P + S_K + S_O + S_H) \times S_E \quad (4.9)$$

where $S_H \approx (A_1 + B_1 + E)$. Thus

$$\Gamma^{\text{total}} = 4A_1 + 5A_2 + 6B_1 + 6B_2 + 12E \quad (4.10)$$

This is the result obtained by Shur [28], who also gives a complete list of eigenvectors.

4.3 Raman spectra of CsDA and CsD*A

The Raman tensors for normal modes of crystals with point group $D_{2d} (\bar{4} 2 m)$ have the form [34],

$$\begin{array}{ccccc} A_1 & B_1 & B_2(Z) & E(Y) & E(X) \\ \begin{bmatrix} a & & \\ & a & \\ & & b \end{bmatrix} & \begin{bmatrix} c & & \\ & -c & \end{bmatrix} & \begin{bmatrix} d & & \\ & d & \end{bmatrix} & \begin{bmatrix} & e & \\ & & \\ e & & \end{bmatrix} & \begin{bmatrix} & & \\ & & \\ & e & \\ & & e \end{bmatrix} \end{array}$$

The direction of infra-red activity is shown in parenthesis.

A_2 modes are Raman and infra-red inactive. It is therefore possible to distinguish all the Raman active modes with four experimental arrangements:-

$$\begin{array}{ll} X(ZZ)Y & - A_1 \\ Z(XX)Y & - A_1 + B_1 \\ X(YX)Y & - B_2 \\ X(ZX)Z \text{ or } X(ZX)Y & - E \end{array}$$

Since the E and B_2 modes are infra-red active it is possible that LO - TO splitting occurs; the geometry $X(ZX)Z$ gives purely TO modes whereas $X(ZX)Y$ gives (TO + LO). Both orientations are studied.

The room temperature spectra for both crystals were recorded with two samples of each, but no significant differences were noted. Figures 4.1 - 4.4 show the spectra in the region 0 - 3000 cm^{-1} . The vibration spectrum may be approximately divided into three regions. The low frequency region ($< 300 \text{ cm}^{-1}$) corresponds to the lattice vibrations; the middle frequency region (300 - 1000 cm^{-1}) to the AsO_4 internal vibrations; and the high frequency region ($> 1000 \text{ cm}^{-1}$) to vibrations of the relatively much lighter hydrogens in the O-H...O bonds. In fact, these regions overlap to a large extent making unequivocal assignments difficult. It is therefore of considerable importance to compare the spectra of the various members of the class obtained by substitution $K \longrightarrow \text{Rb} \longrightarrow \text{Cs}$ and $\text{P} \longrightarrow \text{As}$. In table 4.5 we give a complete list of frequencies and symmetries and the proposed assignment.

4.3.1 Lattice modes

We expect $2B_1 + B_2 + 3E$ translatory external modes. For CsDA we have a B_1 mode at 126 cm^{-1} , a B_2 at 140 cm^{-1} and 3E modes at 55, 84 and 137 cm^{-1} . With the exception of the B_2 mode, the corresponding frequencies for CsD*A are virtually unchanged. The same

modes in KDA occur at 137, 158, 75, 105 and 160 cm^{-1} respectively; further replacement of As with P gives rise to modes at 156, 174, 95, 113 and 190 cm^{-1} in KDP. The only predicted optical lattice mode not observed is a B_1 mode.

We have seen above that free rotations of the AsO_4^{3-} ion give rise to librational modes in the crystal; they have symmetry $A_1 + A_2 + 2E$, and are expected to have frequencies similar to the translatory vibrations. Inspection of figures 4.1 and 4.3 shows that there are no suitable candidates in the low frequency spectra of CsDA and CsD*A. The same applies for KDP and KD*P. Although there is additional splitting in the A_1 spectrum of the arsenates, which increases on deuteration, it is not possible to assign any of the additional modes to librations. It is known that deuteration leads to a weakening of the bonding between adjacent molecular groups, and as a result, we may expect the frequency of librational modes to decrease. No such effect is observed.

Since KDP is ionic we should expect the infra-red active B_2 and E modes to be affected by depolarising fields. The interaction between the LO mode and the depolarising field gives rise to a TO - LO splitting. Cochran and Cowley [40] have obtained a general result which relates the frequencies of these modes to the static and optic dielectric constants of the material,

$$\pi_i \left(\frac{\omega_{LO_i}}{\omega_{TO_i}} \right)^2 = \frac{\epsilon_a(0)}{\epsilon_a(\infty)}$$

where α is the direction of polarisation of the mode, and i includes all the infra-red active modes. Using this relation, Wilson [23] has estimated the splitting for the 95 cm^{-1} E mode in KDP to be $\sim 7 \text{ cm}^{-1}$, and he assigns the 113 cm^{-1} feature as the LO mode. However, his conclusions are not confirmed in CsDA and CsD*A. The mode which corresponds to his LO mode appears at $\sim 85 \text{ cm}^{-1}$ in both X(ZX)Z and X(ZX)Y configurations, as shown in figures 4.1 and 4.3; the latter configuration includes both LO and TO modes while the former contains only TO modes. The predicted splitting is certainly large enough to be observed in our experiment, so we can only conclude that the scattering efficiency for the LO modes may be very low.

The low frequency E spectrum is characterised by a wing on the Rayleigh line in CsDA, which broadens to become a fairly flat plateau in the case of KDP [35]; it is fairly temperature independent and is difficult to interpret in terms of the anomaly in the a-axis dielectric constant which occurs at T_c . Very recently, Scott and Wilson [35] have interpreted this lineshape in KDP as a resonant interference between the discrete state at 95 cm^{-1} and a background continuum extending over $0 - 100 \text{ cm}^{-1}$. They believe the latter to be the E-symmetry projection of the one-phonon density of states; these $q \neq 0$ modes can scatter light because of the disorder present in the crystal due to random proton location. Verification of this proposal requires a similar analysis for the other crystals in the class.

The extremely broad Rayleigh wing in the B_2 spectrum was first observed by Kaminow and Damen [21] in KDP and interpreted by them as an overdamped soft mode responsible for the ferroelectric phase transition. We have studied the temperature dependence of the overdamped modes and the results are discussed in chapters 5 and 6. The sharp dip in the B_2 spectrum of CsDA at $\sim 96 \text{ cm}^{-1}$ and the very asymmetric form of the mode at 140 cm^{-1} have been interpreted as due to a strong coupling between the modes [36].

Deuteration leads to a narrowing of the overdamped spectrum and a splitting of the higher frequency mode. Perry and Agrawal (private communication) have observed that the 213 cm^{-1} peak in the B_2 spectrum of KD*P is highly dependent on the deuterium content in the crystal. The intensity of this band increases as the deuteration increases from 30% to 98%. In addition to this, we have observed the 175 cm^{-1} component to be highly temperature dependent; it decreases rapidly in intensity as the transition is approached. Similar behaviour is observed more clearly in CsD*A where the modes appear at 105 and 195 cm^{-1} . In both cases, the lower frequency mode appears to be closely associated with the phase transition. Because of this complication, we have not attempted an accurate study of the overdamped modes in CsD*A and KD*P.

4.3.2 Internal modes

Several attempts have been made to assign the internal vibrations of the PO_4 group, using both Raman [17, 18, 22, 23, 26, 27, 28] and infra-red [1, 3, 8]

techniques. Stekhanov and Popova [17, 18] give a detailed analysis but were restricted through lack of polarisation information in their Raman data. She et al. [28] have recently considered the possibility of the phosphate ion in KDP behaving as a free molecule, as described in section 4.2. We now consider the possibility in CsDA.

The atomic displacements of the free tetrahedral molecule vibrations are described by Herzberg [38]; the free ions have vibrational frequencies:-

	<u>PO₄</u>	<u>AsO₄</u>
A ₁ (ν_1)	980 cm ⁻¹	700 cm ⁻¹
E (ν_2)	363	320
F (ν_4)	515	390
F (ν_3)	1082	840

In Table 4.4 we have the predicted splitting in a weak crystal field, and inspection of Table 4.5 leads us to make the following assignment:-

	<u>KDP</u>	<u>KD*P</u>	<u>CsDA</u>	<u>CsD*A</u>
ν_1 A ₁	918	887,968,1000	800	756,819,921
A ₂	inactive	inactive	inactive	inactive
A ₁	360	359	220,284	212,284
ν_2 B ₁	-	-	-	-
B ₂	386	385	305	298
B ₁	479	458	349	345
B ₂	510	520	370	406
ν_4 E	490	475	368	-
E	530	517	443	-

the ion groups, whereas the proton executes considerable dynamical motion between them.

It is interesting that Skalyo et al. [39] have observed a considerable distortion of the PO_4 group in KD^*P due to a very low frequency soft mode.

4.3.3 Hydrogen modes

The main types of vibration of the O - H...O system and their typical frequencies are shown in Table 4.6. The two broad bands at 2305 and 2662 cm^{-1} in CsDA, figure 4.2, may be interpreted as a doublet produced by ν_{OH} being split by proton tunneling between the two equilibrium positions along the O - O direction. The origin of their large width is uncertain; interactions of ν_{OH} with very low frequency vibrations such as δ (O - H...O) is one possibility. Combinations of ν_{OH} with other fundamentals, intensified by Fermi resonance, has been proposed; Popova and Savatinova [20] have recently stressed this possibility, but the evidence is far from conclusive. The mode at 1713 cm^{-1} in CsDA may be assigned to be in-plane bending, δ_{OH} ; the out-of-plane bending, γ_{OH} , is expected to be near 800 cm^{-1} - a range which is highly populated with AsO_4 internal modes - and so positive identification is difficult.

The effect of deuteration on these modes is shown below:-

	<u>KDP</u>	<u>KD*P</u>	<u>ρ</u>	<u>CsDA</u>	<u>CsD*A</u>	<u>ρ</u>
δ_{OH}	1830cm ⁻¹	1370cm ⁻¹	1.34	1713cm ⁻¹	1296cm ⁻¹	1.32
ν_{OH}	2390	1780	1.34	2305	1734	1.33
ν_{OH}	2710	2000	1.35	2662	1960	1.36

In addition, as shown in Table 4.5, new modes appear at 709 cm⁻¹ and 688 cm⁻¹ in KD*P and CsD*A respectively which may in fact be γ_{OH} . It is unclear why this mode should be inactive in the normal compounds. The most significant change is the almost harmonic shift in frequency of δ_{OH} and ν_{OH} ; ρ , the ratio of the frequencies in the normal and deuterated crystals, is ~ 1.35 . This would imply that these modes correspond to uncoupled vibrations of the protons in relatively simple potential wells. It is also apparent in figures 4.3 and 4.5 that these modes are active to a fair extent in the E-spectrum. This indicates that the deuterons move out of the a-b plane, which agrees qualitatively with the observations of Skalyo et al. [39]. This conclusion was also reached by Hill and Ichiki on the basis of their infra-red study [7]. It is of interest that Weiner et al. [8] have made a somewhat different assignment on the basis of their infra-red absorption data on polycrystalline samples.

Although our observations are not indicative of a double minimum potential well, this theory cannot be ruled out; such a potential may exist for collective motions of the protons, which are expected to couple strongly with lattice vibrations and occur at very low frequency. The symmetry of the collective modes is given by Blinc [30] (and is discussed in 1.3.3):-

$$\tau^{\text{coll.}} = A_2 + B_2 + E$$

The overdamped B_2 mode is interpreted as the collective mode, or at least a collective proton-phonon mixed mode. The wing on the Rayleigh line in the E spectrum may in fact correspond to the collective mode, but its lack of temperature dependence near T_c is inconsistent with observed dielectric behaviour.

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Table 4.1

Character table for point group $D_{2d}(\bar{4} 2 m)$

D_{2d}	E	$2S_4$	$C_2(z)$	$2C_2'$	$2\sigma_d$	Activity	
						IR	Raman
A_1	1	1	1	1	1	f	$p(xx,yy,zz)$
A_2	1	1	1	-1	-1	f	f
B_1	1	-1	1	1	-1	f	$p(xx,yy)$
B_2	1	-1	1	-1	1	$p(Tz)$	$p(xy)$
E	2	0	-2	0	0	$p(Tx,y)$	$p(xz,yz)$
$\chi(s_K)$	2	2	2	0	0		
$\chi(s_P)$	2	2	2	0	0		
$\chi(s_O)$	8	0	0	0	0		

Table 4.2

Character table for tetrahedral group T_d ($\bar{4}$ 3 m)

T_d	E	$8C_3$	$6\sigma_d$	$6S_4$	$3C_2$	mode	<u>Activity</u>	
							IR	Raman
A_1	1	1	1	1	1	ν_1	f	$p(xx,yy,zz)$
A_2	1	1	-1	-1	1		f	f
E	2	-1	0	0	2	ν_2	f	$p(xx,yy,zz)$
F_1	3	0	-1	1	-1		f	f
F_2	3	0	1	-1	-1	ν_3, ν_4	$p(Tx,yz)$	$p(xy,yz,zx)$

Table 4.3

Character table for point group $S_4 (\bar{4})$

S_4	E	C_2	S_4	S_4^3	<u>Activity</u>	
					IR	Raman
A	1	1	1	1	f	$p(xx,yy,zz)$
B	1	1	-1	-1	$p(Tz)$	$p(xx,yy,xy)$
E	1	-1	i	-i	$p(Tx)$	$p(xz,yz)$
	1	-1	-i	i	$p(Ty)$	$p(xz,yz)$

Table 4.4

Correlation table for PO_4 group with reduced symmetry

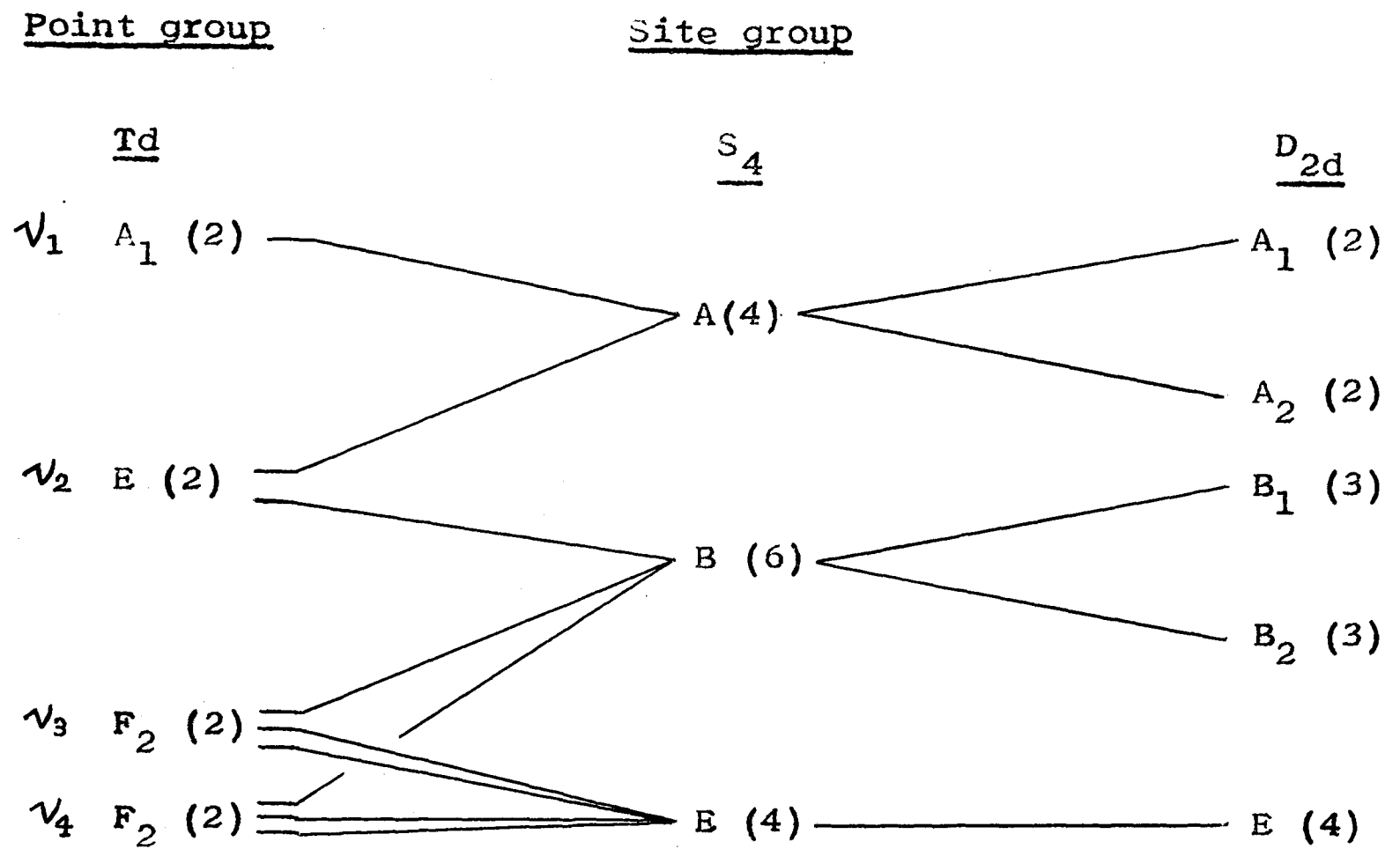


Table 4.5

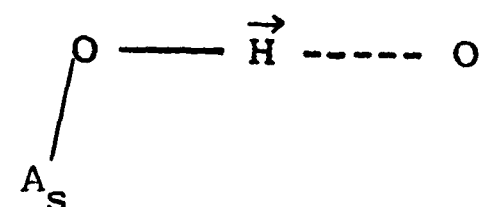
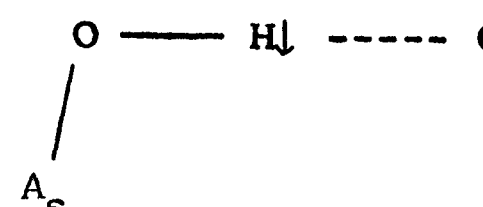
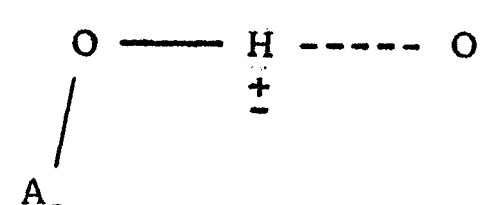
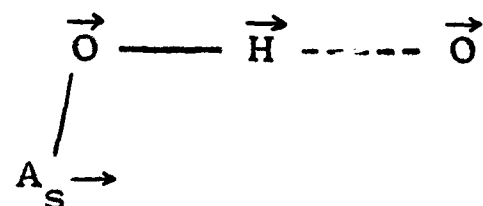
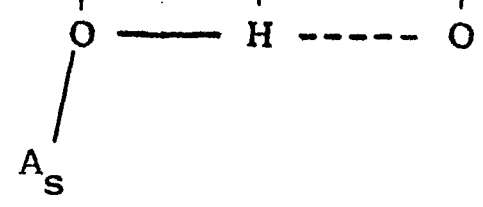
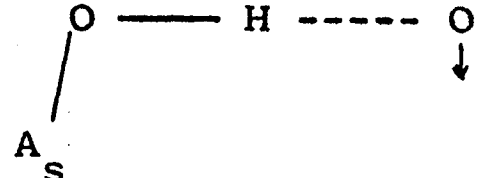
Assignment of Raman Active Mode Frequencies in KDP
and its Isomorphous Crystals at 295°K

Mode frequency (cm ⁻¹)						<u>Species</u>	<u>Assignment</u>
[26]	[27]	[27]	[27]				
RbDP	KDP	KD*P	KDA	CsDa	CsD*A		
				220	212	A ₁	
360	360	359	276	282	284	A ₁	ν ₂
520	514	510	385	372	369	A ₁	
		884*			756	A ₁	
920	918	968*	796	800	819	A ₁	
		1000*			921	A ₁	
123	156	155	137	126	126	B ₁	l
463	479	458	365	349	345	B ₁	ν ₄
520	570	551	455	441	426	B ₁	
		713			688	B ₁	γ _{OH}
	1315*		1330	1260		B ₁	
	1830*	1370*	1750	1713	1296	B ₁	δ OH
	2390*	1780*	2374	2305	1734	B ₁	ν OH
	2710*	2000*	2760	2662	1960	B ₁	ν OH
over'd	over'd	over'd	over'd	over'd	over'd	B ₂	
165	174	175	158	140	105	B ₂	l
		213			195	B ₂	γ(O-H-O)
385	386	385	299	305	298	B ₂	ν ₂
	510	520	433	370	406	B ₂	ν ₄
				762	760	B ₂	
				795	820	B ₂	ν ₃
	1350	1000	1292	1280	925	E ₂	δ OH
67	95	98	75	55	58	E	l
97	113	116	105	84	88	E	l
150	190	188	160	137	138	E	l
	320		300	300		E	
	490	475	365	368	364	E	ν ₄
540	530	517				E	ν ₄
560	568	548	498	440	413	E	
	960	937		775	760	E	ν ₃
	1100*	1130	865	875	886	E	ν ₃

RbDP ^[26]	KDP ^[27]	KD*P ^[27]	KDA ^[27]	CsDA	CsD*A	Species	Assignment
1145	1188	1114			935	E	
1325	1300	1330			1301	E	

*Data taken from [23]

Table 4.6 Vibrations of the Hydrogen atoms

<u>Type of Vibration</u>	<u>Description</u>	<u>Notation</u>
	OH stretching	ν_{OH}
	OH in-plane bending	δ_{OH}
	OH out-of-plane bending	γ_{OH}
	hydrogen bond stretching	$\nu(OH...O)$
	hydrogen bond bending	$\delta(OH...O)$
	hydrogen bond bending	$\gamma(OH...O)$

<u>Mode</u>	<u>Frequency range (cm⁻¹)</u>
ν_{OH}	1700 - 3500
δ_{OH}	1000 - 1700
γ_{OH}	500 - 1000
$\nu_{OH...O}$	50 - 250
$\delta + \gamma(OH...O)$	100

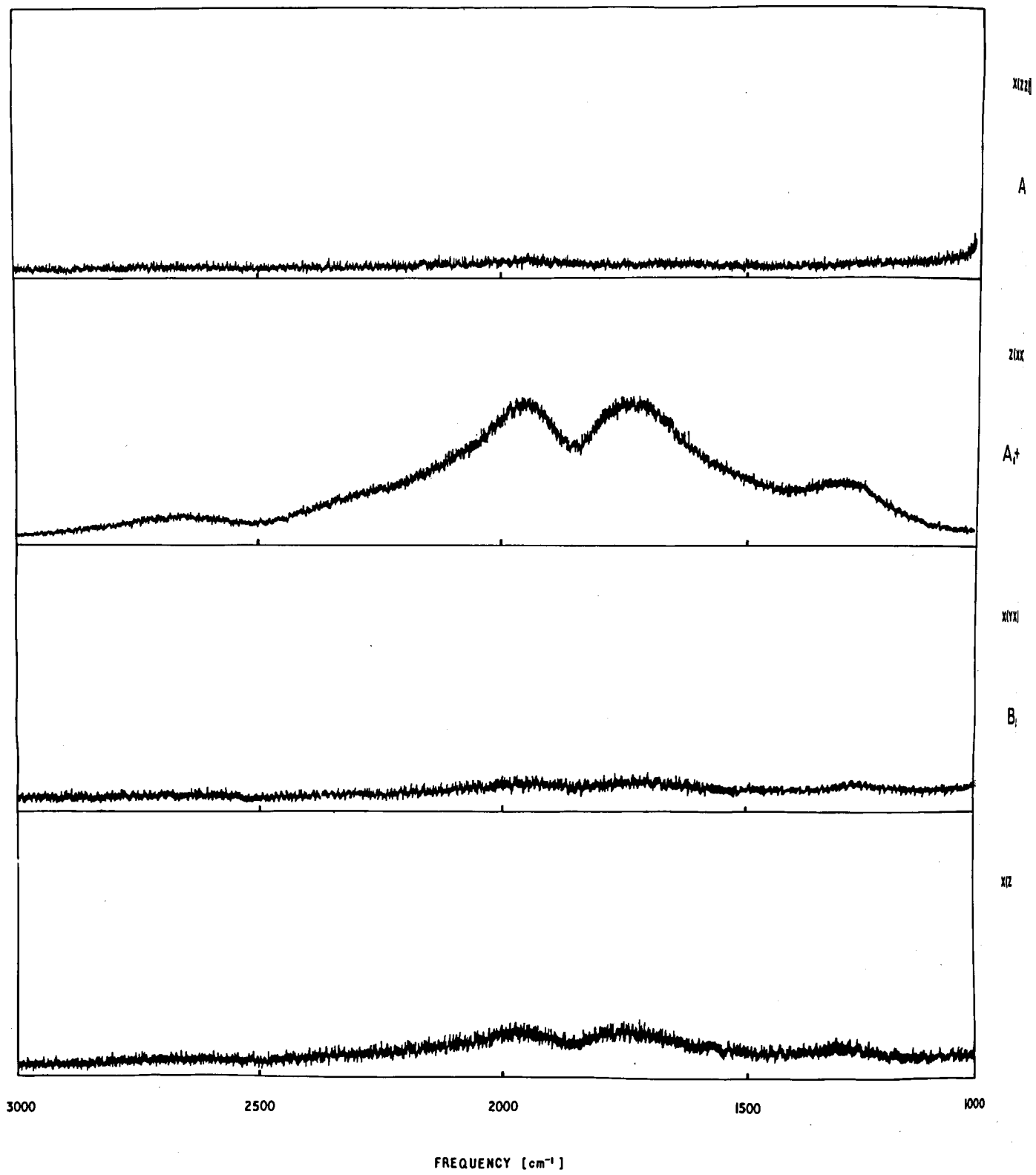


Figure 4.4

Raman spectrum of CsD*A, 1000 - 3000 cm^{-1}

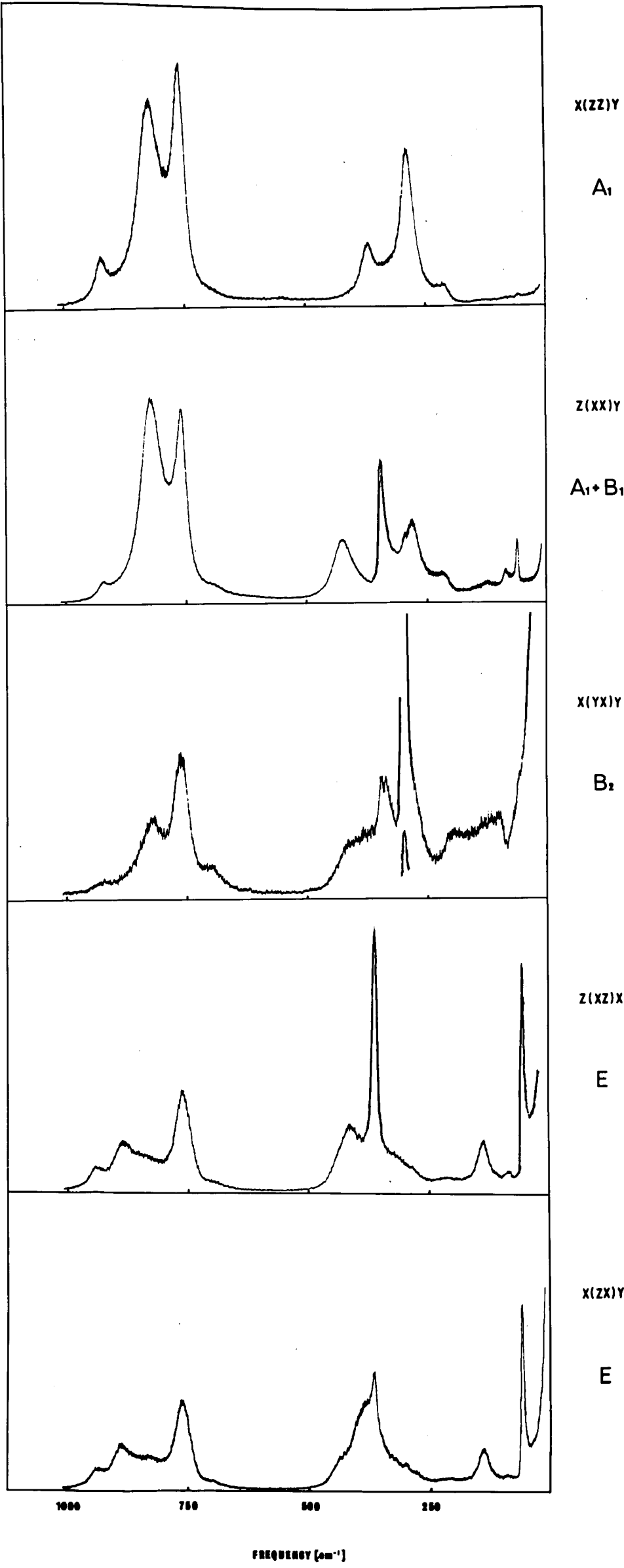


Figure 4.3

Raman spectrum of CsD*A, 0 - 1000 cm^{-1}

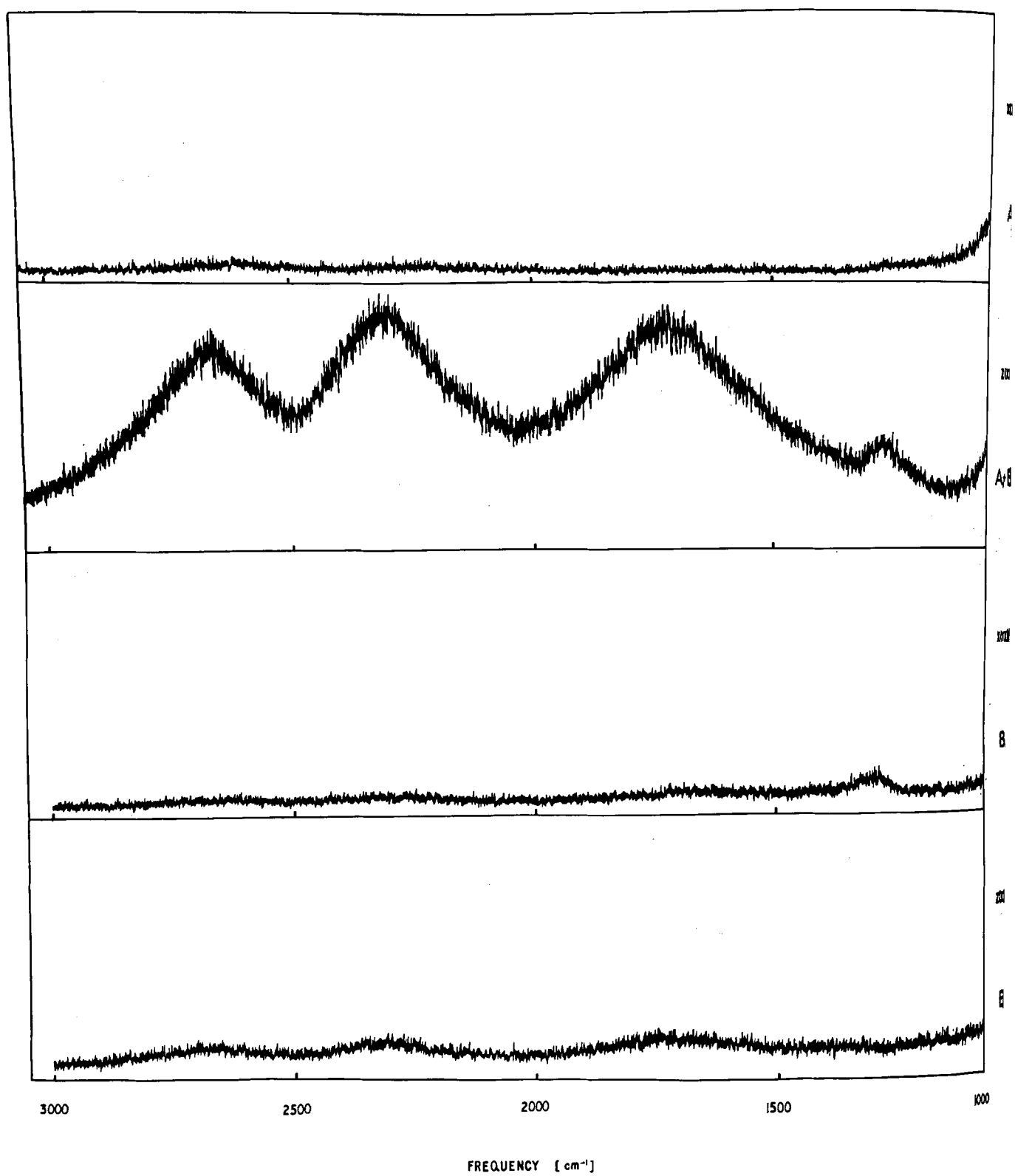


Figure 4.2

Raman spectrum of CsDA, 1000 - 3000 cm^{-1}

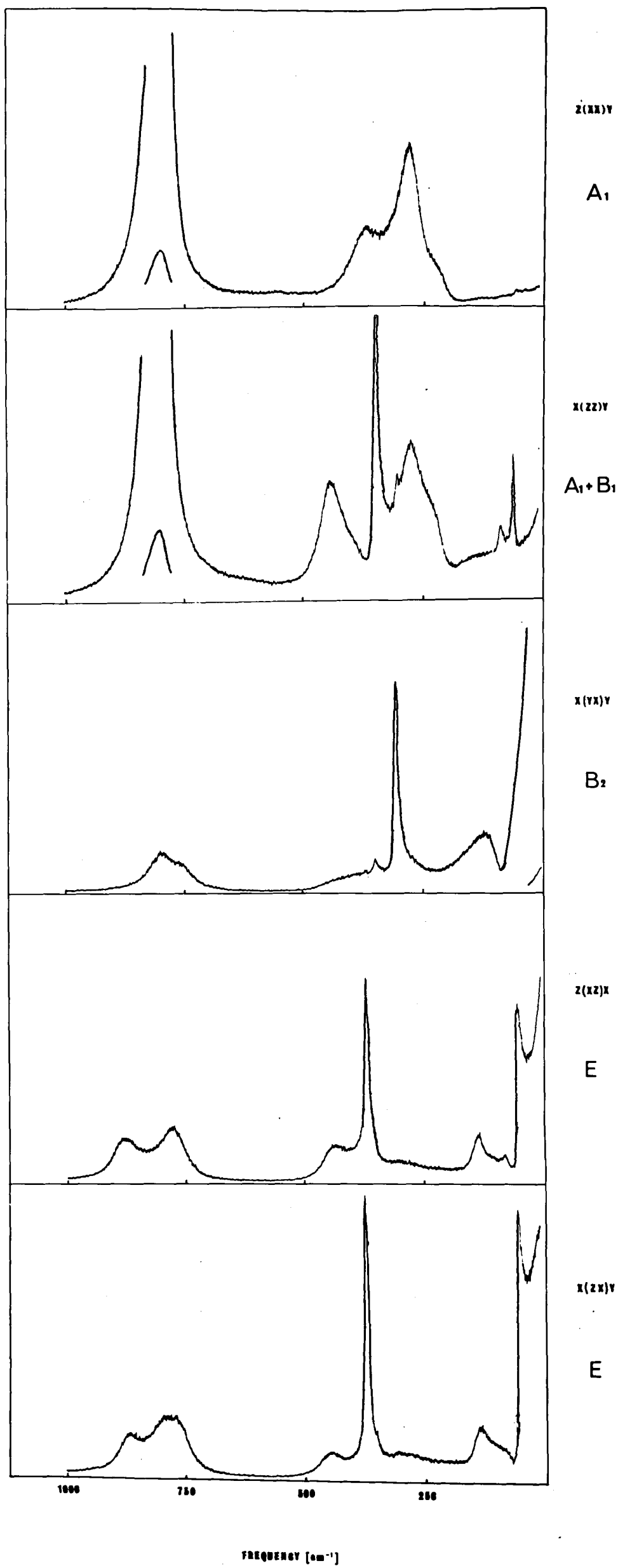


Figure 4.1

Raman spectrum of CsDA, 0-1000 cm^{-1}

CHAPTER 5

The Ferroelectric Mode in KDP-type crystals

5.1 Background

As discussed in Chapter 1 the dielectric anomaly in KDP is associated with an unstable vibrational mode. In Cochran's theory this is a lattice optic mode; the tunneling model predicts a highly temperature dependent collective proton mode whose frequency also tends to zero as the transition is approached. In 1963 Barker and Tinkham [1] observed a highly overdamped mode near 50 cm^{-1} in the far infra-red spectrum of KDP. They were unable to obtain a classical oscillator fit to their data but found a large decrease in frequency with temperature. Kaminow and Damen [2], in 1968, were the first to observe the broad wing in the B_2 symmetry Raman spectrum of KDP and interpreted it in terms of an overdamped mode. The spectrum was fitted to the damped oscillator response function

$$G^{-1}(\omega) = (\omega_0^2 - \omega^2 + i\gamma\omega) \quad (5.1)$$

The imaginary part of this function, multiplied by the Bose population factor and the mode strength, gives the spectral distribution of scattered light; it is plotted in figure 5.1 for $\omega_0 = 100 \text{ cm}^{-1}$ and various values of γ . We see that when $\gamma > \sqrt{2} \omega_0$ the peak in the response is at $\omega = 0$, and the profile becomes more highly overdamped as γ increases. This overdamped lineshape is

similar to that observed by Kaminow and Damen. They found $G(0)$ to have a Curie-Weiss temperature dependence while $\gamma (\approx 170 \text{ cm}^{-1})$ was approximately independent of temperature. As the transition is approached from above they obtained for the undamped frequency:-

$$\omega_0^2 = (99)^2 \left(\frac{T - 117}{T} \right) (\text{cm}^{-1})^2 \quad (5.2)$$

However, the coupling of the ferroelectric mode to the transverse acoustic mode produces a 'level repulsion' which drives the frequency of the latter to zero at $T_c = 122^\circ\text{K}$, the actual transition temperature. The difference between $T'_c = 117^\circ\text{K}$ and $T_c = 122^\circ\text{K}$ corresponds to the free and clamped response as discussed in chapter 1. This acoustic mode instability has been observed directly by Brody and Cummins [3] in the Brillouin spectrum of KDP. They also find for the ferroelectric mode

$$\bar{m} \omega_0^2 = 4.13 \times 10^{-3} (T - 117.7) \quad (5.3)$$

where $\bar{m}$ is an "effective mass density". These different temperature dependencies may not be inconsistent since $\bar{m}$ could be reasonably expected to be temperature dependent in an anharmonic crystal. On the other hand, since the Raman experiment records data from $10 - 100 \text{ cm}^{-1}$ and the Brillouin only the region below 10 cm^{-1} , this difference may indicate some additional frequency dependent factor not included in the analyses.

Also in 1968, Blinc and Zumer [4] observed an anomalous increase in the P^{31} spin-lattice relaxation time in KDP on approaching the phase transition. Assuming a temperature

independent damping for the soft mode they obtained for the undamped frequency a temperature dependence similar to expression (5.2).

The functional form $\omega_0^2 \propto (T - T_c)/T$ is that given by the pseudo-spin model (see equation 1.15). The theoretical significance of the damping constant is not clear, but if it is the same in both KDP and KD*P then we expect the frequency to be much lower in the latter. In this case the mode is highly overdamped, and the scattering occurs at low frequency such that $\omega^2 \ll \omega_0^2$. Equation (5.1) then reduces to

$$G^{-1}(\omega) = \omega_0^2 \left(1 + i \left\{ \frac{\gamma}{2\omega_0^2} \right\} \omega \right) \quad (5.4)$$

This is the form of the Debye response with the quantity γ/ω_0^2 being equivalent to the Debye relaxation time τ . Since the deuteron tunneling frequency is much smaller than that of the proton, the transition mechanism in the deuterated crystals is expected to be order-disorder in character. Therefore, both the highly overdamped phonon and the proton tunneling models predict the same form of response in deuterated crystals.

Magnetic resonance studies of the deuteron in KD*P [5] have shown the existence of deuteron "jumping" within the O-D-O bond, the actuation energy required for this process being consistent with the order-disorder model.

The neutron inelastic scattering study of KD*P by Paul et al. [6] has found the ferroelectric fluctuations to give rise to quasi-elastic scattering which increases with temperature as the transition is approached from above.

The lineshape was found to be of the Debye form but it was impossible to distinguish between both models. They obtained for the undamped frequency

$$\omega_o^2 = (4.6)^2 (T - T_c(q)) (\text{cm}^{-1})^2 \quad (5.5)$$

with $T_c(q)$ being dependent on the momentum transfer q .

In a microwave experiment on KD*P, Hill and Ichiki [7] obtained the real and imaginary parts of the dielectric susceptibility in the range $10^{-3} \text{ cm}^{-1} < \omega < 1 \text{ cm}^{-1}$, and a model which assumes a Gaussian distribution of Debye oscillators was used to fit the data. The distribution arises from the dependence of the local field at any one dipole on neighbouring clusters of dipoles of different sizes and orientations; all the dipoles are Debye oscillators but with different relaxation times. They obtained for the half-width of the distribution $\tau_o = 5 \times 10^{-9} / (T - 213) \text{ sec}$.

Their results can be compared with the low frequency Raman spectra obtained by White et al. [8] in the range $10^{-1} \text{ cm}^{-1} < \omega < 10 \text{ cm}^{-1}$; the distribution of relaxation times proved to be unsatisfactory in this case, and in addition, both the damped oscillator and Debye models failed to describe the Raman measurements over the entire frequency and temperature range studied.

Wilson [9] has conducted an extensive study of the Raman spectrum of KDP in an effort to resolve this problem. At high temperatures the damped oscillator model provided a good fit to the observed lineshape. However, near to and below T_c , the Debye spectrum proved to be more suitable.

This again suggests an additional factor present in the response which is not included in the existing simple models.

In the present experiments we have extended the Raman measurements to the other isomorphs of KDP, and the frequency region studied is extended to 300 cm^{-1} . A broad Rayleigh wing of B_2 symmetry is observed in each case, but in addition there is an underdamped lattice mode situated in the region $100 - 200\text{ cm}^{-1}$. In CsDA and KDA in particular, this underdamped mode lineshape is highly asymmetric, indicating a strong anharmonic interaction with the overdamped ferroelectric mode. That part of the wing below 100 cm^{-1} cannot be described as a damped harmonic oscillator nor as a Debye relaxation spectrum, but we have been able to obtain a fit by including coupling between the two modes.

The problem of mode coupling has in the past [3] caused great difficulty in determining critical exponents and the dynamical parameters ω_0 and γ ; however, it can give rise to lineshape anomalies and level repulsions from which much information can be extracted. There have been several different descriptions [10,11,12,13] of coupled modes in crystals, employing different notations and approximations. We give here a general anharmonic description of coupled oscillators and discuss the approximations and constraints valid in the present problem.

5.2 Coupled-mode analysis

A theory of the Raman scattering process is presented in chapter 2. Excitations in the crystal produce fluctuations in the optical polarisability and a scattering function $I(\omega)$ is obtained which is a measure of the correlation between such fluctuations. Equation (2.13) may be written for two normal modes

$$I(\omega) = K(n(\omega) + 1) [P_1 \ P_2]_{\text{cm}} \begin{bmatrix} G_{11} & G_{12} \\ G_{12} & G_{22} \end{bmatrix} \begin{bmatrix} P_1 \\ P_2 \end{bmatrix} \quad (5.6)$$

$n(\omega)$ is the Bose population factor, $\underline{G}$ is the one-phonon Green's function (discussed in Appendix 1) and P_1, P_2 determine the scattering strength of each mode. K is a constant depending on the experimental conditions and is required only when absolute cross-sections are to be measured. In the harmonic approximation each phonon is statistically independent, and this spectral function then consists of δ -functions at ω_1, ω_2 , the poles of the harmonic Green's function. Anharmonic effects give rise to finite phonon lifetimes and the Green's function then contains an additional self-energy term which describes the resulting frequency shift and width. When phonon modes have the same symmetry a polarisation mixing of states occurs and the off-diagonal elements of $\underline{G}$ may be non-zero. Equation (A1.16) for the case of two normal modes is then:-

$$\underline{G}^{-1}(\omega) = \begin{bmatrix} \omega_1^2 - \omega^2 & \\ & \omega_2^2 - \omega^2 \end{bmatrix} + \begin{bmatrix} 2(\Delta_{11} + i\Gamma_{11}\omega)\omega_1 & 2(\Delta_{12} + i\Gamma_{12}\omega)(\omega_1\omega_2)^{\frac{1}{2}} \\ 2(\Delta_{12} + i\Gamma_{12}\omega)(\omega_1\omega_2)^{\frac{1}{2}} & 2(\Delta_{22} + i\Gamma_{22}\omega)\omega_2 \end{bmatrix} \quad (5.7)$$

The first matrix on the right is the simple harmonic Green's function for two independent oscillators; the second term represents the self-energy contribution. To first order, Δ is frequency independent and linearly temperature dependent, (A1.20) and so we may re-normalise the frequencies:-

$$\hat{\omega}_1^2 = \omega_1^2 + 2 \Delta_{11} \omega_1$$

$$\hat{\omega}_2^2 = \omega_2^2 + 2 \Delta_{22} \omega_2$$

In the same approximation Γ is linearly dependent on both frequency and temperature (A1.21). In this case we can write:-

$$\gamma_{11}\omega = 2\omega_1 \Gamma_{11}$$

$$\gamma_{22}\omega = 2\omega_2 \Gamma_{22}$$

$$\gamma_{12}\omega = 2(\omega_1\omega_2)^{\frac{1}{2}} \Gamma_{12}$$

The Green's function describing the coupled modes is then:-

$$\underline{\underline{G}}^{-1}(\omega) = \begin{bmatrix} \hat{\omega}_1^2 - \omega^2 + i\gamma_{11}\omega & \Delta + i\gamma_{12}\omega \\ \Delta + i\gamma_{12}\omega & \hat{\omega}_2^2 - \omega^2 + i\gamma_{22}\omega \end{bmatrix} \quad (5.8)$$

That is, we assume anharmonic oscillator forms for both modes and include coupling via the real and imaginary off-diagonal terms. This is the form of $\underline{\underline{G}}^{-1}(\omega)$ expected at low frequency only since ω^3 terms in Γ may become important at high frequency. However, we shall assume that over the energy range of interest, i.e. 10 - 300 cm^{-1} , the parameters in (5.8) are frequency independent; more exactly, we replace frequency dependent quantities by their average values over this frequency range.

The Raman spectrum can therefore be calculated for a system of two coupled modes in terms of the seven parameters $\omega_1, \omega_2, \gamma_{11}, \gamma_{22}, \Delta, \gamma_{12}$ and P_1/P_2 . As discussed by Barker and Hopfield [10] there are an infinite number of solutions to the diagonalisation of $\underline{\underline{G}}^{-1}(\omega)$. This is illustrated by performing unitary transformations to obtain a new function $\underline{\underline{G}}^1$:-

$$\underline{\underline{G}}^1 = \underline{\underline{e}} \cdot \underline{\underline{G}} \cdot \underline{\underline{e}}^+$$

for arbitrary elements e_{ij} subject to

$$\underline{\underline{e}} \cdot \underline{\underline{e}}^+ = \underline{\underline{1}}$$

If we have new mode strengths

$$\underline{\underline{P}}' = \underline{\underline{e}} \underline{\underline{P}}$$

then

$$\begin{aligned} \underline{\underline{I}}' &= \underline{\underline{P}}' \cdot \underline{\underline{G}}^1 \cdot \underline{\underline{P}}' \\ &= \underline{\underline{P}} \underline{\underline{e}}^+ \underline{\underline{e}} \underline{\underline{G}} \underline{\underline{e}}^+ \underline{\underline{e}} \underline{\underline{P}} \\ &= \underline{\underline{I}} \end{aligned}$$

We can choose the e_{ij} such that $P_1' = 0$ or $\Delta' = 0$ etc.; we may always diagonalise the real part ($\Delta = 0$) or the imaginary part ($\gamma_{12} = 0$), the choice being equivalent to a choice of phase for the interacting modes. In general it is not possible to make a choice on the basis of data at a single temperature, and measurements over a range of temperatures are required. The constraints applied result from the model being employed and therefore the parameters evaluated will always be model dependent.

For the soft mode interaction in SbSI, Harbeke et al. [11] have used the approximation $\gamma_{12} = 0$ and $\gamma_{11}, \gamma_{22} \ll \hat{\omega}_1, \hat{\omega}_2$. There is then no lineshape anomaly but a

level repulsion occurs. The peaks in the response are given by $\left| \underline{G}(\omega) \right| = 0$, and are found to be

$$\omega_{\pm} = \frac{1}{2}(\hat{\omega}_1^2 + \hat{\omega}_2^2) \pm \frac{1}{2}\sqrt{(\hat{\omega}_1^2 - \hat{\omega}_2^2)^2 + 4\Delta^2} \quad (5.9)$$

$\hat{\omega}_1$ is a temperature dependent underdamped soft mode and the familiar level repulsion or anti-crossing is observed. At the opposite limit of approximation, assuming the line-width of one mode to be infinite, we obtain Fano's theory [14], successfully employed by Rousseau and Porto [12] for coupled modes in BaTiO_3 , and by Scott in AlPO_4 [15].

In the present analysis we have considered three models.

A) Model 1

This corresponds to the Kobayashi coupling scheme where the overdamped mode is the proton tunneling mode which is responsible for the ferroelectric phase transition. There is no dielectric moment associated with it and so $P_1' = 0$. The total dielectric moment must be associated with the transverse optical mode.

B) Model 2

This is analogous to the Barker-Hopfield model. In analysing the infra-red reflection spectra of BaTiO_3 and SrTiO_3 in terms of coupled modes, they chose a set of basis states such that

$$\gamma_1 \neq 0; \quad \gamma_2 = 0; \quad \gamma_{12} = 0$$

i.e. all the damping is associated with one oscillator. This is not always a possible choice since it requires the condition

$$\gamma_{12}^2 = \gamma_1 \gamma_2$$

In our model $\gamma_{12} = 0$; we obtain the result that the damping associated with the overdamped mode is very much greater than that of the underdamped mode, and so the above condition is almost valid.

C) Model 3

Since $\underline{\underline{G}}(\omega)$ describes the dielectric response of the material (see Appendix 2), $\underline{\underline{G}}(0)$ must obey a Curie-Weiss law. The static susceptibility is

$$\chi(0) = \frac{M_1^2 \hat{\omega}_2^2 - 2M_1 M_2 \Delta + M_2^2 \hat{\omega}_1^2}{\hat{\omega}_1^2 \hat{\omega}_2^2 - \Delta^2} \quad (5.9)$$

Inserting the relation $\hat{\omega}_1^2 \propto (T - T_c)$, as predicted by Cochran's theory, and assuming $\hat{\omega}_2^2$ to be temperature independent, we require $\Delta = 0$ to give the Curie-Weiss behaviour.

The calculated spectrum is obtained from a least squares fit of $\underline{\underline{G}}(\omega)$ to the observed spectrum using the constraints described. The results are discussed now in chapter 6.

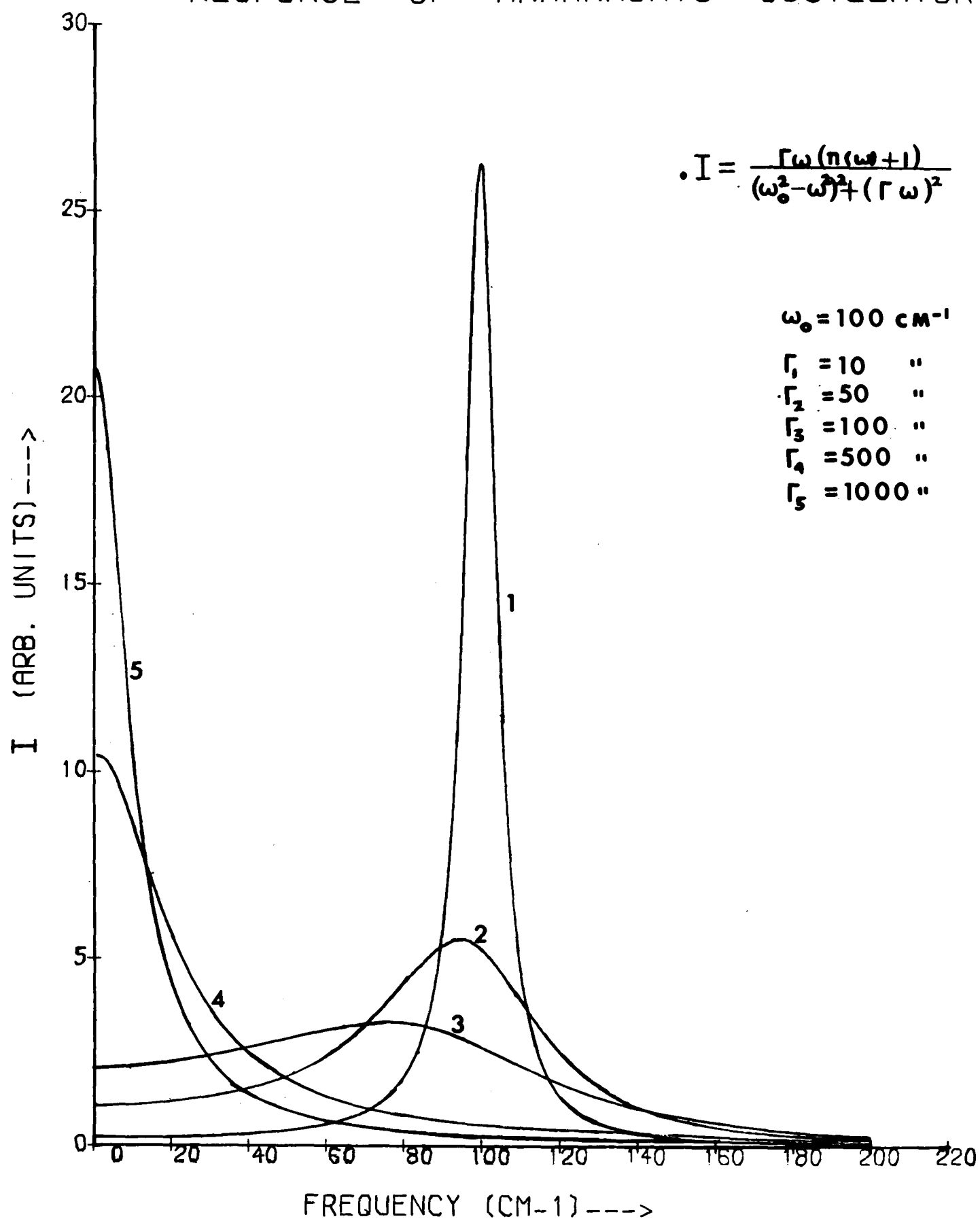
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Figure 5.1

Raman lineshape in the presence of damping.
The curves are plotted for various γ ranging from the lightly damped case to the highly overdamped case. When $\gamma > \sqrt{2} \omega_0$ then the peak in the response occurs at $\omega = 0$.

RESPONSE OF ANHARMONIC OSCILLATOR



CHAPTER 6

Temperature Dependence of the Ferroelectric Mode

6.1.1 Data acquisition

In these experiments we have measured the Raman spectrum in the region $10 - 300 \text{ cm}^{-1}$. The spectrometer used was the double-grating Spex 1400 which employs a linear wavelength scan. The energy scale was converted to frequency in wavenumbers by a simple computer program, and the Raman intensity was corrected for laser power fluctuations. The time constant of the ratemeter was determined by the count rate obtained, and the scan speed was selected accordingly. The slitwidth was chosen to correspond with a resolution of $\approx 10 \text{ cm}^{-1}$. Both the Anti-Stokes and the Stokes regions were studied, but only the latter is presented here.

6.1.2 Data fitting

In fitting the various response functions to the experimental data we have used a computer program developed by Marquandt [1] and modified by R.S. Katiyar. Since $I(\omega)$ is not linear in γ and $\hat{\omega}_0$ a non-linear least squares fit must be made. Initial estimates of the parameters are required which are then adjusted so as to minimise the quantity

$$\chi^2 = \sum_{i=1}^m \left(\frac{I_{o_i} - I_{c_i}}{\sigma_i} \right)^2$$

where I_o is the observed intensity and σ its uncertainty,

and I_c is the calculated intensity. The basic criterion for convergence is that the fractional change in the parameters on successive iterations should be less than some very small value, in our case $\sim 10^{-3}$.

Once the iteration has converged, the program lists the final values of the parameters and their uncertainties. The value of χ^2 at the minimum, χ_M^2 , is given, and the normalised value or agreement factor

$$\phi = \left(\frac{\chi_M^2}{NF} \right)^{\frac{1}{2}} \quad (6.1)$$

provides a comparison of the goodness of fit for different spectra. NF is the number of degrees of freedom given by:-

$$NF = NO - NV + 1$$

where NO is the number of observations or data points, and NV is the number of variable parameters.

Finally, the parameter correlation matrix $\underline{R}$ is also given. This gives an estimate of how well the parameters of the model can be obtained separately. Very large non-diagonal terms indicate a high correlation and suggest that a model with different or fewer parameters would be more satisfactory. This is the situation when a mode is highly overdamped and the two parameters γ and $\hat{\omega}_0$ are better replaced by $\tau = \gamma / \hat{\omega}_0^2$; the damped oscillator model then reduces to the Debye model, with relaxation time τ . When comparing the two models, the variance in τ must include a term arising from the correlation of γ and $\hat{\omega}_0$.

We have then

$$\sigma_\tau^2 = \sigma_{\hat{\omega}_0}^2 \left(\frac{2\omega_0}{\gamma} \right)^2 - 4 \left(\frac{\hat{\omega}_0}{\gamma} \right)^3 R \sigma_{\hat{\omega}_0} \sigma_\gamma + \left(\frac{\hat{\omega}_0}{\gamma} \right)^4 \sigma_\gamma^2$$

The additional term is important when R is large.

6.2 Analysis of KDP spectra

The spectra obtained for KDP at a number of temperatures in the paraelectric phase are shown in figure 6.1. We have the broad Rayleigh wing extending out to 250 cm^{-1} , and at 180 cm^{-1} overlaps an underdamped mode. As the temperature is lowered the wing narrows and increases in intensity at lower frequency. The asymmetry in the lineshape of the other mode suggests an interaction between the two modes. In addition, the intensity between the modes is slightly lower than that on the high frequency side; if the intensities were simply additive, then the converse would be expected. This is a further indication of coupling.

Initially we have analysed the spectra in terms of the damped simple harmonic oscillator (DSHO) and Debye models, and have obtained a comparison with the results of Wilson [2] and Kaminow and Damen [3]. The more complete analysis involves a detailed consideration of coupling.

6.2.1 DSHO model

The lineshape in the region $10 - 100 \text{ cm}^{-1}$ has been fitted with the function

$$I(\omega) = \frac{P^2 \gamma \omega \{n(\omega) + 1\}}{(\hat{\omega}_0^2 - \omega^2)^2 + \gamma^2 \omega^2} \quad (6.2)$$

and the parameters obtained are given in Table 6.1.

The room temperature values of γ and $\hat{\omega}_0$ are 233 and 99 cm^{-1}

respectively; the corresponding values obtained by Kaminow and Damen are 170 and 75 cm^{-1} . The difference arises mainly from the correlation between the parameters ($R = 0.7$), and by constraining the upper limit of allowed values of γ and $\hat{\omega}_0$ we can obtain results similar to those of Kaminow and Damen. The fairly large value of R indicates that we should replace the two parameters by the Debye relaxation time. The above two sets of data then give for τ , 0.8×10^{-12} sec. and 1.0×10^{-12} sec. In figure 6.2 we compare the temperature dependence of T/τ for both experiments. A linear relation of the form :-

$$\frac{T}{\tau} = A(T - T_0) \quad (6.3)$$

gives a good description: we find $T_0 = 120\text{K}$, while Kaminow and Damen obtain the value of 117K.

However, we find also - in agreement with Wilson - that the quality of the fit becomes poorer as the transition is neared. The agreement factor, ϕ , increases from 0.7 at $T = 295\text{K}$, to 1.7 at $T = 126\text{K}$. A slight improvement is found when we analyse only the data in the region 10 - 70 cm^{-1} .

6.2.2 Debye model

The above results suggest that the Debye relaxation spectrum may give a better description of the overdamped mode lineshape. The response function is then:-

$$I(\omega) = \left\{ n(\omega) + 1 \right\} \frac{P^2 \omega \tau}{1 + \omega^2 \tau^2} \quad (6.4)$$

The parameters obtained are given in Table 6.2. As the transition is approached both P and γ diverge. In figure 6.2 we have plotted I/γ for the different spectra and compare the result with that of the DSHO model and Kaminow and Damen's data. Agreement with the latter is very good.

Once again, we find that the quality of the fit deteriorates near the transition. In addition, the fit is poor if all the data with $10 \text{ cm}^{-1} < \omega < 100 \text{ cm}^{-1}$ is employed and only the region below 70 cm^{-1} can be described satisfactorily. The intensity at higher frequency is greater than that predicted by the Debye model. To account for this we must include in the analysis the scattering from the higher frequency underdamped mode. Initially we consider both modes to be independent.

6.2.3 Two uncoupled oscillators

The scattering from two independent modes is given by an extension of equation (6.2):-

$$I(\omega) = \{n(\omega) + 1\} \left[\frac{P_1^2 \gamma_1 \omega}{(\hat{\omega}_1^2 - \omega^2)^2 + \gamma_1^2 \omega^2} + \frac{P_2^2 \gamma_2 \omega}{(\hat{\omega}_2^2 - \omega^2)^2 + \gamma_2^2 \omega^2} \right] \quad (6.5)$$

The values of the six parameters for the 295K spectrum are listed in Table 6.3 and the fit obtained is shown in figure 6.3. The result is rather unsatisfactory; it is apparent that the lineshape in the region $100 - 200 \text{ cm}^{-1}$ cannot be reproduced by this model. We have also attempted to obtain a fit combining a Debye relaxation spectrum and a classical oscillator response, but the

results show no improvement.

Therefore, as the preliminary inspection of the spectra indicated, we must extend this simple treatment and consider the full form of the coupled mode response expressed in equation (5.8).

6.2.4 Coupled mode analysis

The response function for two coupled modes is given by equation (5.8):-

$$\begin{aligned}
 I(\omega) = & \{n(\omega) + 1\} \omega [(\gamma_1 \Delta_2 \hat{\omega}_2^2 + \gamma_2 \Delta_1 \hat{\omega}_1^2 - 2 \Delta \gamma_{12}) \\
 & (P_1^2 \Delta_2 \hat{\omega}_2^2 + P_2^2 \Delta_1 \hat{\omega}_1^2 - 2P_1 P_2 \Delta) - (\Delta_1 \Delta_2 \hat{\omega}_1^2 \hat{\omega}_2^2 + \omega^2 \\
 & \{ \gamma_{12}^2 - \gamma_1 \gamma_2 \} - \Delta^2) (P_1^2 \gamma_2 + P_2^2 \gamma_1 - 2P_1 P_2 \gamma_{12})] / \\
 & [\Delta_1 \Delta_2 \hat{\omega}_1^2 \hat{\omega}_2^2 + \omega^2 \{ \gamma_{12}^2 - \gamma_1 \gamma_2 \} - \Delta^2)^2 + \\
 & \omega^2 (\gamma_1 \Delta_2 \hat{\omega}_2^2 + \gamma_2 \Delta_1 \hat{\omega}_1^2 - 2 \Delta \gamma_{12})^2] \quad (6.6)
 \end{aligned}$$

where $\Delta_1 = 1 - \frac{\omega^2}{\hat{\omega}_1^2}$ and $\Delta_2 = 1 - \frac{\omega^2}{\hat{\omega}_2^2}$. Making use of unitary transformations we have shown in chapter 5 that there are an infinite number of solutions to this problem. We can, however, arrive at unique solutions by applying suitable constraints, which are determined by the choice of model. We have already discussed the situation where $\Delta = \gamma_{12} = 0$ and the two modes are uncoupled. We now consider the three models illustrated in chapter 5 where the coupling is non-zero.

(i) $P_1 = 0$

This model is analogous to the Kobayashi theory for KDP-structure hydrogen-bonded ferroelectrics in which

the pseudo-spin tunneling mode is viewed as having no direct contribution to the dielectric function, only indirect through phonon coupling. The oscillator parameters obtained with $P_1 = 0$ are shown in Table 6.4. While we obtain algebraic solutions, they are physically different from Kobayashi's theory. The data can be fitted by two modes, one having zero polarisability and underdamped (this corresponds to the tunneling mode which is overdamped in the prevailing view of KDP structures), and the other having non-zero polarisability and overdamped (this corresponds to the phonon mode). We conclude that the coupled modes in KDP do not correspond closely to the Kobayashi theory, and that it will be necessary to associate greater polarisation with the tunneling mode than with the phonon in order to obtain a physically realistic model.

$$(ii) \quad \underline{\gamma_{12} = 0}$$

We see from Table 6.4 that $\gamma_2 \approx 0$ when $\gamma_{12} = 0$, and so the model corresponds closely to that of Barker and Hopfield, i.e. all the damping is due to one oscillator. In figure 6.4 we have the spectral response of the coupled and uncoupled modes. The lineshape over the entire frequency range is now described very accurately. The underdamped TO mode occurs near the dip in the spectrum and is much weaker than the overdamped mode. At room temperature the soft mode is almost underdamped ($\gamma_1 = 1.5 \hat{\omega}_1$), and $\tau = 0.4 \times 10^{-12}$ sec.; the relaxation time is therefore reduced by a factor of 2 on that determined by the DSHO

model in 6.2.1. The temperature dependence of T/τ is plotted in figure 6.5; once again a linear relationship provides a good description, but now the intercept is at $T_0 = 53\text{K}$. This differs considerably from the actual transition temperature, $T_c = 122\text{K}$.

(iii) $\Delta = 0$

The coupled and uncoupled modes corresponding to this model are shown in figure 6.6. The response of the uncoupled overdamped mode is now very close to the observed lineshape, and the underdamped mode is extremely broad with frequency near to the peak in the spectrum. The minimum in the observed intensity at 150 cm^{-1} we see is quite different from a simple addition of the contribution from both modes and illustrates well the effect of coupling. The width of this mode and the coupling constant decrease with temperature in a well-behaved manner, while the frequency hardens slightly. As shown in figure 6.5, (T/τ) for the overdamped mode decreases linearly to zero at 112K .

6.3 Analysis of KDA spectra

Replacement of phosphorous by arsenic in KDP lowers the transition temperature to $T_c = 92\text{K}$. The Raman spectra in figure 6.7 are similar to the KDP spectra in figure 6.1, but now overdamped mode is narrower and the underdamped mode is shifted from 180 cm^{-1} to 160 cm^{-1} . However, this feature is now very asymmetric and the dip in the intensity at 130 cm^{-1} is much more pronounced.

This may be understood qualitatively in terms of a stronger anharmonic interaction due to the modes being closer in frequency. The coupled mode analysis has been repeated as for KDP and the parameters are given in Table 6.5

$$(i) \quad \underline{P_1 = 0}$$

Again, we find a contradiction with Kobayashi's theory in that the mode with zero polarisability is underdamped and largely temperature independent. The ferroelectric mode is overdamped and has a large non-zero polarisability.

$$(ii) \quad \underline{\gamma_{12} = 0}$$

At $T = 295K$, $\tau = 0.5 \times 10^{-12}$ sec. which is very close to the value of 0.4×10^{-12} found for KDP. The coupled modes are shown in figure 6.8 and once more we see that the underdamped mode occurs at the minimum in the intensity, but now its strength is increased and the effect of coupling on the observed lineshape much larger. The temperature dependence of T/τ is plotted for the overdamped mode in figure 6.9 and has an intercept with T-axis at $T_0 = 75K$.

$$(iii) \quad \underline{\Delta = 0}$$

We see from figure 6.10 that the lattice mode is almost overdamped at 295K ($\gamma_1 \approx 1.25 \hat{\omega}_1$) and the soft mode is distorted considerably from the observed overdamped lineshape. The temperature dependence of the soft mode is shown in figure 6.9 and τ diverges at $T_0 \approx T_c = 92K$. However, the parameters for the underdamped mode are largely temperature independent but its polarisability is greater than that of the ferroelectric mode.

6.4 Analysis of CsDA spectra

Further replacement of potassium by caesium to produce CsDA now gives rise to a peak in the spectrum at $\sim 110 \text{ cm}^{-1}$, (see figure 6.11). The Rayleigh wing is very narrow and the TO mode lineshape is extremely asymmetric. The parameters derived from the coupled mode analysis are given in Table 6.6.

(i) $P_1 = 0$

What we have already said for KDP and KDA also applies for CsDA. Although algebraic solutions are obtained, the parameters are quite different from those predicted by Kobayashi's theory.

(ii) $\gamma_{12} = 0$

The coupling coefficient Δ is now much larger than in KDP or KDA and the uncoupled underdamped mode in figure 6.12 occurs nearer the peak in the spectrum. The frequency of this mode is not significantly temperature dependent. T/τ for the overdamped mode is plotted in figure 6.13 and the intercept is found to occur at $T_0 = 69\text{K}$, whereas the transition occurs at 143K .

(iii) $\Delta = 0$

This decoupling is illustrated in figure 6.14 for $T = 295\text{K}$. Again, the second mode is nearly overdamped ($\gamma_1 = 1.34 \hat{\omega}_1$), but it is now temperature dependent. This must be taken into account when comparison is made with the static dielectric susceptibility. The relaxation time of the ferroelectric mode is shown in figure 6.13, and we obtain $T_0 = 61\text{K}$.

6.5 Discussion

The extension of the lineshape analysis of the overdamped mode to include coupling with the lowest frequency TO phonon therefore indicates a new effect which has not previously been considered. We find that the Debye relaxation time diverges at a temperature below the actual transition temperature. This cannot arise because of the difference between the free and clamped Curie temperatures since we know from chapter 1 that this amounts to no more than about 5K. Likewise, the difference between T_0 and T_c does not arise from the first order nature of the transition since it is well established that the transition is very nearly second order. We are therefore led to examine more closely the response function used in our description. Since the oscillator parameters are obviously model dependent, it is convenient to discuss each model separately.

6.5.1 Model 1

In the mode coupling scheme proposed by Kobayashi the collective proton mode responsible for the phase transition interacts with a phonon mode. The former has zero dielectric moment but the coupled mode which softens possesses a component indirectly through coupling. Our Raman spectra show that the ferroelectric mode is overdamped, while the lattice mode is underdamped and temperature independent. The view is then that the proton tunneling mode is overdamped.

The solutions we have obtained to this model produce the conflicting result that the ferroelectric mode is

overdamped but has a large polarisability. In addition, the infra-red reflectivity analysis of CsDA in Appendix 2 indicates that the dielectric moment associated with the overdamped mode has a large non-zero value. Although it has been established that the proton displacement has a component in the c direction, approximately $0.02A$, it is not sufficient to give rise to this effect. However, the Kobayashi description may yet be valid if the collective proton mode occurs at very low frequency and is not resolved in our experiment. It is interesting that Mossbauer experiments by Brunstein et al. [4] have indicated the presence of a mode at 10^7 Hz.

6.5.2 Model 2

We have seen in chapter 5 that a consideration of real coupling only, i.e. $\Delta \neq 0$, $\gamma_{12} = 0$, gives a good description of the level repulsion observed when the two interacting modes are underdamped. In our case, although the level repulsion cannot be observed with the overdamped mode, this model provides a convenient description of the observed spectrum. The ferroelectric mode is overdamped while the second mode is underdamped. However, the Debye relaxation time of the overdamped mode is found to diverge at some temperature below the actual transition temperature:-

	T_C (K)	T_O (K)	$\Delta^{\frac{1}{2}}$ (cm^{-1})
KDA	92	75 ± 4	110
KDP	122	53 ± 5	110
CsDA	147	69 ± 7	170

To compare T_0 and T_c we must examine the static response of the coupled mode system:-

$$\chi(0) = \frac{P_1^2 \hat{\omega}_2^2 - 2P_1 P_2 \Delta + P_2^2 \hat{\omega}_1^2}{\hat{\omega}_1^2 \hat{\omega}_2^2 - \Delta^2} \quad (6.7)$$

When $\Delta = 0$, we obtain $\chi(0) = \frac{P_1^2}{\hat{\omega}_1^2} + \frac{P_2^2}{\hat{\omega}_2^2}$, and with $\hat{\omega}_1^2 \propto (T - T_c)$

the simple Curie Weiss form is obtained for $\chi(0)$. However, when the coupling is non-zero the full form of this expression must be considered. It may be re-written (when $\hat{\omega}_2$ is constant):-

$$\frac{C}{T - T_c} = \frac{\hat{\omega}_1^2 + A}{\hat{\omega}_1^2 - B}$$

where $A = (P_1^2 \hat{\omega}_2^2 - 2P_1 P_2 \Delta) / P_2^2$

$$B = \Delta^2 / \hat{\omega}_2^2$$

$$C = C' \cdot \hat{\omega}_2^2 / P_2^2$$

and $\chi(0) = C' / (T - T_c)$

The result is then:-

$$\hat{\omega}_1^2 = \frac{A(T - T_0)}{T_1 - T} \quad (6.8)$$

with $T_0 = T_c - \frac{BC}{A}$

$$T_1 = T_c + C \quad (6.9)$$

The constants A and C are difficult to estimate since the polarisabilities P_1 and P_2 are known only in arbitrary units (absolute intensity measurements would be required to estimate the value of K in equation (5.6) and so give absolute values of P_1 and P_2). But, if C is large then

the denominator will not vary much with temperature over the range studied. The model then predicts that $\hat{\omega}_1^2$, or T/τ , will go to zero at $T_0 < T_c$.

The singularity in the susceptibility then occurs when $\hat{\omega}_1^2 = B$, or more fully:-

$$(\omega_1^2 + 2 \Delta_{11} \omega_1)(\omega_2^2 + 2 \Delta_{22} \omega_2) = \Delta_{12}^2$$

This is a significant departure from the conventional soft mode picture since the generalisation of the Lyddane-Sachs-Teller relation in (1.23) indicates that the product is zero at T_c . We see now that the off-diagonal elements of the self-energy matrix are important, and must be included in the discussion. However, when there is no such coupling of the ferroelectric mode to other phonons, the normal behaviour is expected.

6.5.3 Model 3

When the coupling is purely imaginary i.e. $\gamma_{12} \neq 0$, $\Delta = 0$, the static dielectric susceptibility reverts to the simplified expression:-

$$\chi(0) = \frac{P_1^2}{\hat{\omega}_1^2} + \frac{P_2^2}{\hat{\omega}_2^2} \quad (6.10)$$

Since $\chi(0)$ obeys a Curie-Weiss temperature dependence we expect the frequency to follow the simple dependence $\hat{\omega}_1^2 \propto (T - T_c)$. However, our results above have shown that in fact there are departures from the Lyddane-Sachs-Teller behaviour:-

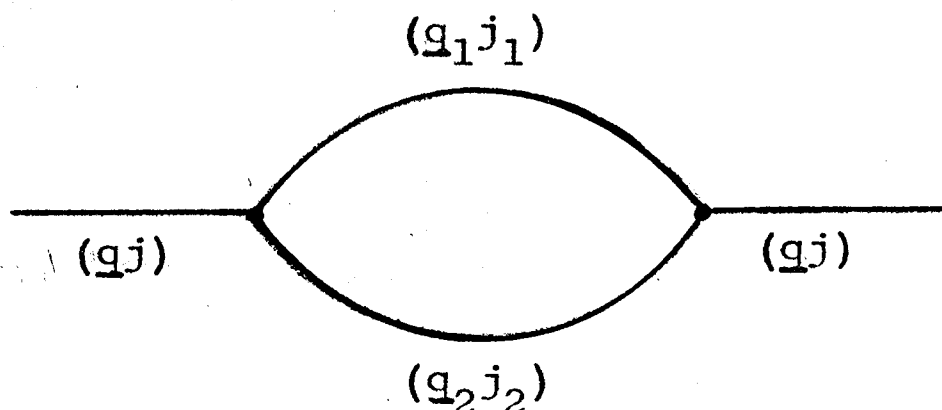
	T_0 (K)	T_c (K)
KDA	92 ± 4	92
KDP	112 ± 4	122
CsDA	61 ± 6	143

Previously the effect was explained in terms of coupling between two modes, but this no longer applies here. It would appear then that the damped harmonic oscillator of the soft mode is not an adequate description.

In the anharmonic theory of lattice dynamics the damping of modes arises from decay of the phonon into other modes. As discussed in Appendix 1, the self-energy consists of a summation over all the possible interaction vertices, and the one-phonon response function becomes:-

$$G^{-1}(\underline{q}j, \omega) = [\omega(\underline{q}j)^2 - \omega^2 + 2\omega(\underline{q}j) \{ \Delta(\underline{q}j, \omega) + i \Gamma(\underline{q}j, \omega) \}] \quad (6.11)$$

where $(\underline{q}j, \omega)$ and $(\underline{q}j, \omega)$ are the resulting frequency shift and width. In first order perturbation theory only the cubic anharmonic interaction is important:-



From equation (A1.18) we see that the anharmonic perturbation is then:-

$$H_A = \sum_{\underline{q}, \underline{q}_1, \underline{q}_2} v\left(\frac{\underline{q}}{j} \frac{\underline{q}_1}{j_1} \frac{\underline{q}_2}{j_2}\right) A(\underline{q}j) A(\underline{q}_1j_1) A(\underline{q}_2j_2) \quad (6.12)$$

and consequently:-

$$\Delta(\underline{q}j, \omega) = - \frac{18}{\hbar^2} \sum_{\underline{q}_1j_1, \underline{q}_2j_2} \left| v\left(\frac{\underline{q}}{j} \frac{\underline{q}_1}{j_1} \frac{\underline{q}_2}{j_2}\right) \right|^2 \{ (n_1 + n_2 + 1)$$

$$\left[\frac{1}{(\omega_1 + \omega_2 + \omega)_p} + \frac{1}{(\omega_1 + \omega_2 - \omega)_p} \right] + (n_2 - n_1) \left[\frac{1}{(\omega_1 - \omega_2 + \omega)_p} + \frac{1}{(\omega_1 - \omega_2 - \omega)_p} \right] \} \quad (6.13)$$

and

$$\Gamma(qj, \omega) = \frac{18\pi}{\hbar^2} \sum_{\substack{q_1 j_1 \\ q_2 j_2}} |v(\begin{smallmatrix} q & q_1 & q_2 \\ j & j_1 & j_2 \end{smallmatrix})|^2 \{ (n_2 + n_1 + 1) \}$$

$$\left[\delta(\omega_1 + \omega_2 - \omega) - \delta(\omega_1 + \omega_2 + \omega) \right] + (n_2 - n_1) \left[\delta(\omega_2 - \omega_1 + \omega) - \delta(\omega_1 - \omega_2 + \omega) \right] \} \quad (6.14)$$

(c.f. equations A1.19 and A1.21).

The high frequency response is the well known classical damped harmonic oscillator. However, we see from these two equations that the self-energy is not well defined for $j_1 = j_2$ in the limit $q \rightarrow 0$, $\omega \rightarrow 0$, unless $v(\begin{smallmatrix} 0 & q & -q \\ j & j_1 & j_2 \end{smallmatrix})$ is zero. In ferroelectric crystals we are concerned basically with processes occurring near this limit.

By definition:-

$$v(\begin{smallmatrix} 0 & q & -q \\ j & j_1 & j_1 \end{smallmatrix}) = v(\begin{smallmatrix} 0 & -q & q \\ j & j_1 & j_1 \end{smallmatrix}) \quad (6.15)$$

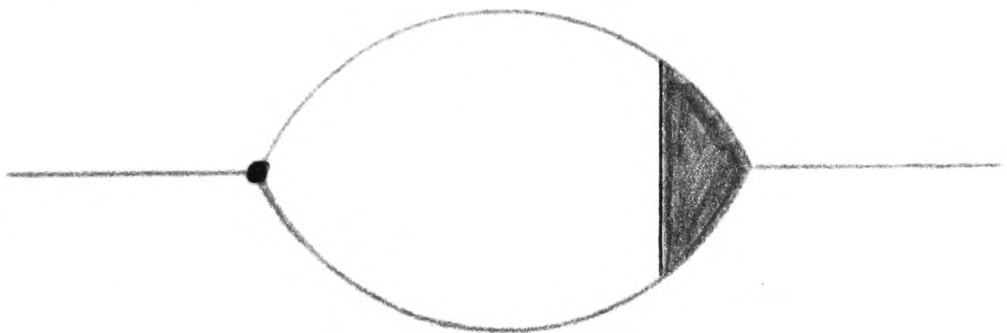
In addition, if the mode $(0j)$ gives rise to dielectric fluctuations, i.e. is infra-red active, then for non-piezoelectric crystals:-

$$v(\begin{smallmatrix} 0 & q & -q \\ j & j_1 & j_1 \end{smallmatrix}) = -v(\begin{smallmatrix} 0 & -q & q \\ j & j_1 & j_1 \end{smallmatrix}) \quad (6.16)$$

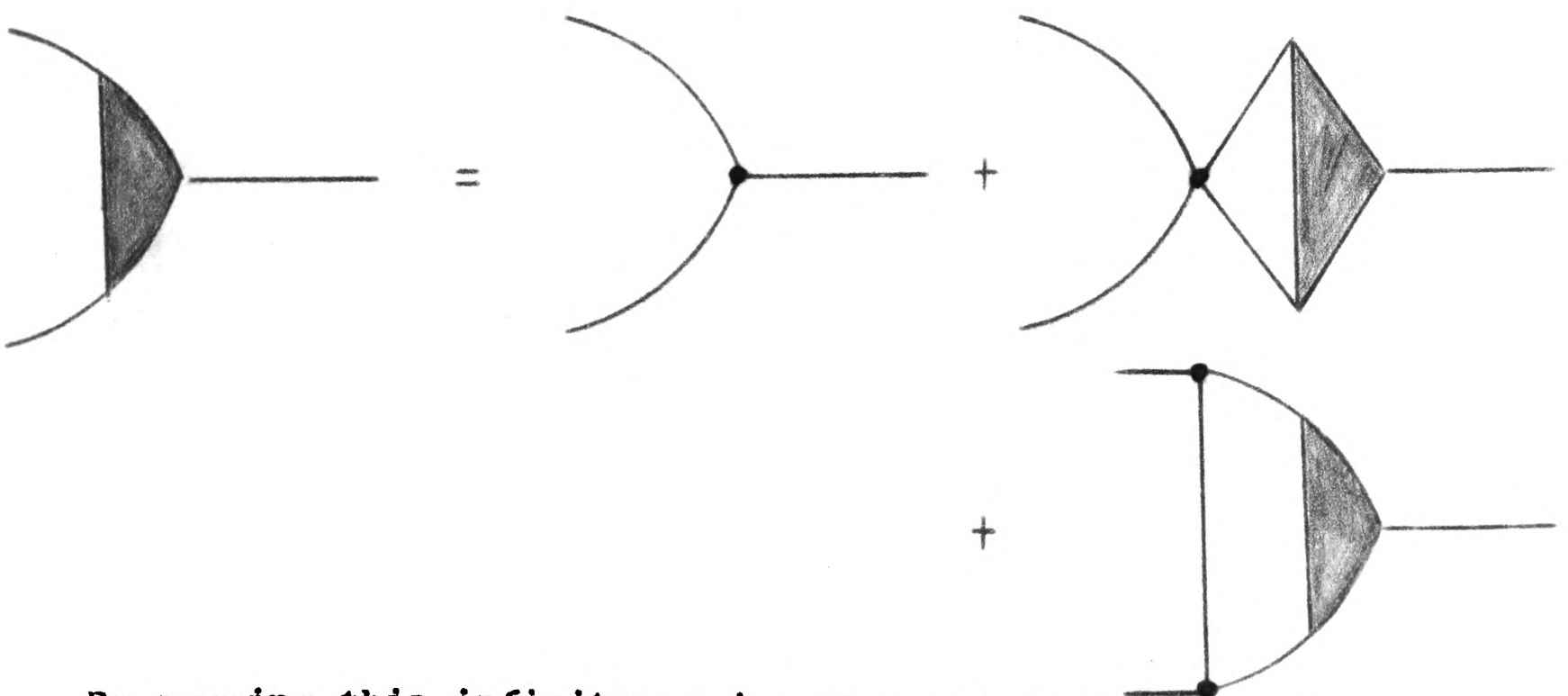
and therefore they must be identically zero. In the perovskite ferroelectrics, for example, we expect then that the response function is well described by the damped

harmonic oscillator model, but in piezoelectric crystals we expect an additional contribution to the soft mode response at low frequency. This was first pointed out by Cowley [5].

Since the KDP-type ferroelectrics are piezoelectric, the correct form of Δ and Γ must be used in equation (6.11). The above self-energy diagram must be reevaluated with the internal harmonic lines being replaced by thermal phonon lines. Cowley and Coombs [6] have shown that more complex processes must be considered:-



where the re-normalised vertex is given by the diagrams:-



By summing this infinite series they obtain the result:-

$$G^{-1}(0j, \omega) \propto [\hat{\omega}(0j)^2 - \omega^2 + i\gamma\omega - \frac{\alpha T}{1 + i\omega\tau^*}] \quad (6.17)$$

where α is a positive quantity and τ^* is an average phonon lifetime.

At high frequency this response is identical with classical oscillator form; and for the soft mode we have $\hat{\omega}_0^2 = k(T - T_c)$. At low frequency, $\omega \tau^* \ll 1$, fluctuations in the phonon distribution function caused by the ferroelectric mode have time to decay within each period of the wave, and the response is determined by $(\hat{\omega}_0^2 - \alpha T) = k(T - T_c)$. The mode appears to become soft at a temperature T_0 given by:-

$$T_0 = \left(\frac{k - \alpha}{k}\right) T_c$$

Since $\alpha > 0$, we have $T_0 < T_c$, which is in agreement with the results of the above experiments. We find:-

	CsDA	KDP	KDA
$(1 - \frac{\alpha}{k})$	0.4	0.9	1.0

The increasing value of $\frac{\alpha}{k}$ with T_c can be understood qualitatively as follows. Whereas both the ferroelectric mode and final phonon state population densities increase with temperature, the fluctuations in the latter caused by decay of the former will be much larger at higher temperature. Consequently, the coupling between the ferroelectric mode and deviations from local thermodynamic equilibrium is stronger.

Cowley and Coombs have also shown that scattering arising from the response function in (6.17) depends sensitively on the parameters, and in some cases it may show a peak centred at $\omega = 0$ in addition to the two usual phonon side-bands. This central peak is confined

to the region $\omega \lesssim 10 \text{ cm}^{-1}$, and in the case of an overdamped phonon mode may be indistinguishable. Certainly, higher resolution studies of the low frequency spectrum of these materials have been unable to detect such a mode, and so we assume that both features coalesce to produce a lineshape corresponding to a highly damped oscillator.

6.6 Soft modes in antiferroelectric ADP and AD*P

Although ADP and AD*P are members of the isomorphous series of tetragonal salts they are antiferroelectric at low temperatures. As we have seen in chapter 1, the dielectric constants ϵ_{11} and ϵ_{33} rise only slightly with decreasing temperature, and both drop suddenly at the transition. Not much is known about the properties of the antiferroelectric phase since the crystals shatter completely, but the large shift in the transition temperature with deuteration suggests that proton ordering is important. Nagamiya [7] proposed the ordering illustrated in figure 1.5, and Paul and Montgomery [8] have shown that this corresponds to a zone boundary, M_{34} , mode. Meistner et al. [9] have observed quasi-elastic scattering of neutrons near the M point and they ascribe this to an overdamped M_{34} mode which produces polarisation fluctuations in the ab-plane.

This mode, however, cannot be observed in our 1st - order Raman scattering experiments, but the temperature dependence of the static susceptibility indicates that zone

centre modes may also be temperature dependent. In these experiments we have in fact observed overdamped soft modes of both B_2 and E symmetry, and a lineshape analysis has provided us with the Debye relaxation times. A comparison is made with the static and microwave dielectric measurements.

6.6.1 Raman spectrum of ADP

The low frequency E-symmetry mode giving rise to polarisation fluctuations in the ab-plane is found to be highly damped. The spectra presented in figure 6.15 show that the wing extends to 200 cm^{-1} and overlaps three underdamped modes. As the temperature decreases the wing narrows, but the other modes change only slightly.

In Fig. 6.16 we see that the B_2 symmetry spectrum is somewhat similar to that found in the ferroelectric materials, but the scattering is extremely weak and there is no marked change with temperature.

An analysis of these lineshapes has been made in the same way as discussed previously. Anharmonic interactions between the modes is now a considerable problem, especially for the four E-symmetry modes. In the latter case the response function for such a system of coupled oscillators contains twenty four variable parameters, but since at least two of the modes are well defined we may ignore any coupling in a first approximation. The response function has then twelve parameters and the analysis is relatively straightforward. In the case of the B_2 spectrum the

coupled mode analysis is exactly analogous to that for the ferroelectric isomorphs.

The parameters describing the E-spectra are listed in Table 6.7. The underdamped mode frequencies and widths vary little with temperature but the Debye relaxation time for the overdamped mode increases as the transition is approached. In figure 6.19 we have (T/τ) v.s. T and find that it extrapolates to $T_0 = 54 \pm 5K$.

The coupled mode analysis for the B_2 -spectra again has two solutions which must be considered. The parameters obtained for the models are given in Table 6.8 and the decoupling illustrated in figures 6.17 and 6.18. The relaxation times obtained are plotted in figure 6.20 and yield $T_0 = 28K$ for the case of real coupling, and $T_0 = 104K$ for imaginary coupling. The latter result is comparable with the values obtained for KDP and KDA.

6.6.2 Raman spectrum of AD*P

The corresponding spectra for AD*P are shown in figures 6.21 and 6.22. The wings are now narrower but the underdamped modes are only shifted slightly. The analysis has been repeated and the only significant difference is that the B_2 spectrum, as shown in figure 6.23, can be satisfactorily described in terms of uncoupled modes. This can be understood qualitatively if we regard the overdamped mode frequency to be lower in the deuterated crystal; the modes are then well separated and the interaction much weaker. The parameters obtained from the fitting are given in Tables 6.9 and 6.10, and the relaxation

times plotted in figures 6.24 and 6.25. We find:-

$$\begin{aligned} T_0 &= 168^\circ\text{K} & \text{E mode} \\ \text{and } T_0 &= 44^\circ\text{K} & \text{B}_2 \text{ mode} \end{aligned}$$

However, the spread in the data is somewhat greater now, and the uncertainties in the values of T_0 are therefore higher, being approximately 20K.

6.6.3 Discussion

In addition to the soft zone boundary mode, these antiferroelectrics possess also zone centre modes which decrease in frequency with temperature. Our Raman measurements indicate that the $E(\Gamma_5)$ mode would become unstable before the $B_2(\Gamma_4)$ mode. Although this agrees qualitatively with the dielectric data, a direct comparison of the two is difficult. In figs. 6.19, 6.20, 6.24 and 6.25 we have included both the microwave and static dielectric susceptibilities in an attempt to compare results. In the case of ADP the data does not appear to be of the Curie-Weiss form; we have plotted $\chi^{-1}(T) = \frac{1}{\epsilon - \epsilon(\infty)}$ which is not quite linearly temperature dependent. The corresponding data for AD*P is almost linear in T . It is apparent that in each case the singularity in the dielectric constant occurs at negative temperatures. In AD*P this negative temperature is very small, but in ADP it is significantly large (Nagamiya [7] quotes values of -17K and -55K for ϵ_{33} and ϵ_{11} respectively. However, our attempt to obtain a least squares fit to the data of Mason [10] failed, and the three parameters required had extremely large uncertainties.

The main reason for this is that the available data covers only a small part of the temperature range being considered). In contrast to this, the Raman measurements provide relatively accurate values of T_0 which are positive.

Because the transition is first order we expect T_0 to be quite different from the transition temperature. In addition, we would also expect it to be lower than T_A , the temperature at which the frequency of the zone boundary mode drops to zero. Meistner et al. [9] obtain for AD*P the value $T_A = 188^\circ \text{K}$, with the transition being at 234K. We obtain $T_0 = 168\text{K}$ for the E (Γ_5) mode in AD*P, which indicates that both extremities of the $\Gamma_5 - M_{34}$ branch (see figure 1.8) are highly temperature dependent and go to zero at nearly the same point. However, the transition which occurs here is quite different from the displacive type where a zone centre mode can condense after the zone boundary mode: AD*P cannot simultaneously order according to M_{34} and Γ_5 , and in fact ordering by a zone boundary occurs at $\sim 240\text{K}$ resulting in a first order transition. On the other hand, the B_2 mode - which is responsible for the ferroelectric transition in KDP - is much weaker and "condenses" at a lower temperature. It is not possible to discuss the significance of the two values of T_0 obtained with Δ , $\gamma_{12} = 0$, since T_c is not known accurately. However, the basic difference in behaviour of the antiferroelectric and ferroelectric isomorphs must arise from the presence of the NH_4^+ ion.

If we assume M_{34} ordering, then the coupling coefficient $J(q = \pi/c)$ in equation 1.14 must be a maximum. It is impossible to say, but we may speculate at this stage as to the importance of the NH_4^+ librational motion. Certainly, the isotope effect on T_0 for the E mode is much larger than observed in any of the other materials. It may be possible to explain this in terms of the much larger moment of inertia of the ND_4^+ ion causing the frequency to be smaller and so condenses at a higher temperature.

To obtain further information about the nature of the transition mechanism it is necessary to obtain data in the low temperature phase. As we have stated before, this is not possible in the material; however, it is interesting that AD*A undergoes the phase transition at $\sim 304K$, which means that the crystal may be grown in the antiferroelectric phase. The zone centre and zone boundary modes may therefore be studied in detail in the low temperature phase.

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Table 6.1

KDP : Damped Harmonic Oscillator Model (0 - 70 cm⁻¹)

T (K)	P (cm ⁻¹)	γ (cm ⁻¹)	$\hat{\omega}_0$ (cm ⁻¹)	τ	(x $\frac{10^{-2}}{c}$ sec)
295	2152	233	99	23.8	
260	2651	248	99	25.3	
210	2684	251	86	33.9	
172	2072	253	71	50.2	
141	2068	249	45	123	
126	2417	249	41	148	

Table 6.2

KDP : Debye Oscillator Model (10 - 70 cm⁻¹)

T(K)	P(cm ⁻¹)	τ (x $\frac{10^{-2}}{c}$ sec)
295	565	20.3
260	836	22.0
210	1106	31.8
172	924	48.9
141	2359	134
126	4290	182

Table 6.3

KDP B₂ spectrum, T = 295K; two uncoupled oscillators

	cm ⁻¹	
P ₁	1242	
γ ₁	81.5	$\tau = 20.3 \times \frac{10^{-2}}{c} \text{ sec.}$
$\hat{\omega}_1$	63.5	
P ₂	864	
γ ₂	26.0	
$\hat{\omega}_2$	189	

Table 6.4

KDP - Coupled Oscillator Model (units cm^{-1})

T (K)	295			260			210		
	1	2	3	1	2	3	1	2	3
Model									
P_1	0	2013	1576	0	2250	1783	0	2222	1814
γ_1	12.3	177	128	10.4	159	115	9.0	150	115
$\hat{\omega}_1$	149	118	79	152	117	74	153	106	62
P_2	2024	209	1269	2259	206	1387	2233	223	1303
γ_2	175	10.5	60	158	9.2	53	149	7.6	43
$\hat{\omega}_2$	129	157	180	127	159	183	118	162	184
γ_{12}	-17	0	76	-14	0	68	-14	0	62
$\Delta^{1/2}$	113	109	0	117	113	0	119	114	0
T (K)	172			141			126		
	1	2	3	1	2	3	1	2	3
model									
P_1	0	1828	1461	0	1791	1478	0	2032	1678
γ_1	10.6	158	122	10.1	142	115	9.1	132	107
$\hat{\omega}_1$	150	101	53	154	91	38	154	91	38
P_2	1851	285	1136	1810	261	1046	2054	300	1185
γ_2	154	7.1	43	140	7.3	35	130	6.4	32
$\hat{\omega}_2$	121	164	186	112	167	186	112	168	187
γ_{12}	-23	0	64	-19	0	55	-18	0	51
$\Delta^{1/2}$	124	116	0	125	116	0	126	116	0

Table 6.5

KDA - Coupled Oscillator Model (units cm^{-1})

T (K)	295			245			189		
	1	2	3	1	2	3	1	2	3
Model									
P_1	0	2440	2156	0	2552	2253	0	2551	2066
γ_1	20.3	372	235	23.3	422	266	21.4	333	170
$\hat{\omega}_1$	126	161	189	129	167	197	130	143	184
P_2	2470	380	1205	2583	398	1262	2581	398	1547
γ_2	363	11.8	149	412	13.7	169	326	13.9	177
$\hat{\omega}_2$	172	140	99.3	179	145	99.8	156	145	86.5
γ_{12}	-55	0	175	-62	0	198	-49	0	160
$\Delta^{1/2}$	105	112	0	116	119	0	113	115	0

T (K)	137			120		
	1	2	3	1	2	3
Model						
P_1	0	2165	1562	0	3509	3064
γ_1	18.4	273	105	33.8	947	573
$\hat{\omega}_1$	132	119	174	135	176	214
P_2	2191	337	1537	3550	547	1795
γ_2	267	12.2	180	925	11.6	386
$\hat{\omega}_2$	134	146	71.4	191	154	93.7
γ_{12}	-40	0	125	-142	0	450
$\Delta^{1/2}$	112	110	0	127	135	0

Table 6.6

CsDA - Coupled Oscillator Model (units cm^{-1})

T (K)	295			247			235		
	1	2	3	1	2	3	1	2	3
Model									
P_1	0	4487	4878	0	3539	3527	0	5773	5744
γ_1	29.2	2375	2303	36.6	2944	2838	24.5	2225	2135
$\hat{\omega}_1$	77	403	409	78	434	442	79	369	377
P_2	4902	379	481	3550	275	405	5790	448	132
γ_2	2361	15.1	87.1	2927	19.2	125	2212	11.2	102
$\hat{\omega}_2$	407	96	65.6	439	103	60	374	98.2	63.3
γ_{12}	-182	0	406	-226	0	547	-171	0	438
$\Delta^{1/2}$	126	167	0	147	189	0	131	165	0
T(K)	200			184			153		
	1	2	3	1	2	3	1	2	3
Model									
P_1	0	4172	4158	0	6251	6191	0	8258	8221
γ_1	40.1	4120	3973	24.5	2256	2134	51	4566	4387
$\hat{\omega}_1$	80	480	488	83.6	354	364	77.8	474	484
P_2	4185	324	66.8	6270	485	990	8283	641	394
γ_2	4095	15.6	103	2243	11.1	134	4539	23.9	203
$\hat{\omega}_2$	485	109	57.9	359	104	61.6	480	108	51
γ_{12}	-316	0	764	-173	0	510	-350	0	884
$\Delta^{1/2}$	163	209	0	141	171	0	168	212	0

Table 6.7

ADP E-spectrum; 4 uncoupled oscillators (units cm^{-1})

T	297	248	193 ℓ	168
P ₁	912	951	962	987
γ_1	130	112	105	93.8
$\hat{\omega}_1$	72.3	68.3	62.5	57.5
P ₂	276	275	276	281
γ_2	16.0	13.5	12.3	10.2
$\hat{\omega}_2$	67.4	68.8	68.8	68.7
P ₃	658	655	656	668
γ_3	44.7	39.9	38.7	39.1
$\hat{\omega}_3$	110	108	107	103
P ₄	1140	1157	1159	1181
γ_4	38.3	34.0	30.0	27.9
$\hat{\omega}_4$	174	177	178	179

Table 6.8

ADP - Coupled Oscillator Model							B ₂ spectra		
T	295			248			227		
Model	1	2	3	1	2	3	1	2	3
P ₁	0	1318	1230	0	1137	965	0	1357	1176
Y ₁	65.7	480	317	51.6	355	182	48.8	378	202
$\hat{\omega}_1$	177	208	230	171	183	221	169	187	224
P ₂	1353	305	563	1167	263	657	1393	314	747
Y ₂	457	43.6	206	338	35.4	208	361	31.0	207
$\hat{\omega}_2$	220	191	163	200	189	142	204	188	141
Y ₁₂	-96	0	211	-70	0	159	-76	0	174
$\Delta^{1/2}$	100	113	0	116	120	0	117	123	0

T	200			153		
model	1	2	3	1	2	3
P ₁	0	1524	1347	0	1176	918
Y ₁	60.0	416	238	41.7	329	133
$\hat{\omega}_1$	166	190	225	171	164	215
P ₂	1564	353	796	1207	272	785
Y ₂	397	410	219	313	26.3	222
$\hat{\omega}_2$	207	185	140	184	189	129
Y ₁₂	-82	0	187	-66	0	146
$\Delta^{1/2}$	117	125	0	121	119	0

Table 6.9

AD*P E-spectrum; 4 uncoupled oscillators (units cm^{-1})

T(K)	387	343	294	281	265	252
P_1	8122	8575	10027	10097	10079	10056
γ_1	10938	12476	16809	20239	20079	20032
$\hat{\omega}_1$	545	552	569	581	585	597
P_2	241	254	297	299	299	298
γ_2	14	13	12	13	12	11
$\hat{\omega}_2$	69	69	70	70	70	70
P_3	576	660	711	716	715	713
γ_3	37	38	40	42	40	39
$\hat{\omega}_3$	115	115	115	115	115	115
P_4	978	980	1146	1154	1151	1149
γ_4	44	42	42	44	43	42
$\hat{\omega}_4$	162	163	166	167	167	167

Table 6.10

AD*P B₂ spectrum; two uncoupled oscillators (units cm⁻¹)

T(K)	251	265	282	296	347	387
P ₁	1496	1529	1526	1430	1714	1855
γ ₁	1742	1917	2033	1671	2161	3121
[^] ω ₁	180	187	188	181	212	241
P ₂	855	874	872	817	980	1060
γ ₂	129	137	147	134	171	218
[^] ω ₂	229	229	228	226	228	237

Figure 6.1

The low frequency B_2 symmetry Raman spectrum of KDP at several temperatures in the para-electric phase. $T_c = 122K$.

[In all the spectra presented here the vertical axis is labelled in arbitrary units]

RAMAN SPECTRUM OF KDP B₂-SYMMETRY

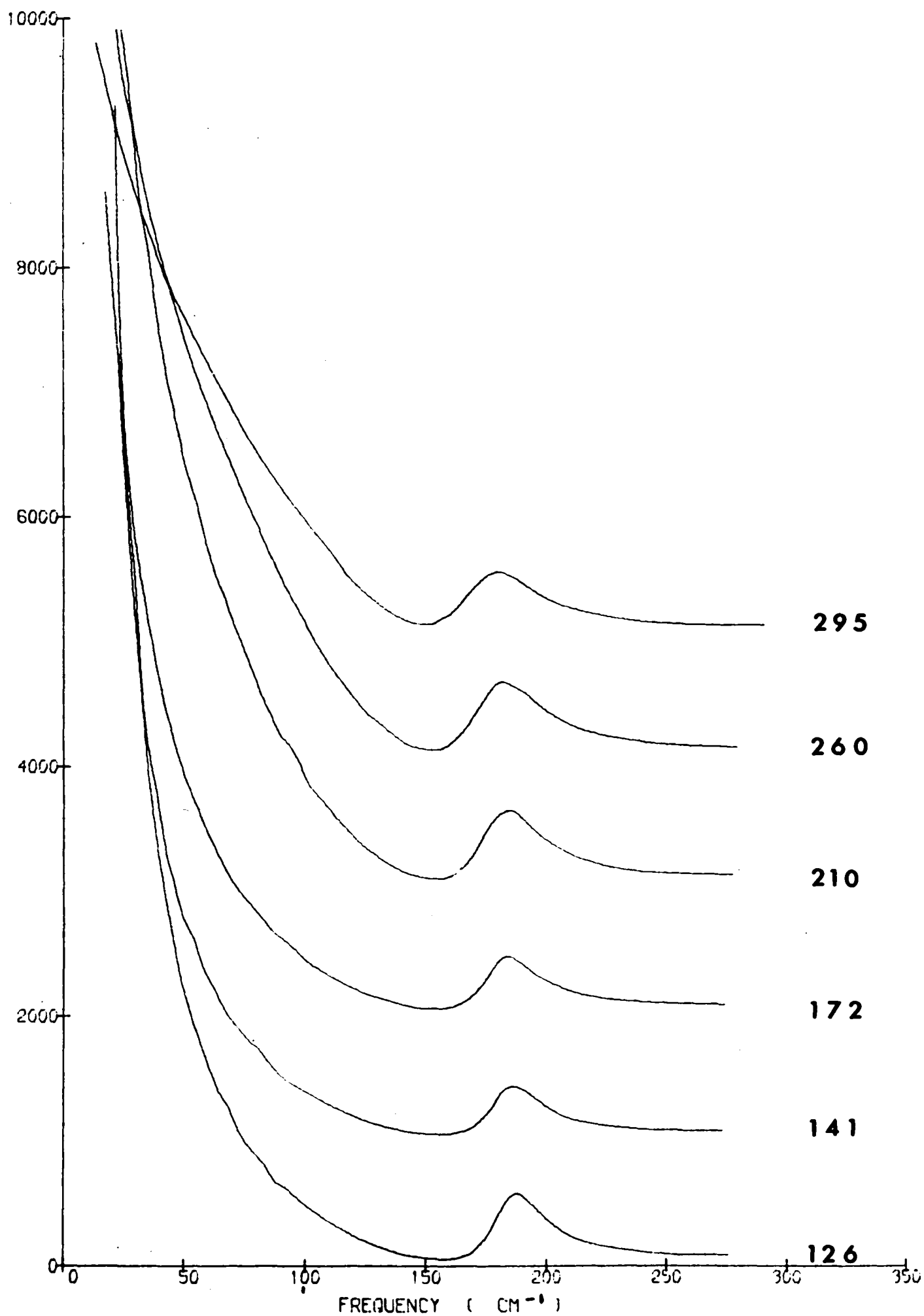


Figure 6.2

Temperature dependence of the Debye relaxation
time of the ferroelectric mode in KDP
(frequency region $\omega < 70 \text{ cm}^{-1}$)

- ⊖ DSHO model
- Debye model
- ▼ Kaminow and Damen [3]

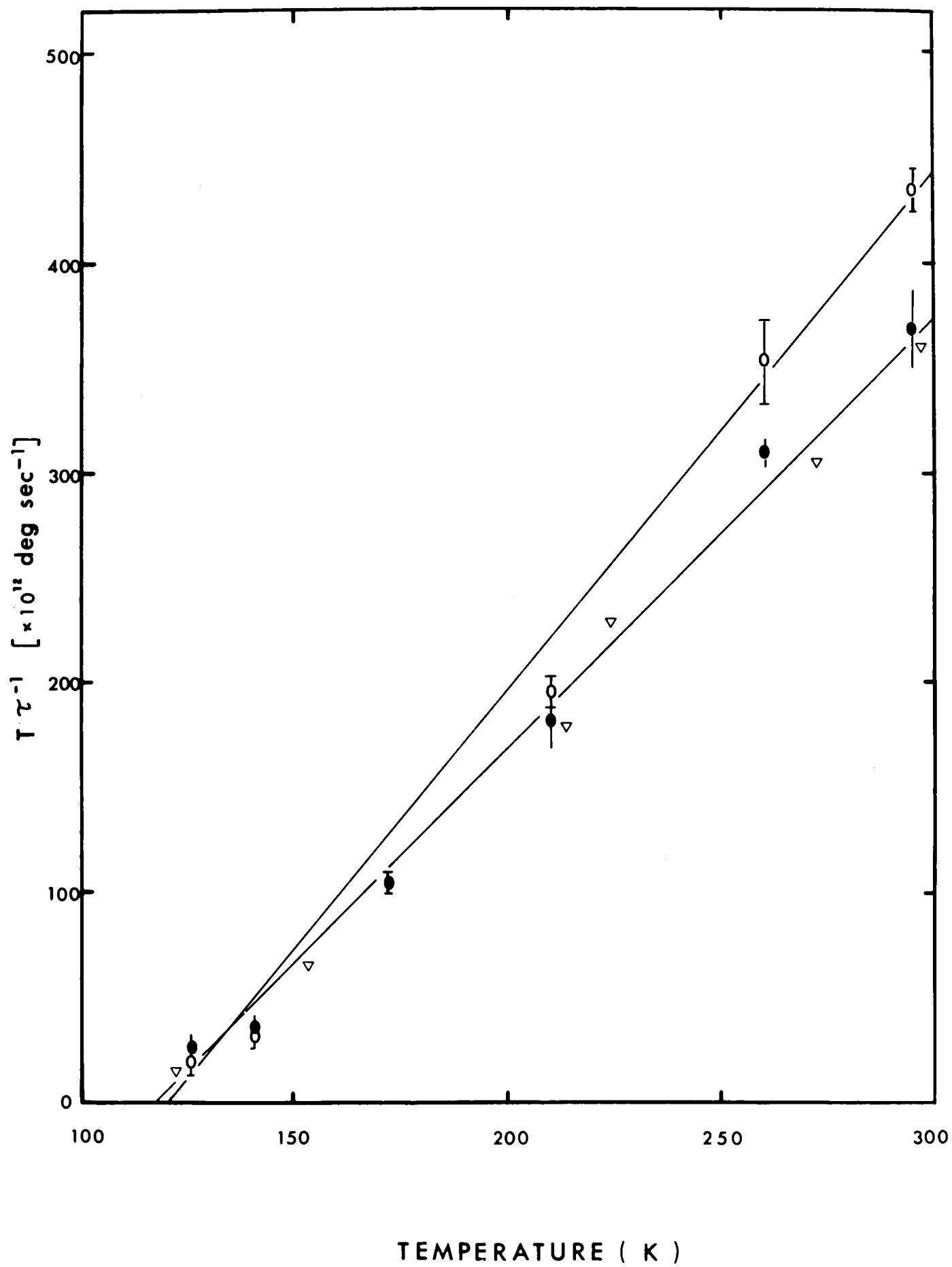


Figure 6.3

Raman spectrum of KDP, B_2 symmetry, $T = 295\text{K}$. The open circles are the data points used in the least squares fitting, and the solid line is the best fit produced by a model with two uncoupled oscillators. The oscillator parameters are listed in Table 6.3

RAMAN SPECTRUM OF KDP B_2 -SYMMETRY

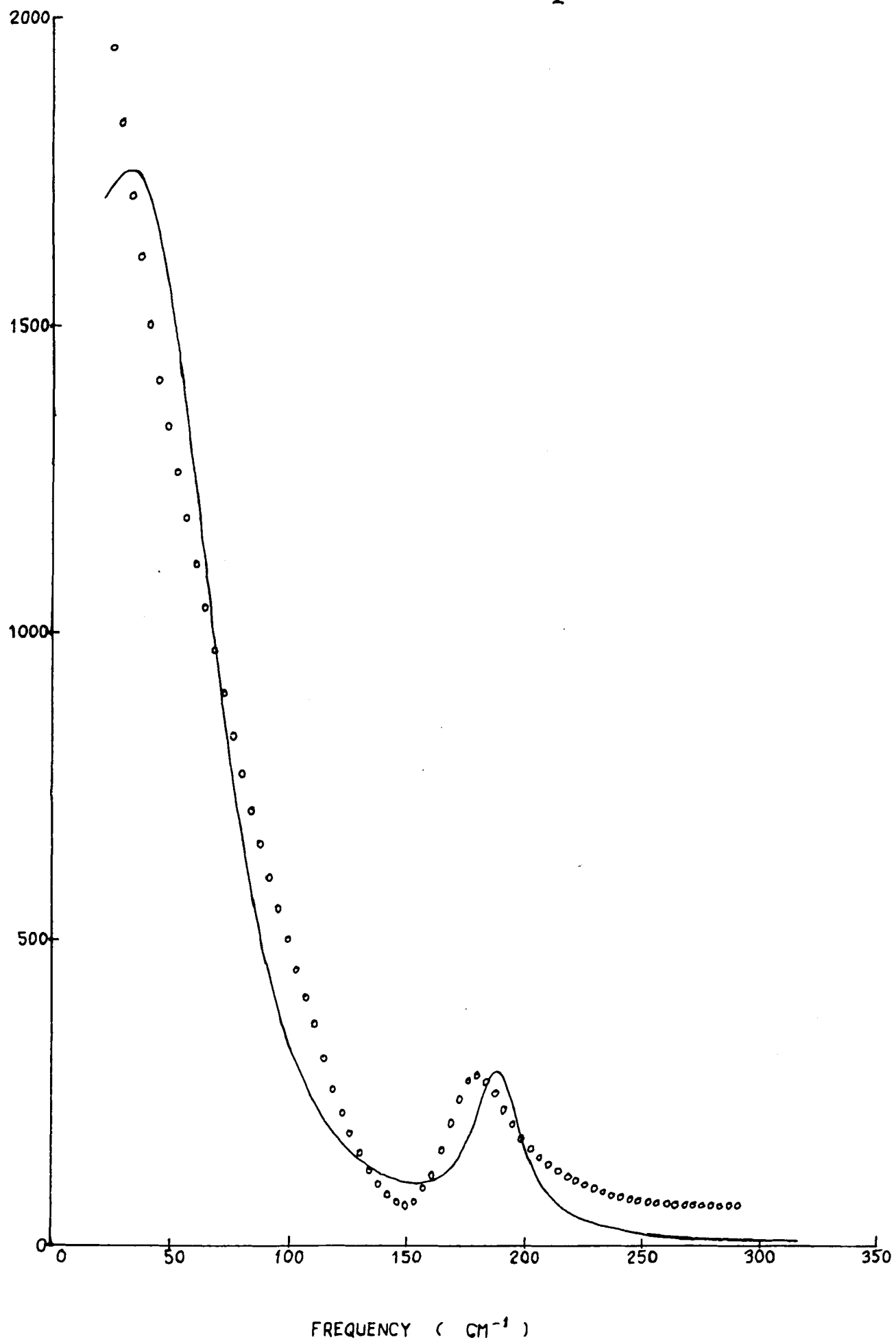


Figure 6.4

Coupled oscillator fit to the B_2 symmetry Raman spectrum of KDP at $T = 295K$. The broken lines represent the response of the uncoupled modes when $\gamma_{12} = 0$ and with the parameters in Table 6.4. The solid curve is produced when the two modes are coupled

RAMAN SPECTRUM OF KDP B_2 -SYMMETRY

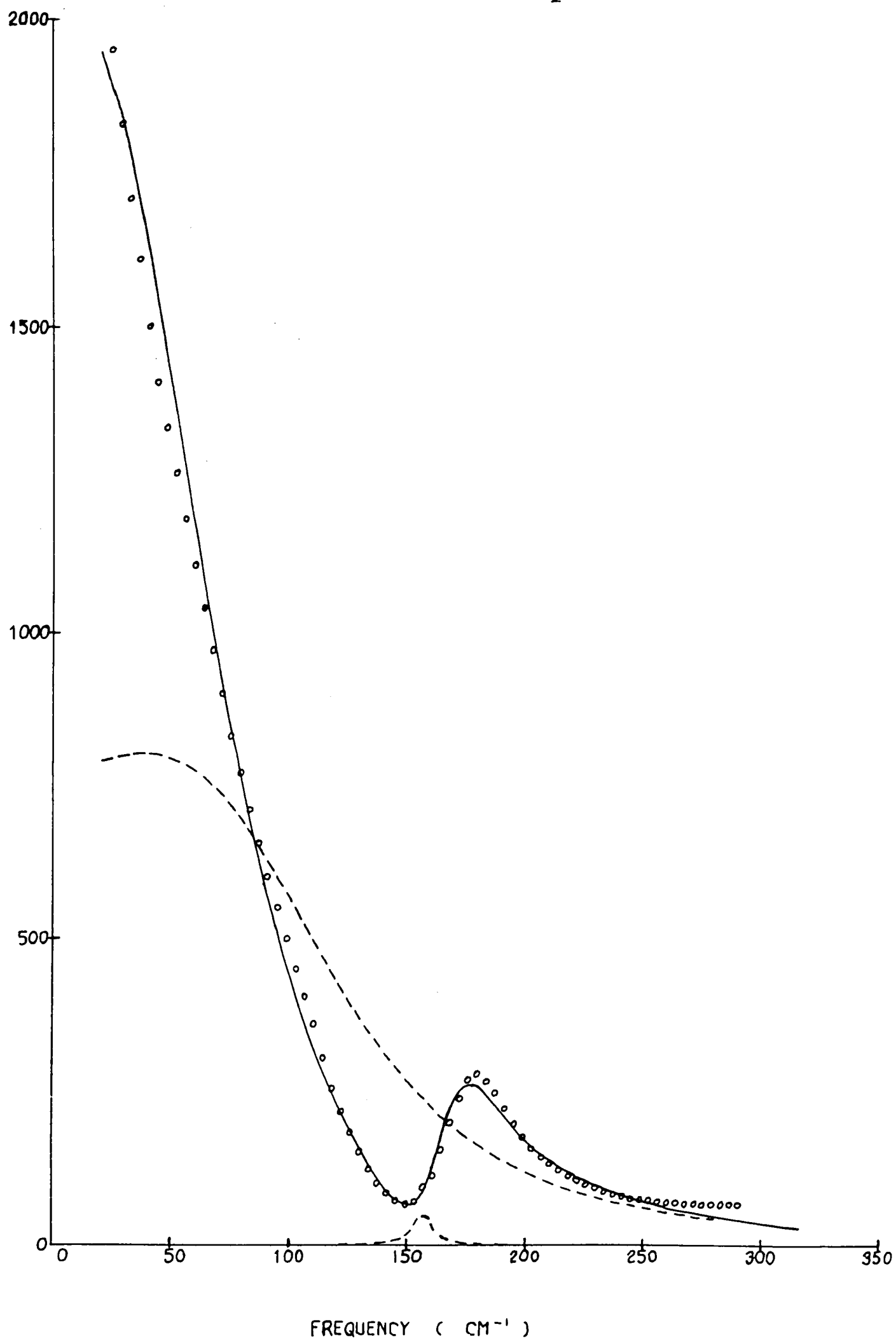


Figure 6.5

Debye relaxation time of the ferroelectric
mode in KDP - after decoupling

$$\begin{array}{l} \bullet \\ | \end{array} \quad \gamma_{12} = 0 ; \quad T_O = 53 \pm 6 \text{ K}$$

$$\begin{array}{l} \bullet \\ \circ \\ | \end{array} \quad \Delta = 0 ; \quad T_O = 112 \pm 5 \text{ K}$$

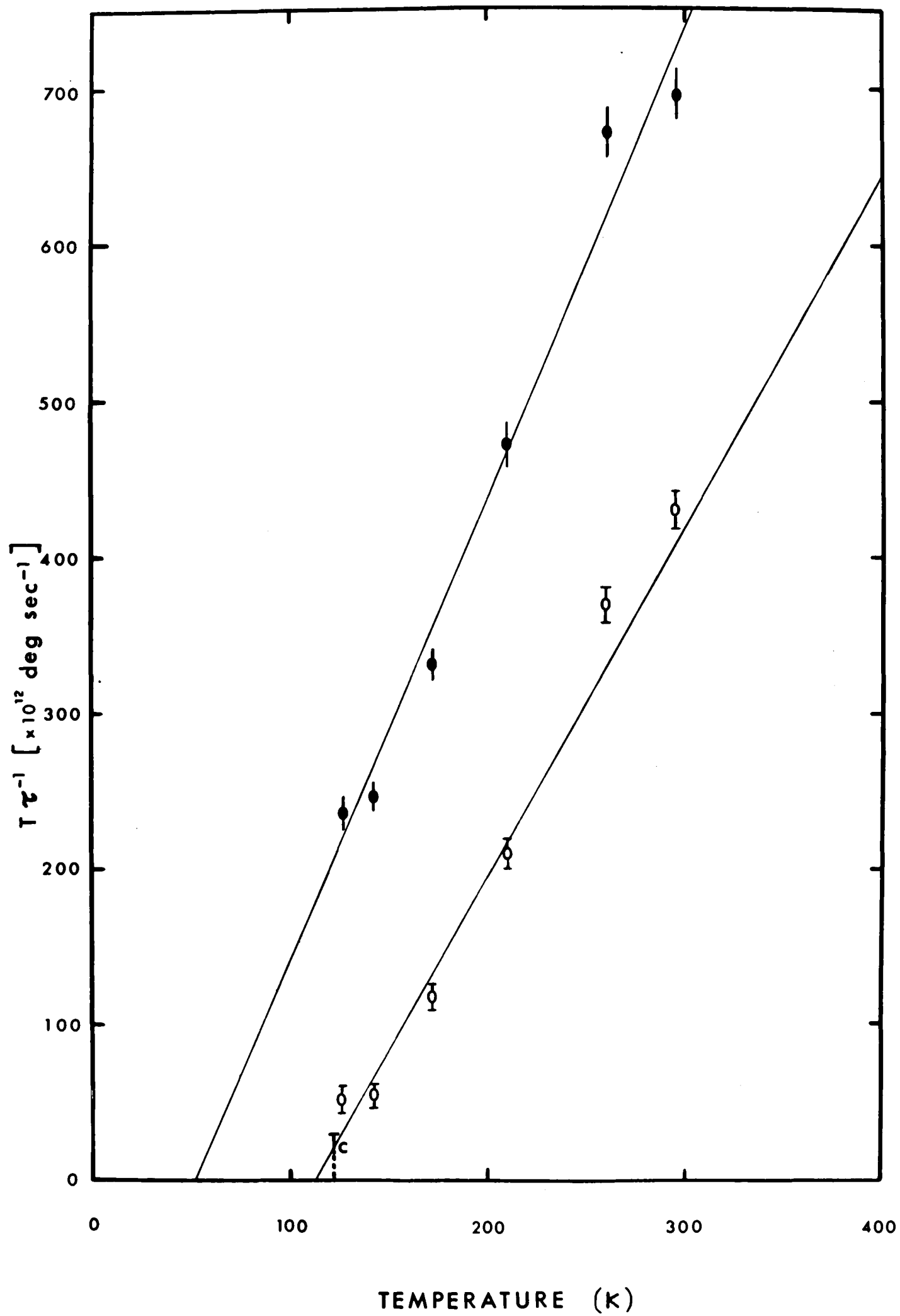


Figure 6.6

Coupled oscillator fit to the B_2 symmetry
Raman spectrum of KDP at $T = 295\text{K}$. The
uncoupled modes here are obtained with $\Delta = 0$.

RAMAN SPECTRUM OF KOP B_2 -SYMMETRY

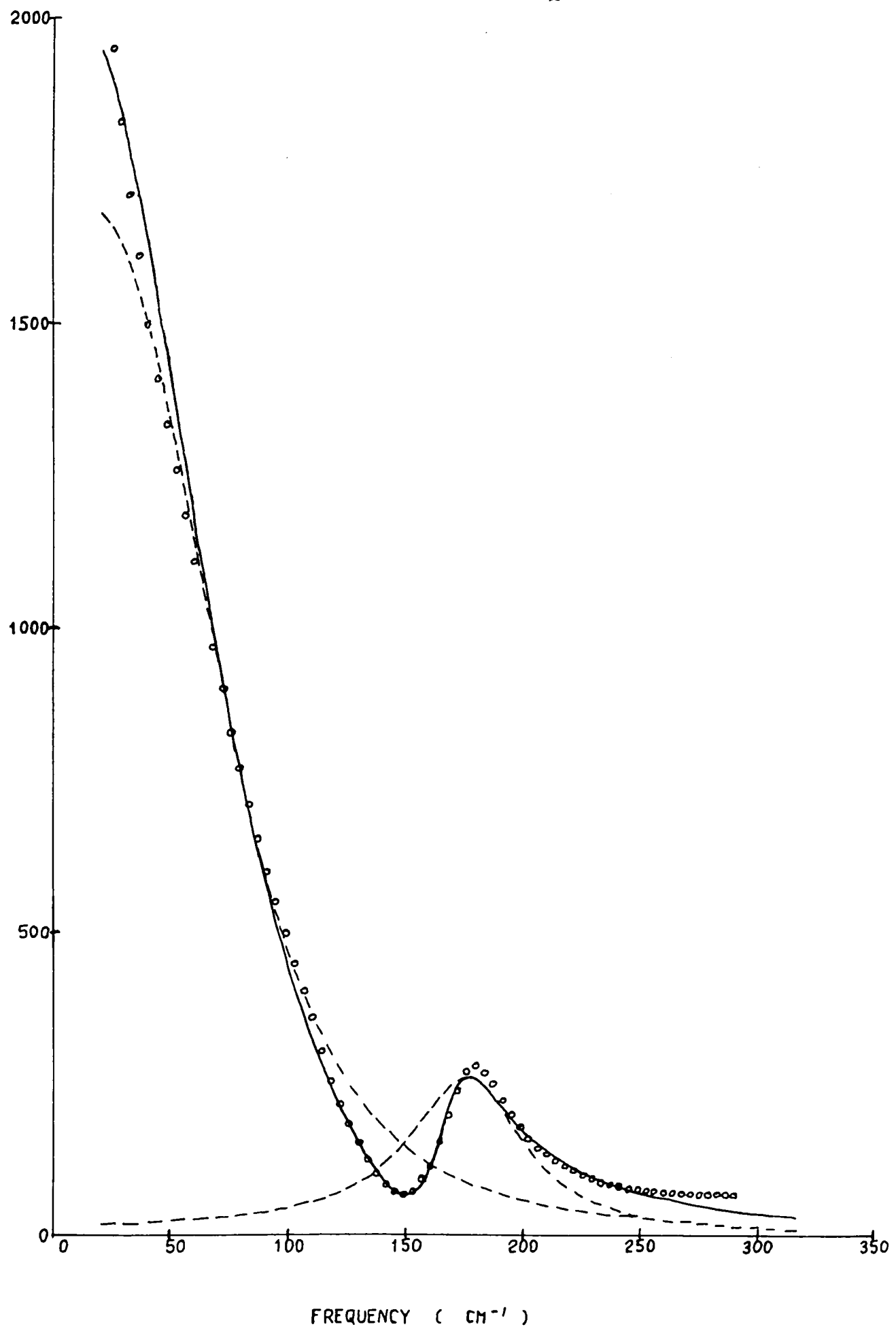


Figure 6.7

The low frequency B_2 symmetry Raman spectrum of KDA at several temperatures in the para-electric phase. $T_c = 92K$.

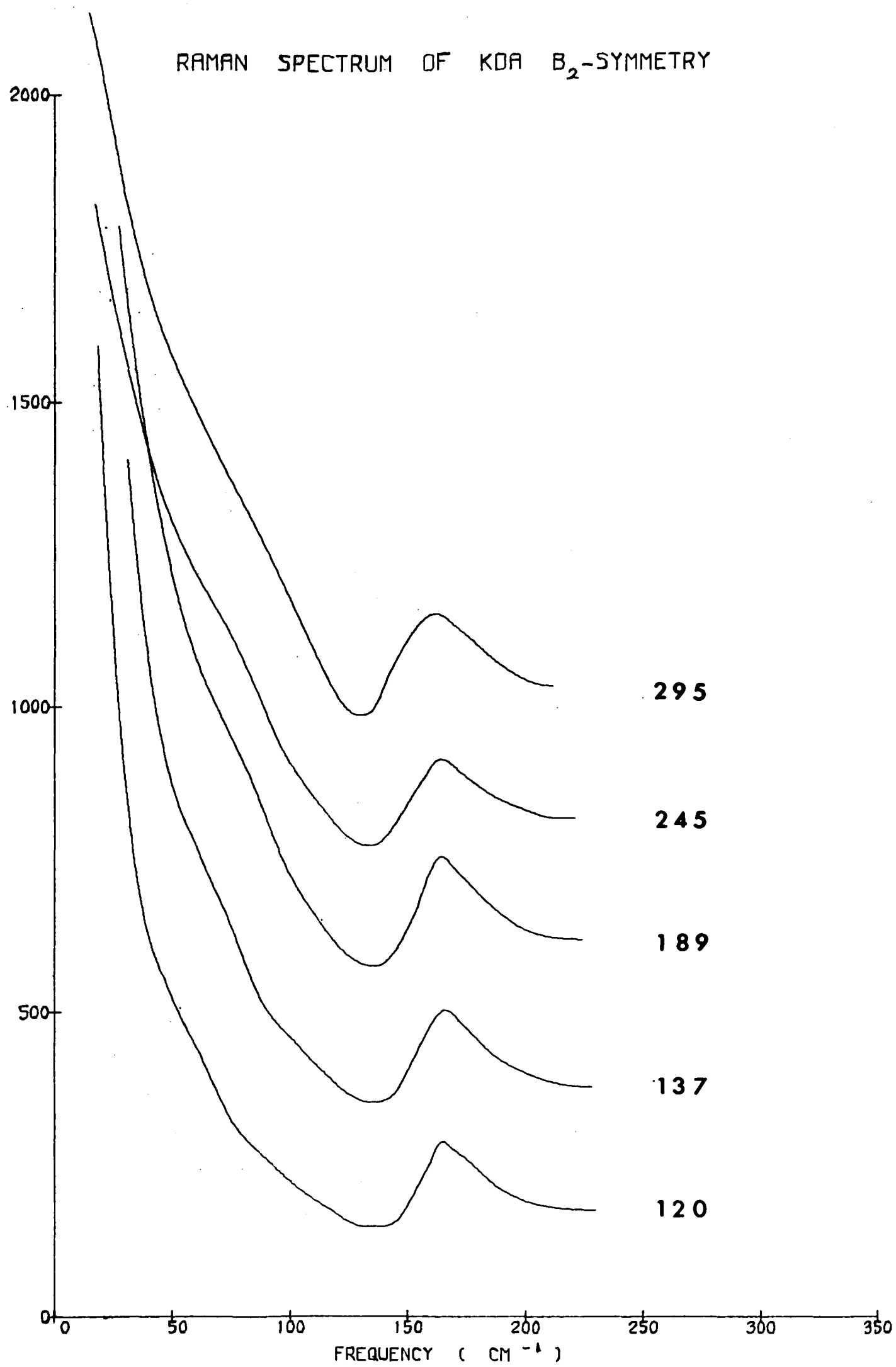


Figure 6.8

Decoupling of the modes in KDA at $T = 295\text{K}$
with $\gamma_{12} = 0$. The parameters are listed
in Table 6.5.

RAMAN SPECTRUM OF KDA B₂-SYMMETRY

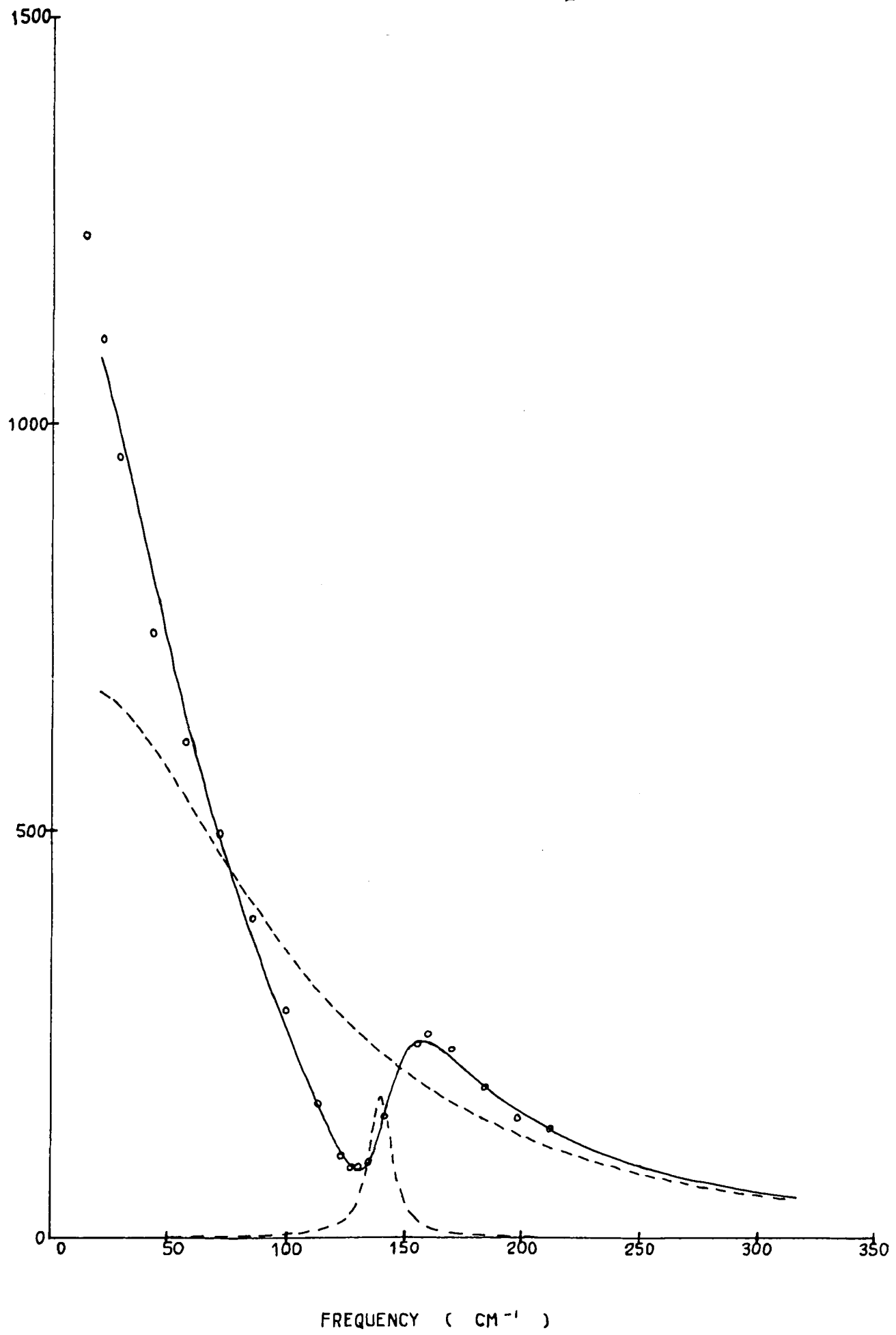


Figure 6.9

Temperature dependence of the Debye relaxation
time of the ferroelectric mode in KDA.

$$\bullet \quad \gamma_{12} = 0 ; \quad T_0 = 75 \pm 4K$$

$$\circ \quad \Delta = 0 ; \quad T_0 = 92 \pm 5K$$

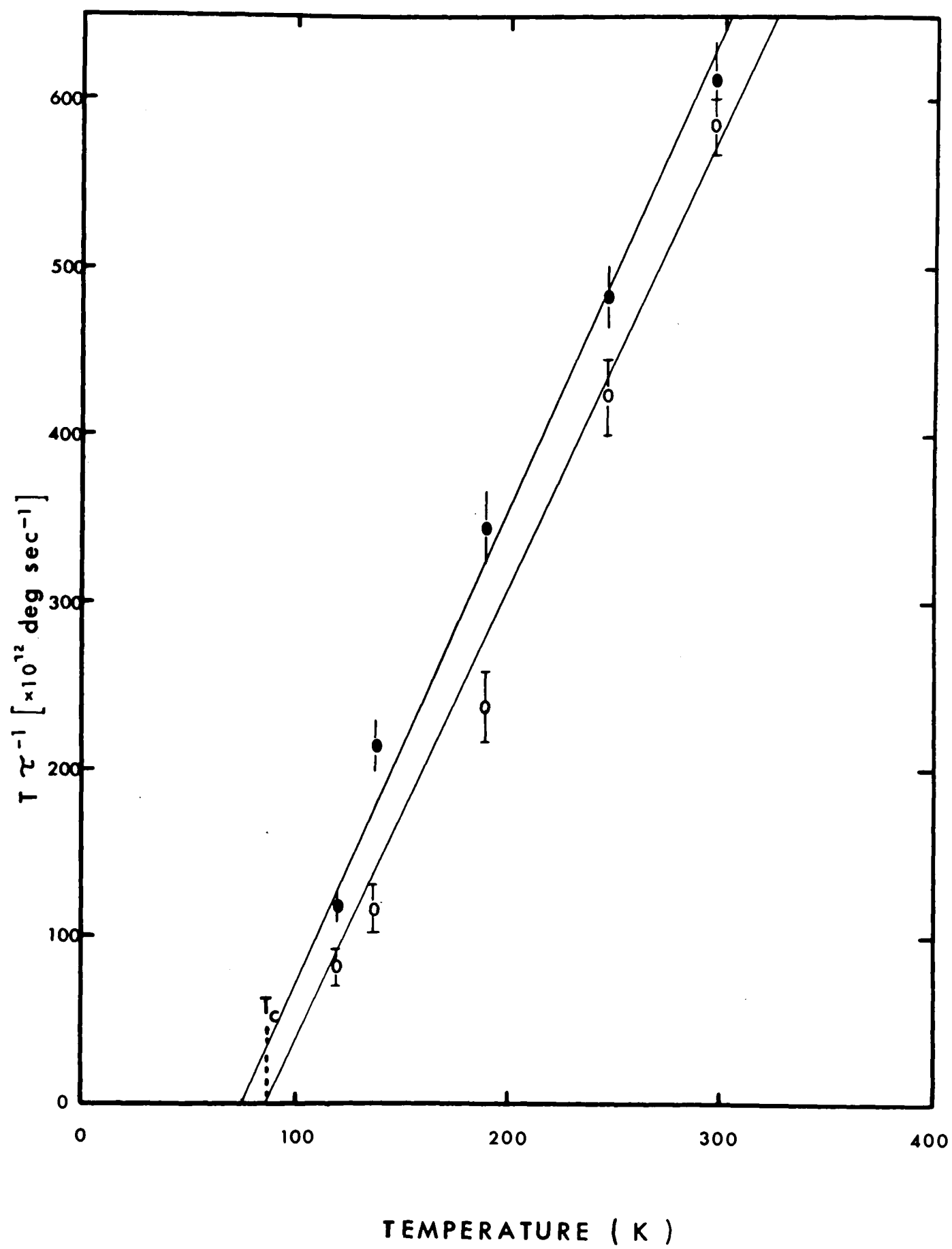


Figure 6.10

Coupled oscillator fit to the B_2 symmetry spectrum of KDA at $T = 295$. The uncoupled modes are obtained with $\Delta = 0$.

RAMAN SPECTRUM OF KDA B_2 -SYMMETRY

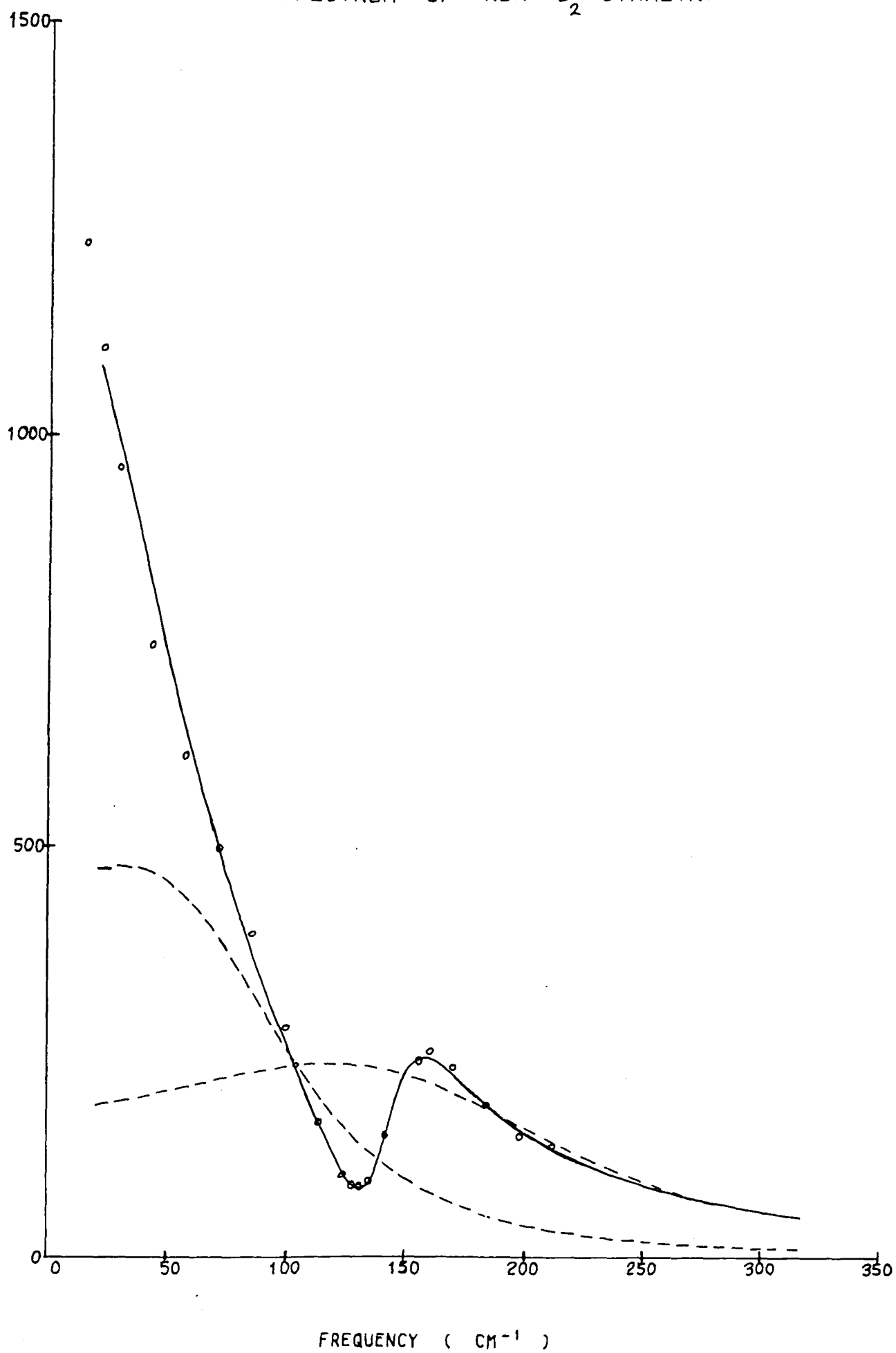


Figure 6.11

The low frequency B_2 symmetry Raman spectrum of CsDA at several temperatures in the paraelectric phase. $T_c = 143K$.

RAMAN SPECTRUM OF CSDA B₂-SYMMETRY

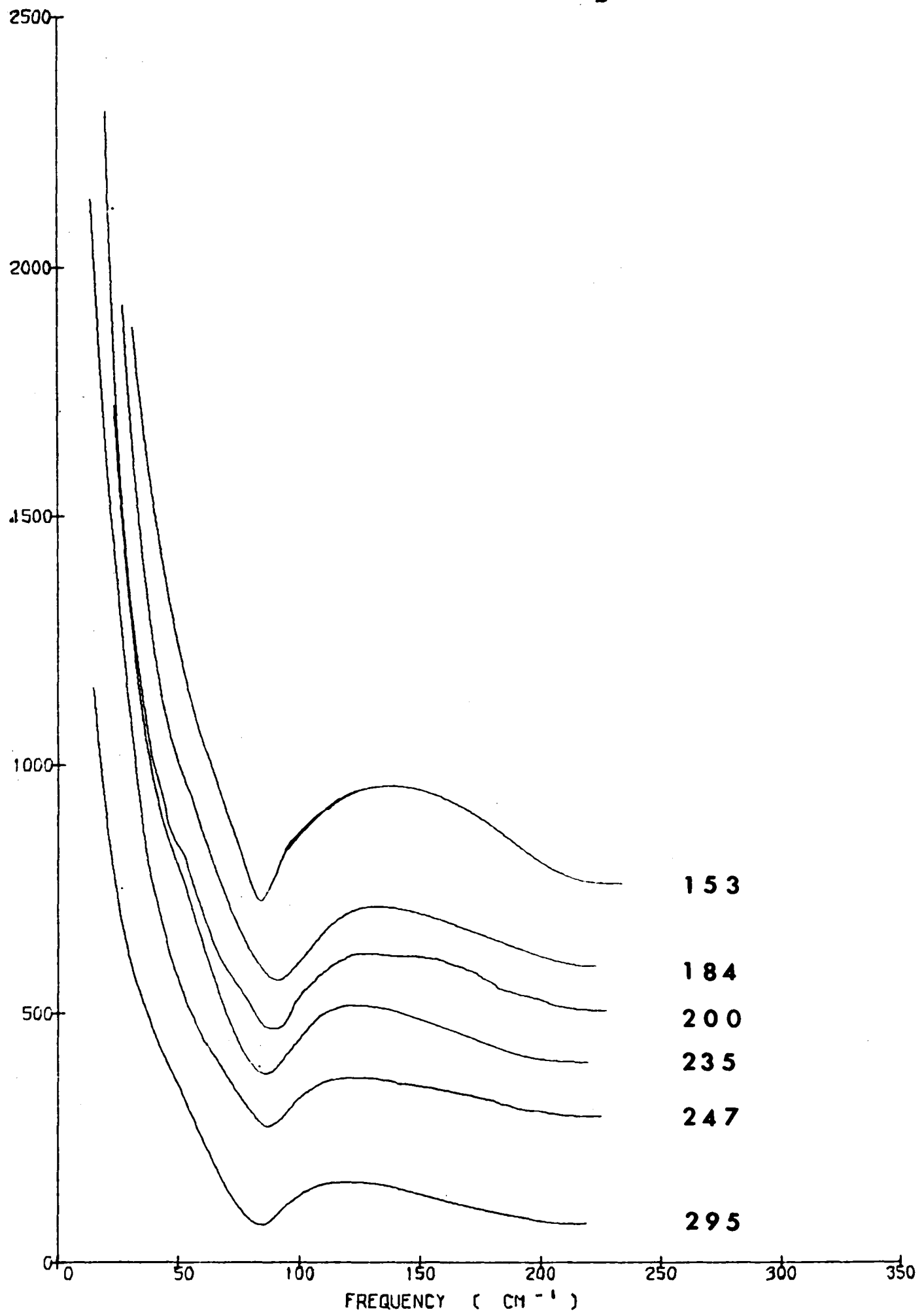


Figure 6.12

Decoupling of the modes in CsDA at $T = 295\text{K}$
with $\gamma_{12} = 0$

RAMAN SPECTRUM OF CSDA B₂-SYMMETRY

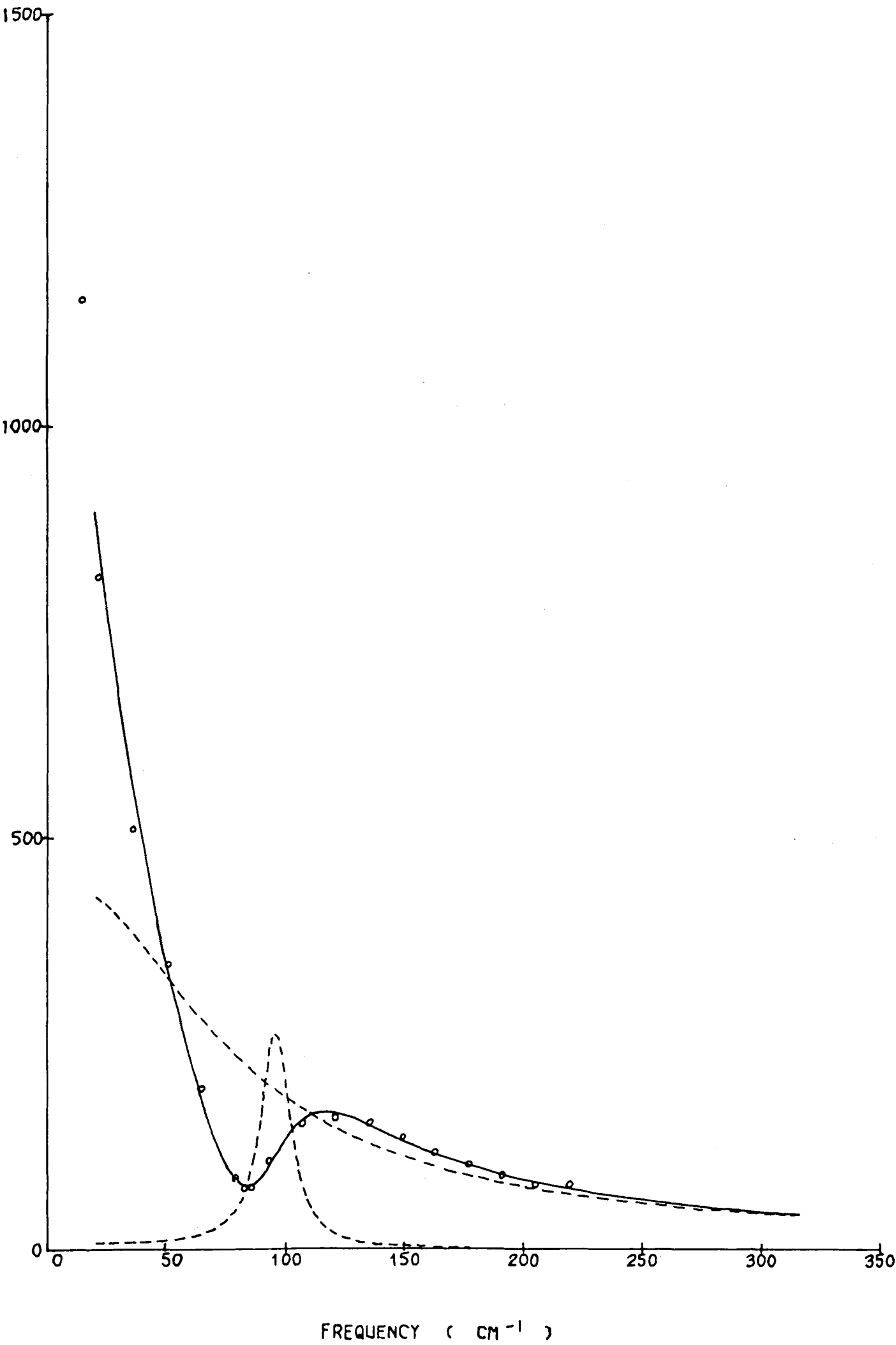


Figure 6.13

Temperature dependence of the Debye relaxation
time of the ferroelectric mode in CsDA

$$\begin{array}{lcl}
 \bullet & \Delta & = 0 ; \quad T_0 = 69 \pm 7 \text{ K} \\
 \circ & \gamma_{12} & = 0 ; \quad \text{ferroelectric mode, } T_0 = 61 \pm 4 \text{ K} \\
 \gamma & \gamma_{12} & = 0 ; \quad \text{underdamped mode}
 \end{array}$$

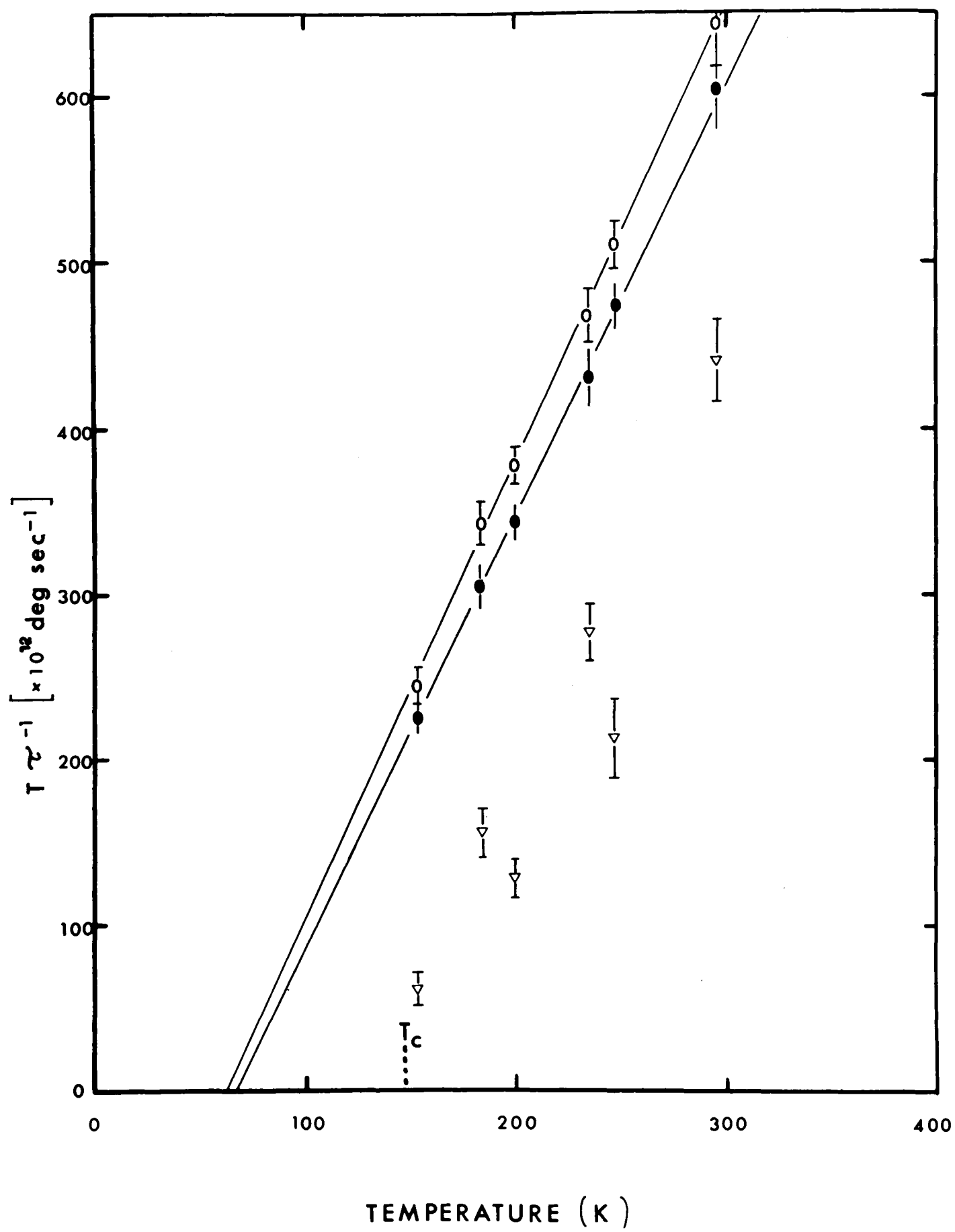


Figure 6.14

Decoupling of the modes in CsDA at $T = 295\text{K}$
with $\Delta = 0$.

RAMAN SPECTRUM OF CSDA B_2 -SYMMETRY

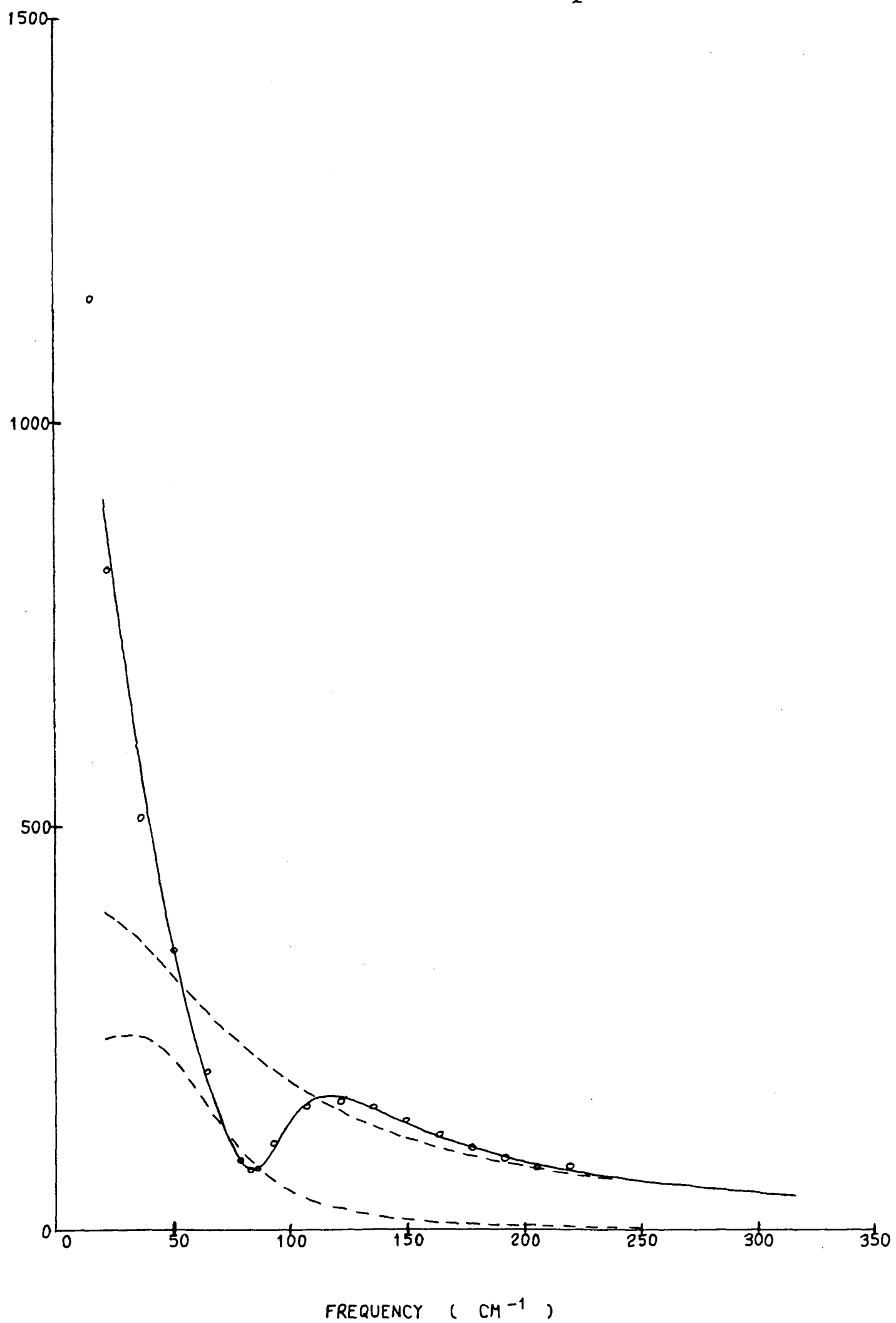


Figure 6.15

E-symmetry Raman spectrum of ADP at several temperatures in the paraelectric phase. The antiferroelectric transition occurs at $T_A = 147\text{K}$.

RAMAN SPECTRUM OF ADP E-SYMMETRY

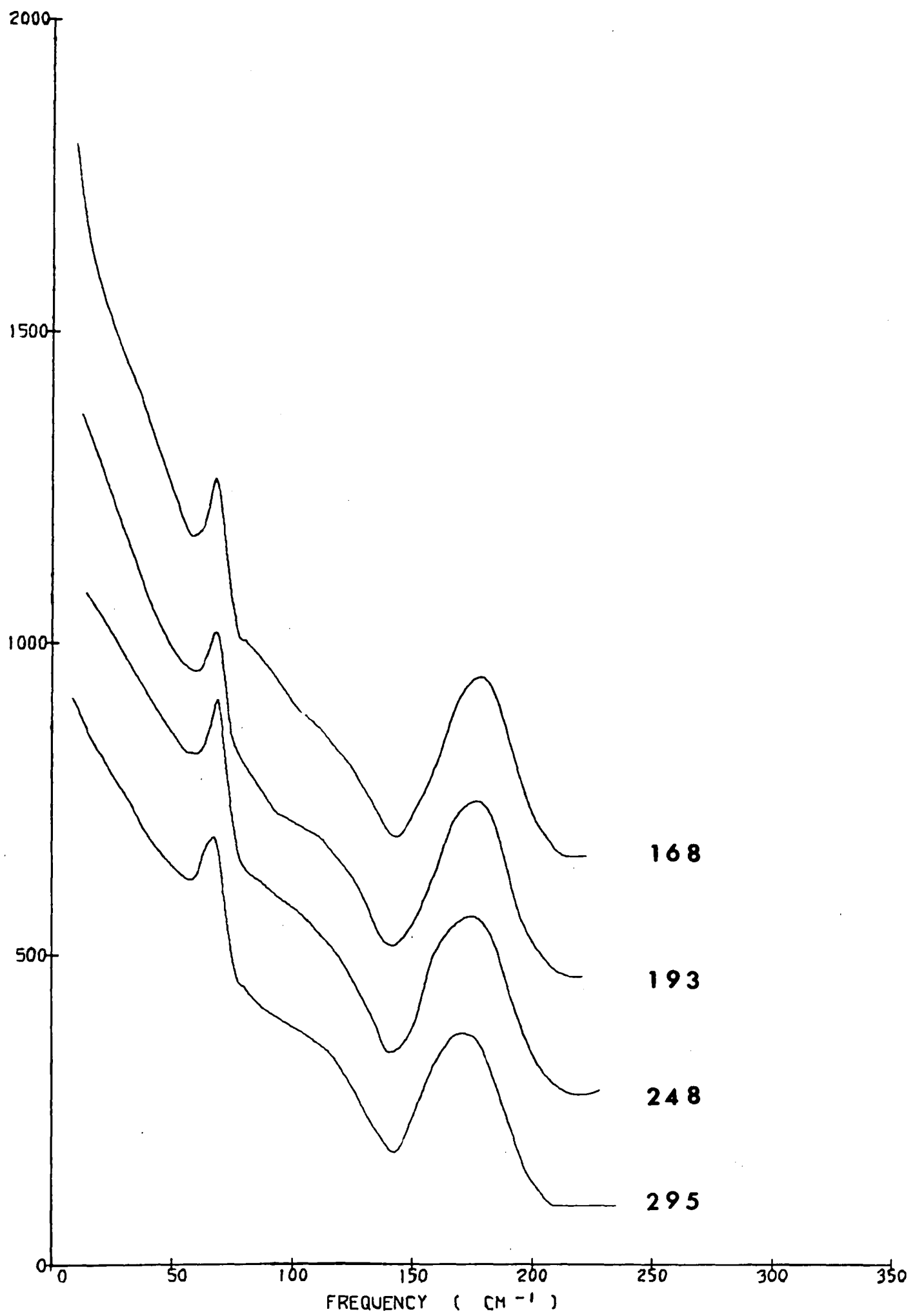


Figure 6.16

B_2 - symmetry Raman spectrum of ADP in the paraelectric phase. The overdamped mode is considerably weaker than the corresponding E- symmetry mode

RAMAN SPECTRUM OF ADP B_2 -SYMMETRY

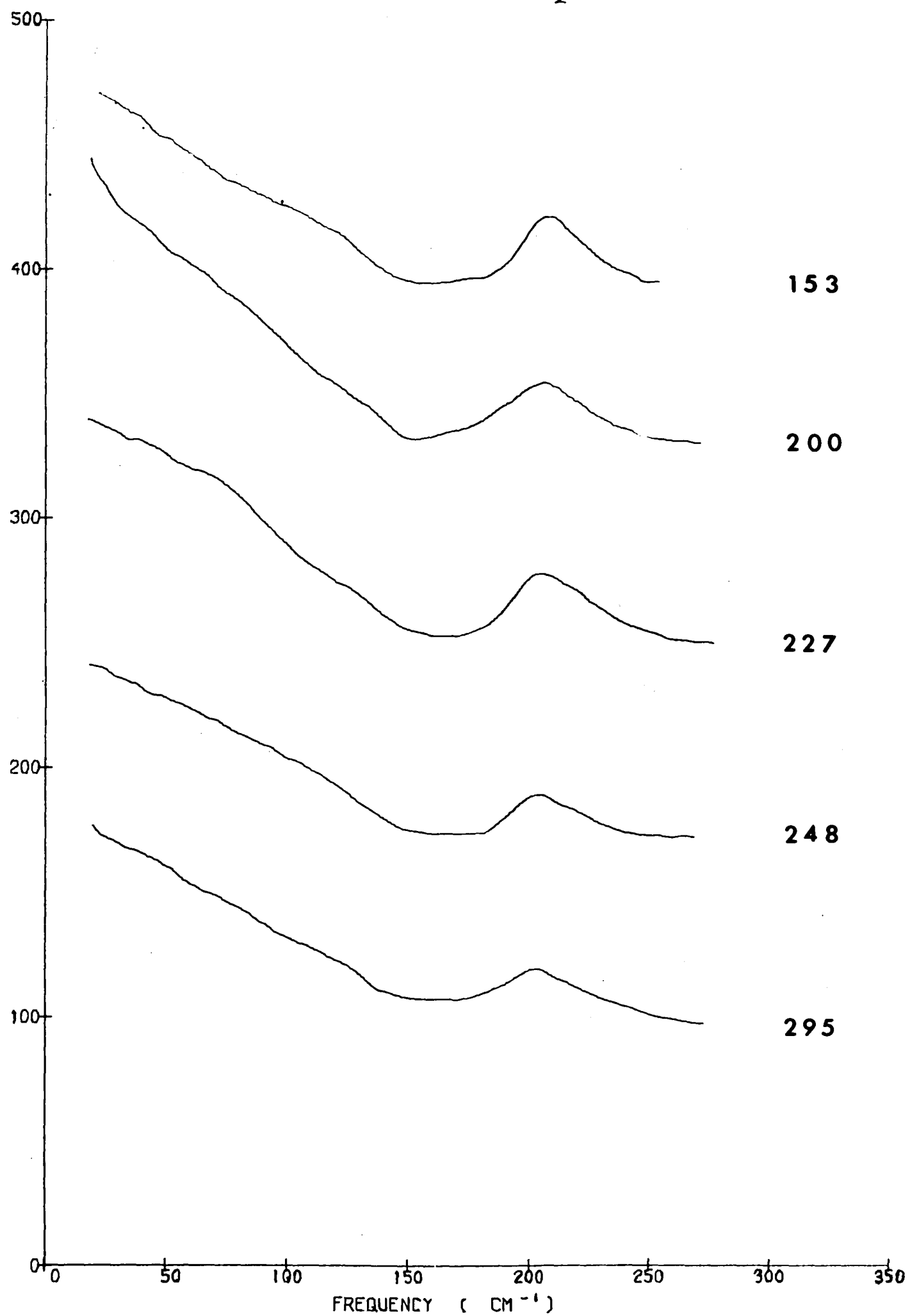


Figure 6.17

Decoupling of the modes in the B_2 symmetry spectrum of ADP at $T = 295K$ with $\gamma_{12} = 0$. Parameters are given in Table 6.8.

RAMAN SPECTRUM OF ADP B_2 -SYMMETRY

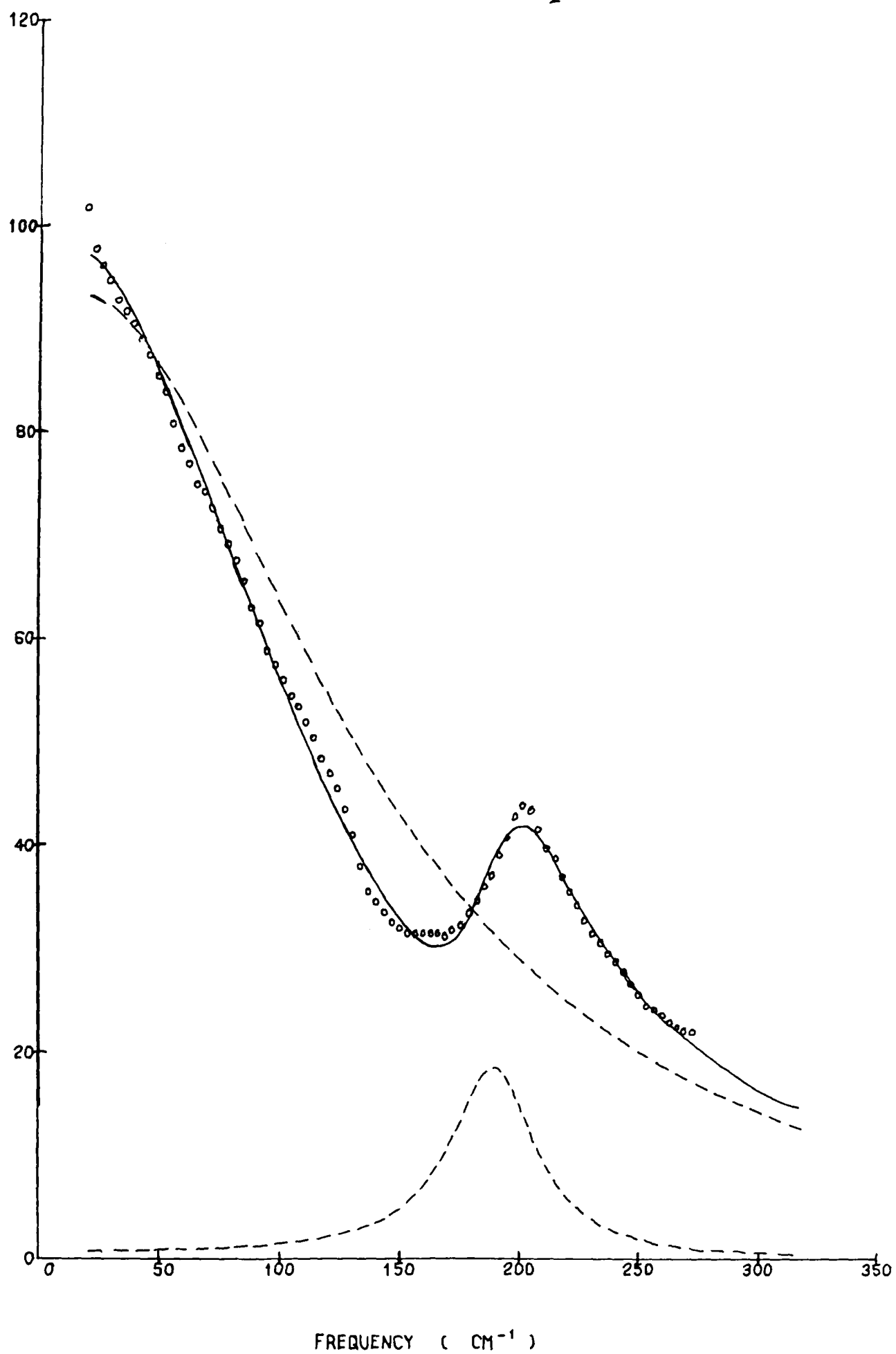


Figure 6.18

Decoupling of the modes in the B_2 symmetry
spectrum of ADP at $T = 295\text{K}$ with $\Delta = 0$.

RAMAN SPECTRUM OF ADP B_2 -SYMMETRY

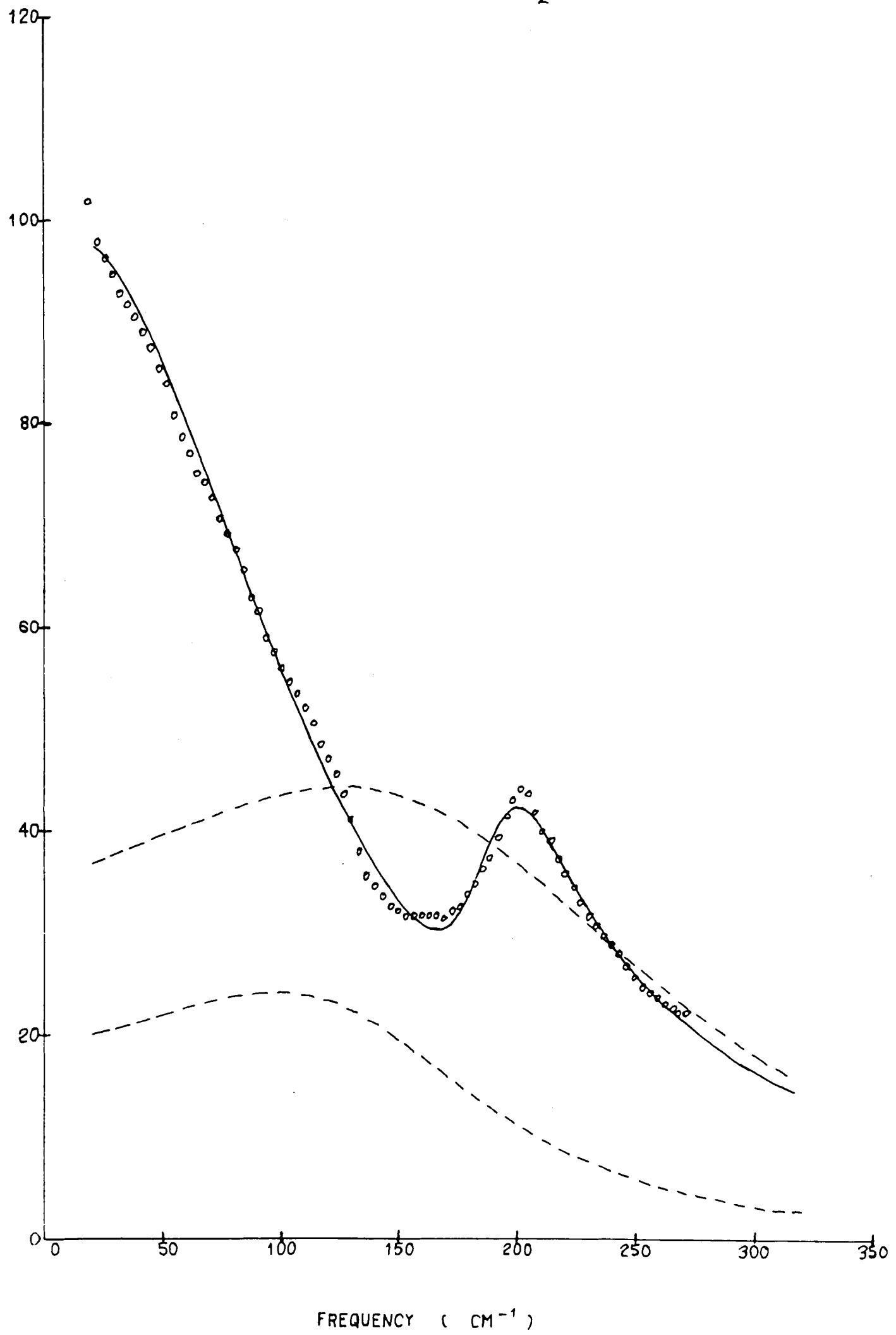


Figure 6.19

The Debye relaxation time for the E-symmetry overdamped mode in ADP; $T_o = 54 \pm 5K$.

Comparison is made with the static dielectric constant measurements of Mason [10] and the microwave data of Kaminow [12], both of which give negative values of T_o .

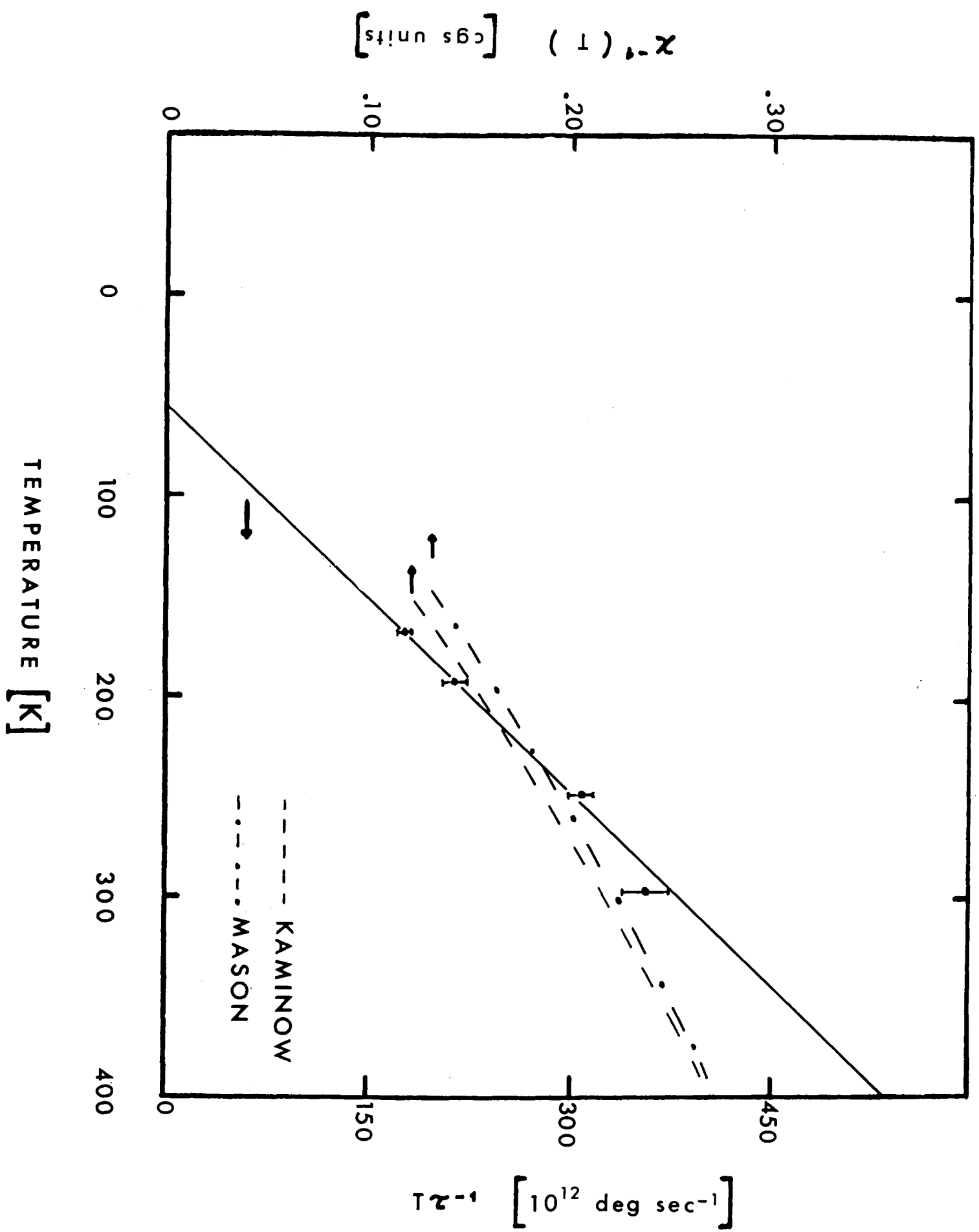


Figure 6.20

The temperature dependence of the Debye relaxation time for the B_2 -symmetry soft mode in ADP; $T_0 = 29 \pm 3\text{K}$ when $\gamma_{12} = 0$, and $110 \pm 5\text{K}$ when $\Delta = 0$.

Again the measurements of Mason [10] and Kaminow [12] give negative temperatures for T_0 .

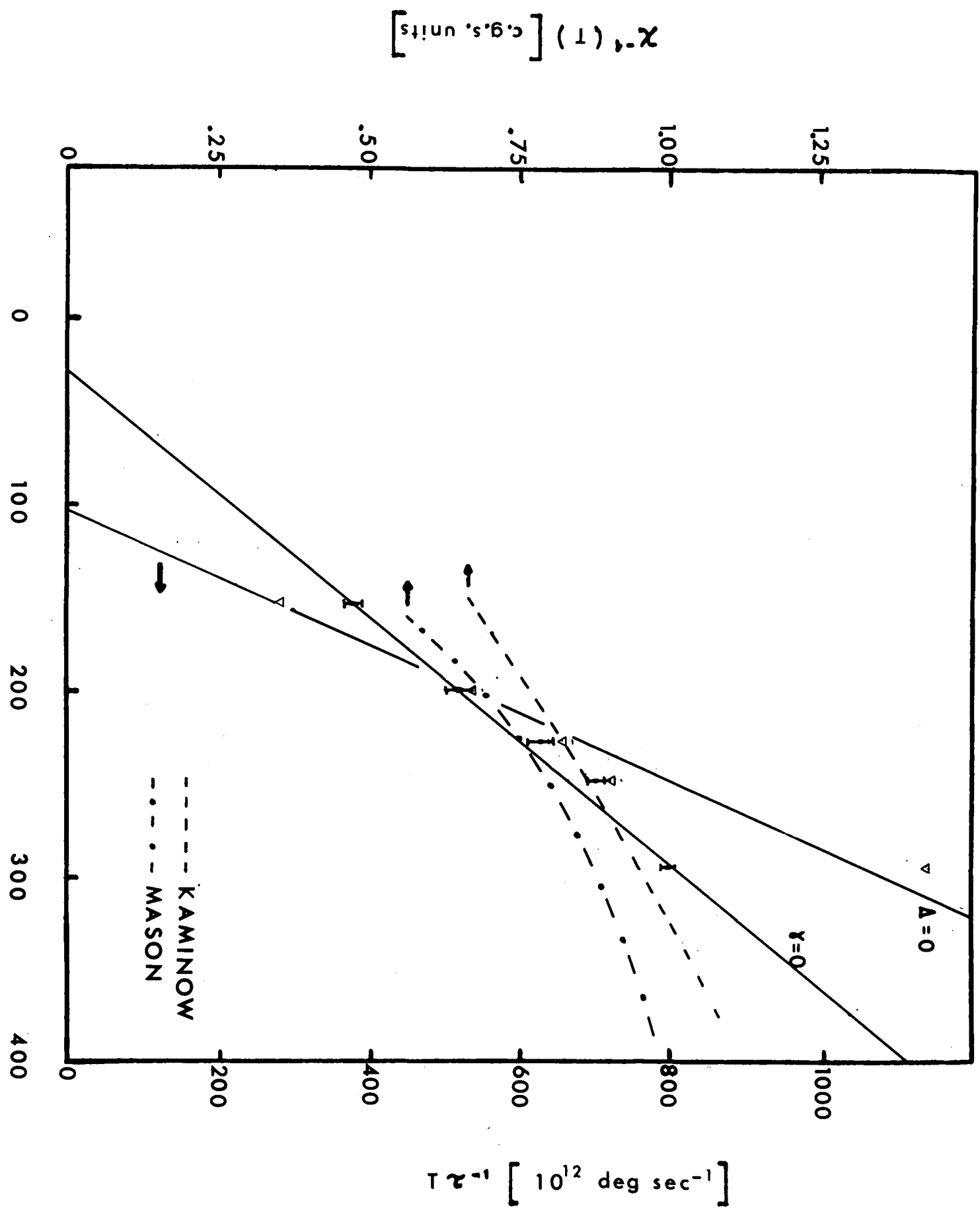


Figure 6.21

The low frequency E-symmetry Raman spectrum
of AD*P for several temperatures $T > T_A \approx$
240K.

RAMAN SPECTRUM OF AD*P E-SYMMETRY

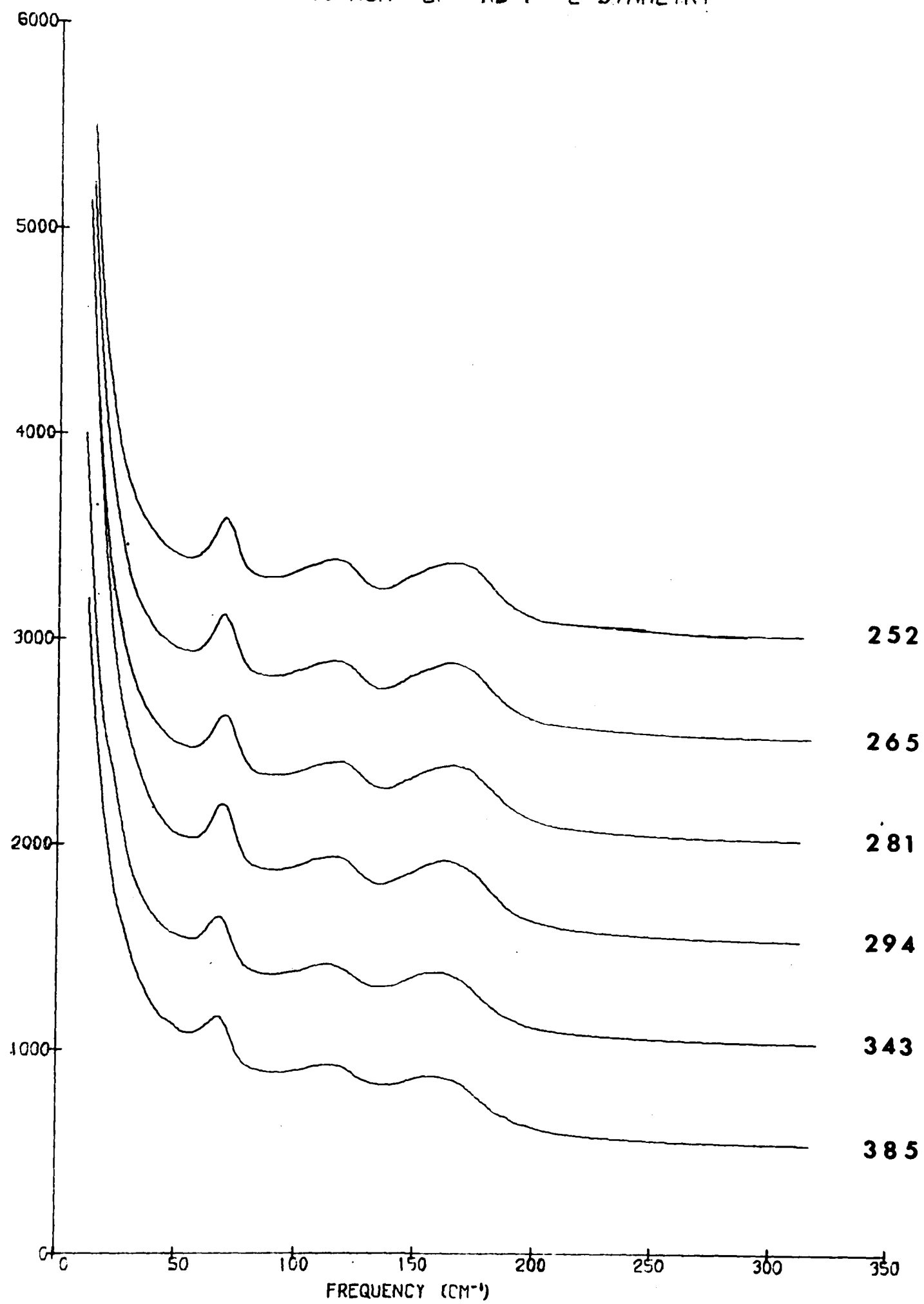


Figure 6.22

The B_2 -symmetry of AD*P in the paraelectric phase

RAMAN SPECTRUM OF AD*P B₂-SYMMETRY

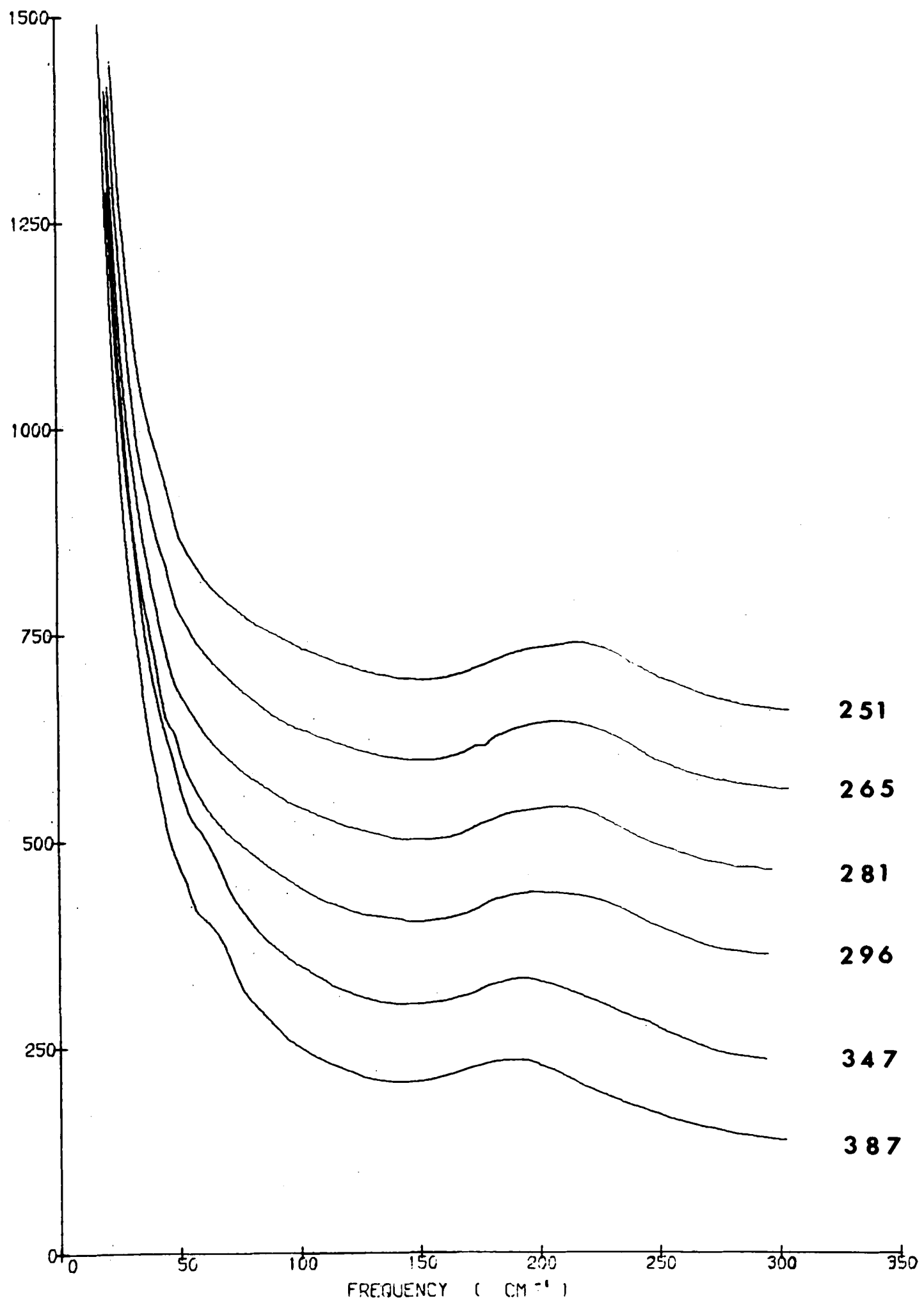


Figure 6.23

Classical oscillator fit to the B_2 spectrum
of AD*P at $T = 296K$.

In this case two uncoupled modes is
sufficient.

RAMAN SPECTRUM OF AD*P B_2 -SYMMETRY

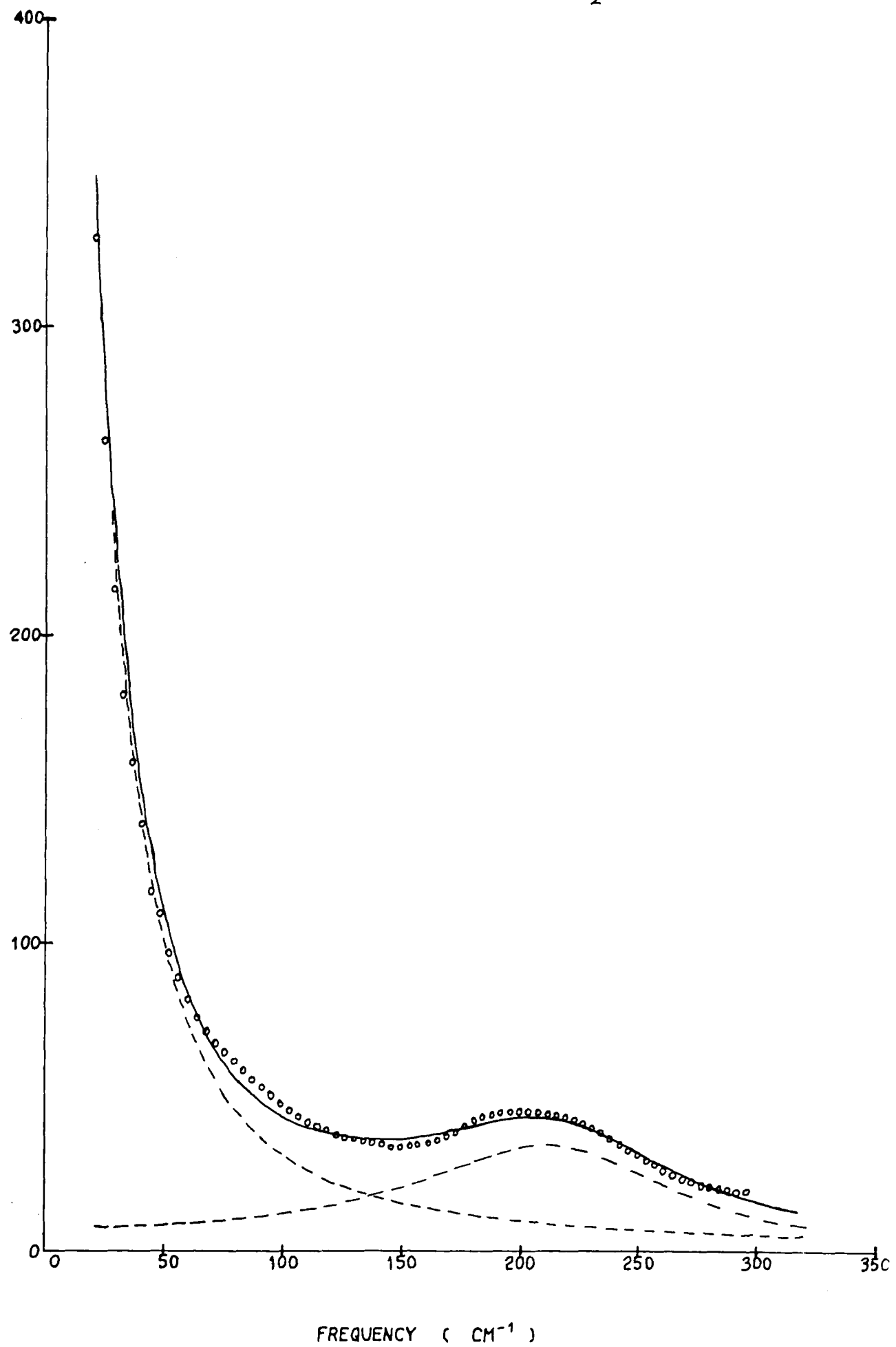


Figure 6.24

Debye relaxation time of the E-symmetry mode in AD*P; $T_0 = 168 \pm 20\text{K}$. The static dielectric data is that of Mason and Matthias [11]; once again there is considerable disagreement between the static and optical frequency measurements.

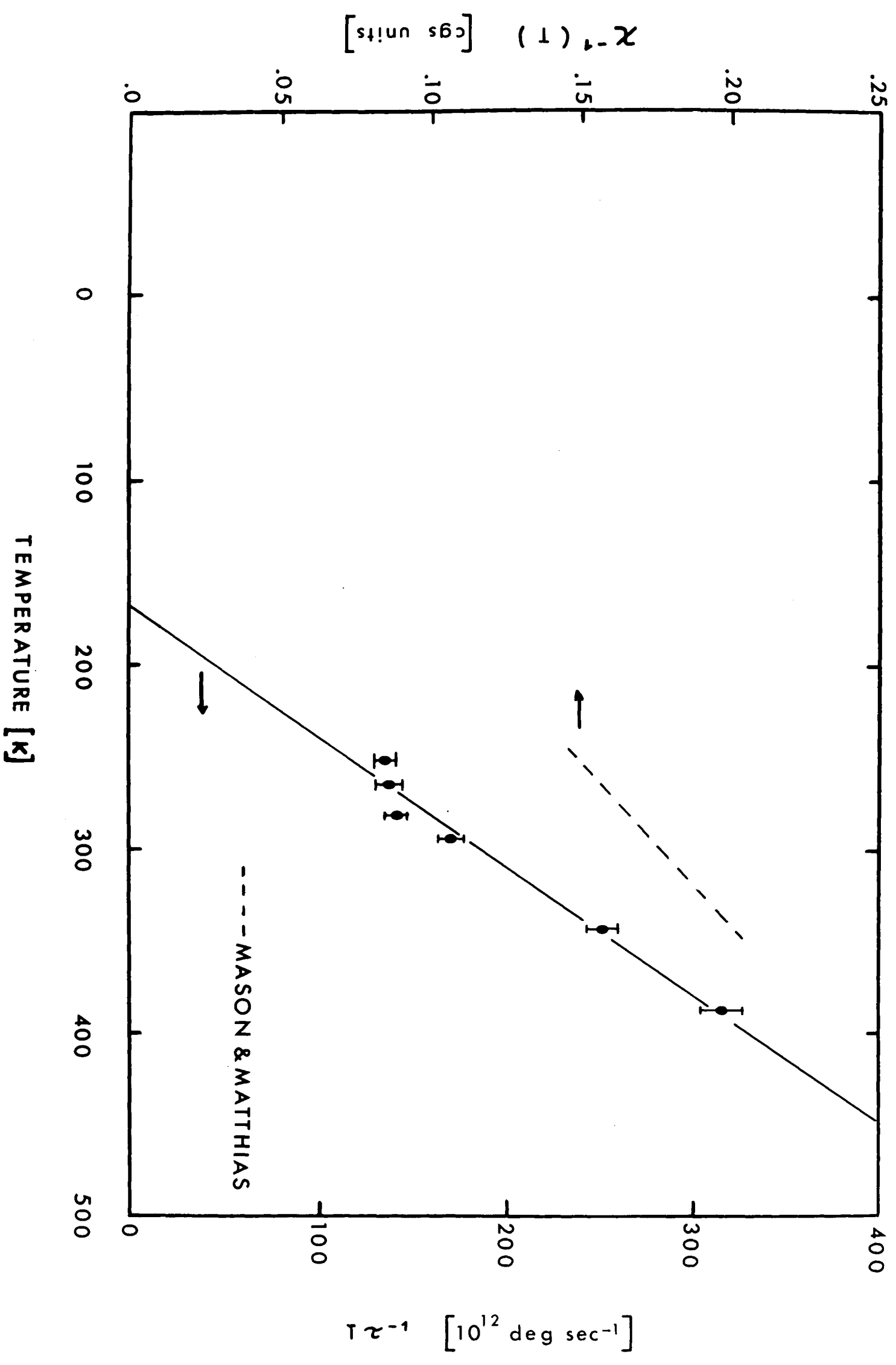
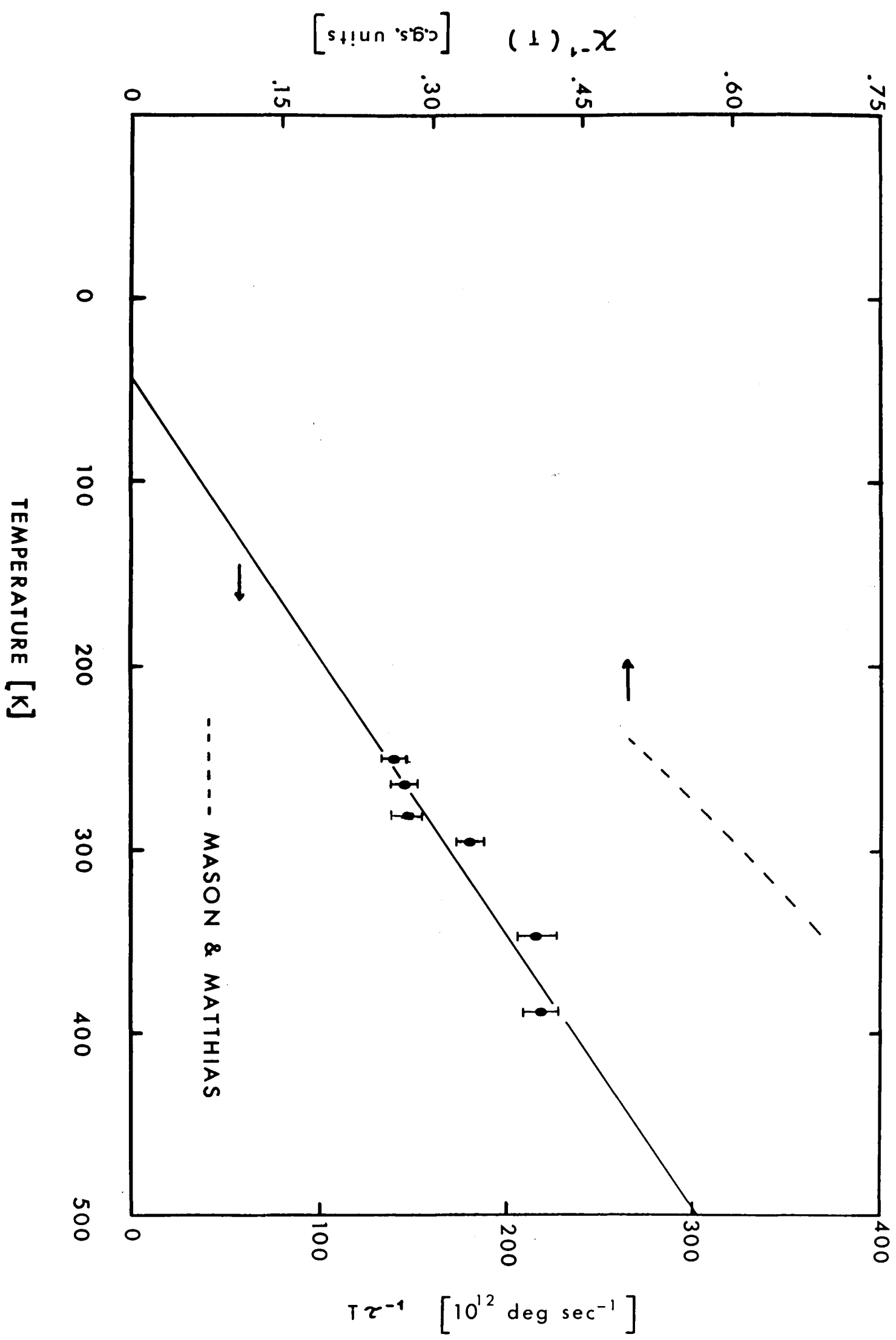


Figure 6.25

The temperature dependence of (T/γ) for the B_2 overdamped mode of AD*P yields $T_0 = 55 \pm 20\text{K}$. These measurements are compared with the dielectric data of Mason and Matthias [11].



CHAPTER 7

Mode Coupling and Quasi-elastic scattering in $5\text{PbO} \cdot 3\text{GeO}_2$

7.1 Introduction

The physical properties of lead germanate ($5\text{PbO} \cdot 3\text{GeO}_2$) have been the subject of much study since the synthesis was first reported [1]. It was found to be ferroelectric [2,3], having a large anomaly in the c-axis dielectric constant (ϵ_{33}) at $T_c = 451\text{K}$, whereas the a-axis dielectric constant (ϵ_{11}) remained virtually unchanged. Measurements of the spontaneous polarisation indicate that the transition is continuous [2], but so far no accurate study of the thermal properties has been reported. The piezoelectric constant (d_{31}) and the elastic compliance (S_{11}^E) have also been observed to exhibit anomalies at T_c [4]. At room temperature the crystal space group is $P3 (C_3^1)$ and that of the non-polar paraelectric phase is $P\bar{6} (C_{3h}^1)$. Lead germanate is the only known ferroelectric possessing this symmetry, and the high temperature phase is the first known structure with $P\bar{6}$ symmetry. Optical activity parallel to the c-axis has been observed [5] with the gyration coefficient

changing sign on reversal of the spontaneous polarisation. Again, it is the only ferroelectric exhibiting this enantiomorphic transformation.

The optical lattice vibrations are closely linked with the phase transition [6], and inelastic light scattering from temperature dependent-'soft'-transverse optic modes has been observed in a number of ferroelectrics. In some cases e.g. BaTiO_3 [7] and KH_2PO_4 (as discussed in chapters 5 and 6), the spectrum of radiation scattered by the ferroelectric mode is relatively broad, and the mode is overdamped at all temperatures. In other cases, e.g. SbSI [8], the mode is underdamped at all temperatures. In $5\text{PbO} \cdot 3\text{GeO}_2$ we have observed a soft mode which is underdamped far away from the transition, but broadens, decreases in frequency, and becomes overdamped near T_c . However, a mode coupling observed to occur between the soft mode and modes of higher frequency, complicates the determination of the dynamical parameters; an analysis similar to that given previously for KH_2PO_4 etc., is presented below.

In view of our discussion of a central component in the soft mode response (in chapter 6), the low frequency spectrum of lead germanate has been studied very closely. We have observed quasi-elastic scattering whose width is resolution limited and whose intensity diverges at T_c . The results are discussed in terms of the theory proposed by Cowley and Coombs [9], and a comparison is made with critical scattering observed in other systems.

7.2 Experimental

The experimental set up is that described in chapter 3. Since the material absorbs quite strongly in the region 400 - 600 nm [10], Raman scattering was measured using the 632.8 nm line of the He-Ne laser. The spectrometer slitwidth was set at 3 cm^{-1} , enabling us to collect data to within 5 cm^{-1} of the exciting line.

In the region below 5 cm^{-1} the Raman spectrum is obscured by very strong parasitic Rayleigh scattering. The intrinsic linewidth of this elastic scattering is determined by the laser but the observed linewidth is broadened by the resolution function of the spectrometer. A technique has recently been developed [11] which filters out this Rayleigh component and enables the low frequency inelastic scattering to be observed. Iodine vapour has a vibration-rotation line (O-43 P(12)) which lies within the Doppler gain curve of the 514.5 nm Ar^+ laser line. The laser, operating at this frequency, is single-moded by an intra-cavity etalon; this effectively forces all the energy into a single cavity mode of width $\sim 10^7 \text{ Hz}$, instead of the 80 modes spread over the region of $\sim 10^{10} \text{ Hz}$ under the gain profile. The etalon is tuned to the iodine absorption line (width $\sim 10^8 \text{ Hz}$) so that an optical cell filled with iodine vapour can be used to remove the parasitic scattering. An absorption factor of $\sim 10^3$ has been achieved.

Since the crystal absorbs strongly at 514.5 nm, much of the Raman signal is lost. In addition, there is a large local heating in the neighbourhood of the focussed laser

beam, so that the temperature at the sample surface is no longer a true measure of the actual temperature. To overcome this problem we have performed two sets of experiments. Firstly, using the 632.8 nm excitation, the Raman spectrum from 5 - 50 cm^{-1} is recorded at several temperatures in the ferroelectric phase; the spectra are analysed in terms of a response function for coupled modes, as described in 7.3, and the temperature dependence of the soft mode frequency, width and intensity are obtained. Secondly, the 514.5 nm exciting line is used in conjunction with the iodine filter, and the frequency of the soft mode is used to indicate the true temperature. A local heating of $\approx 22\text{K}$ was measured with a beam power of 200 mW.

7.3.1 Coupled mode analysis

Figure 7.1 shows the Stokes part of the spectrum for a number of temperatures below T_c . The scattering geometry is, in the usual notation, $X(ZZ)Y$. The irreducible representation of the phonon participating in this scattering process therefore transforms as ZZ , which for $P3$ is totally symmetric. The ferroelectric mode is expected to appear in this spectrum since the pattern of atomic displacements it produces leaves the direction of the spontaneous polarisation unchanged, and so forms the basis of a totally symmetric representation. It is clearly evident in figure 7.1 that mode A is highly temperature dependent, becoming overdamped above $\sim 400\text{K}$. There is no evidence of a soft mode in the Raman spectrum above T_c ,

and it must therefore belong to the Raman inactive A'' irreducible representation of $P\bar{6}$. Near 270K modes A and B interact, leading to a level repulsion and a characteristic intensity transfer whereby the soft mode is always the more intense. While A softens, B remains fixed in frequency, but its strength decreases to zero as the transition is approached, and it is Raman inactive above T_c . Mode C is only slightly temperature dependent and is active in both phases.

In order to extract the temperature dependence of the soft mode frequency and width and evaluate the critical exponent, it is necessary to uncouple the two modes. This process has now been carried out successfully for several systems, e.g. SbSI [12] and KH_2PO_4 (as described in chapters 5 and 6), and has been reviewed recently by Scott [13]. Recalling equation (2.13), the Raman intensity is given by

$$I(\omega) = K. \left\{ n(\omega) + 1 \right\} \sum_{jj'} P(j) P(j') \text{Im}(G_{jj'}(\omega)) \quad (7.1)$$

where we have changed the notation only slightly. In the case of lead germanate we consider coupling between the two lower frequency modes A and B, while the third mode, C, remains uncoupled. The Green's function is then:-

$$G^{-1}(\omega) = \begin{bmatrix} \omega_1^2 - \omega^2 & 0 & 0 \\ 0 & \omega_2^2 - \omega^2 & 0 \\ 0 & 0 & \omega_3^2 - \omega^2 \end{bmatrix} +$$

$$\begin{bmatrix} 2(\Delta_{11}+i\Gamma_{11})\omega_1 & 2(\Delta_{12}+i\Gamma_{12})(\omega_1\omega_2)^{\frac{1}{2}} & 0 \\ 2(\Delta_{12}+i\Gamma_{12})(\omega_1\omega_2)^{\frac{1}{2}} & 2(\Delta_{22}+i\Gamma_{22})\omega_2 & 0 \\ 0 & 0 & 2(\Delta_{33}+i\Gamma_{33})\omega_3 \end{bmatrix} \quad (7.2)$$

The first matrix on the right is the simple harmonic response function for the three modes, while the second matrix represents the self-energy. Δ and Γ are frequency dependent in a rather complex fashion, as discussed in Appendix 1, but we can make the simplifying approximation that Δ is frequency independent while Γ is linearly dependent on frequency. Writing $2\omega_1 \Gamma_{11} = \gamma_{11}\omega$ etc., and renormalising the frequencies $\hat{\omega}_1^2 = \omega_1^2 + 2\Delta_{11}\omega_1$ etc., we obtain:-

$$G^{-1}(\omega) = \begin{bmatrix} \hat{\omega}_1^2 - \omega^2 + i\gamma_{11}\omega & \Delta + i\gamma_{12}\omega & 0 \\ \Delta + i\gamma_{12}\omega & \hat{\omega}_2^2 - \omega^2 + i\gamma_{22}\omega & 0 \\ 0 & 0 & \hat{\omega}_3^2 - \omega^2 + i\gamma_{33}\omega \end{bmatrix} \quad (7.3)$$

The spectra in figure 7.1 can therefore be described by this response function in terms of the 11 parameters. Since mode C is Raman active above T_c we may expect $P(3)$ to be approximately temperature independent. Therefore, by monitoring the ratios $P(1)/P(3)$ and $P(2)/P(3)$ we can study the temperature dependence of the mode strengths. The number of parameters is further reduced if we assume $\gamma_{12} = 0$. The values of Δ then obtained do not appreciably affect the static response $G(0)$, so that the Curie-Weiss form is recovered if we assume the soft mode frequency to have the temperature dependence predicted by Cochran [6]

$$\hat{\omega}_1^2 = \text{const.} \times (T_c - T) \quad (7.4)$$

We have carried out a least squares fit to the observed spectra using the response function and constraints described above. The values of the parameters obtained are shown in Table 7.1.

7.3.2 Results

The frequencies of the three modes, and of two others not shown in figure 7.1, are plotted in figure 7.2 as a function of temperature. The level repulsion can be seen very clearly. It is also obvious that the mode with highest frequency is quite temperature dependent and this would indicate that the decoupling process should involve three modes. However, since the strength of the interaction is inversely proportional to the frequency difference, we may expect the coupling between A, B and the mode of highest frequency to be smaller than that between A and B.

None of the individual frequencies varies in the manner predicted by (7.4), but we find that the product of the squares of the frequencies $\prod \omega_j^2$ for the five modes is proportional to $(T_c - T)$, as shown in figure 7.3. This is consistent with the generalised Lyddane-Sachs-Teller relation as derived by Cochran and Cowley [14]

$$\prod_j \left| \frac{\omega_T(Z)}{\omega_L(Z)} \right|_j^2 = \frac{\epsilon_{33}(\infty)}{\epsilon_{33}(0)} \quad (7.5)$$

$\omega_T(Z)$ and $\omega_L(Z)$ are respectively the transverse and longitudinal optic mode frequencies for which the polarisation

is parallel to z , and $\epsilon_{33}(0)$ and $\epsilon_{33}(\infty)$ are the static and optical dielectric tensor elements. It is expected that $\omega_L(z)$ and $\epsilon_{33}(\infty)$ do not vary much with temperature, so that insertion of the Curie-Weiss form for $\epsilon_{33}(0)$ yields the appropriate result. It is important that the uncoupled frequencies are used and not the frequencies corresponding to the peaks in the spectra.

The effect of coupling on the strengths of the modes is shown in figure 7.4. A transfer of intensity from the higher to the lower frequency mode occurs after which both decrease to zero as the transition is approached. The ferroelectric mode strength appears to have a temperature dependence similar to that of the spontaneous polarisation, but accurate numbers are difficult to obtain above 400°K when the mode becomes overdamped.

Above 300°K only mode A varies with temperature; the frequency and width vary as predicted by the soft mode theory until, as shown in figure 7.5, it becomes overdamped. When the damping is large it is difficult to obtain unique values of the parameters due to a high correlation that arises between them. It may be expected that a simple extrapolation of the parameters from their low temperature underdamped values should provide suitable values to describe the overdamped spectrum, but we have found this to be insufficient. The width γ_{11} increases rapidly as the transition is approached, in a fashion quite different from the linear behaviour predicted by anharmonic theory [15].

7.3.3 Discussion

An apparent divergence of the soft mode damping constant has been observed in PbTiO_3 by Burns and Scott [16], and has been explained by Silverman [17] in terms of a frequency dependent damping constant. The proposed mechanism giving rise to this effect involves the enhancement near T_c of soft mode scattering with the annihilation of a transverse acoustic phonon and creation of a longitudinal acoustic phonon. Tani [18] has also predicted critical behaviour of the damping constant near the paraelectric Curie point in SrTiO_3 . From a consideration of third-order anharmonic forces present in special symmetry directions he was able to show an anomalously large increase in the damping as the transition is approached. However, this singular behaviour is not obtained with a three-dimensional model Hamiltonian [19].

Gesi et al. [20] have observed a diverging damping constant for the soft zone corner, R_{25} , mode in KMnF_3 , and a recent investigation [21] has shown that it arises from a central component in the response. Riste et al. [22] first observed this mode near the 105K phase transition in SrTiO_3 and found it to narrow and increase in intensity near T_c . Feder [13] has suggested that the scattering originates from non-propagating entropy fluctuations which increase in the "critical region"; in this case it is not the adiabatic but the isothermal susceptibility which determines the form of the response. In a higher resolution study of this mode in SrTiO_3 and

KMnF_3 , Shapiro et al. [21] have made a quantitative comparison of the lineshape with a more fundamental microscopic model.

Therefore, the presence of a central mode in the spectrum has been identified very clearly; that it can give rise to an apparent divergence of the soft mode damping constant is also now understood. The similarity of the KMnF_3 results with lead germanate suggests that the low frequency region of the Raman spectrum should be examined at higher resolution.

In figure 7.6 the spectrum at $T = 373\text{K}$ is shown together with the best fit (solid line) to the data above 15 cm^{-1} . There is a large discrepancy between the observed and calculated intensity in the region $\omega < 15\text{ cm}^{-1}$. The lower curve shows this low frequency region of the spectrum obtained at $T = 115\text{K}$, and emphasises that the elastic Rayleigh scattering extending to 5 cm^{-1} rises very sharply and therefore cannot account for the large discrepancy. In figure 7.7 we compare the observed and calculated intensities at several temperatures between room temperature and T_c and we see that this additional low frequency scattering is temperature dependent, being narrower and stronger as the transition is approached.

In view of these results we have performed a second set of experiments on lead germanate. The iodine cell is used to absorb the Rayleigh light and the spectrometer resolution is improved. The results of these experiments are discussed in the next section.

7.4.1 Quasi-elastic scattering in lead germanate

Figure 7.8 shows the spectra obtained at three temperatures in the ferroelectric phase. At 385K the phonon mode appears as a fairly broad feature extending to 30 cm^{-1} . Below 10 cm^{-1} we have resolved additional scattering but it is not well separated from the side band. At 413K the soft mode is overdamped but now a central component is clearly visible. As the temperature is raised further the two profiles merge, and the resultant profile is similar to that of a highly overdamped oscillator. In these spectra some Rayleigh light is still present; complete extinction can be achieved by increasing the vapour cell temperature, but at the same time the broad band absorption also increases. The "noise" in the spectra in fact arises chiefly from a changing absorption produced by temperature fluctuations in the cell.

The integrated intensity is shown in figure 7.9. Here the cell temperature has been raised to give optimum Rayleigh absorption. Below 400K the intensity is mainly that of residual Rayleigh scattering, but there is also present a quasi-elastic component. As the sample temperature is raised the quasi-elastic intensity increases and is a maximum at T_c . Above the transition the intensity drops sharply; that it occurs over 15 degrees or so we believe may be due to the temperature gradient which exists along the beam path in the crystal.

7.4.2 Classical critical scattering

It is of interest that classical theory predicts a divergence of the integrated intensity at T_c . In the high temperature approximation the intensity of Raman light scattered per unit frequency interval is given by [7]

$$I(\omega) \propto k_B T P_s^2 \frac{\chi''(\omega)}{\omega} \quad (7.6)$$

Comparing this expression with equation (7.1) we have replaced $(n(\omega) + 1)$ by $(k_B T / \hbar \omega)$, where k_B is Boltzmann's constant. $\chi''(\omega)$ is the imaginary part of the susceptibility arising from the ferroelectric mode, and is directly proportional to $G_{11}(\omega)$. In equation (2.12) the polarisability operator $P_{\alpha\beta}(0j)$ is proportional to the spontaneous polarisation P_s , when j refers to the ferroelectric mode. The integrated intensity is then:-

$$\begin{aligned} I &\propto k_B T P_s^2 \int_{-\infty}^{+\infty} \frac{\chi''(\omega)}{\omega} d\omega \\ &\propto k_B T P_s^2 \chi'(0) \end{aligned} \quad (7.7)$$

where $\chi'(0)$ is the static dielectric susceptibility.

Here we have made use of the Kramers-Kronig relation

$$\chi'(\omega) = \frac{2}{\pi} \int_0^{+\infty} \frac{\omega' \chi''(\omega')}{\omega'^2 - \omega^2} d\omega'$$

with $\omega = 0$.

For most second-order transitions $P_s \propto (T_c - T)^{\frac{1}{2}}$, and

$\chi'(0)$ has a Curie Weiss temperature dependence. The intensity does not then diverge at T_c . It is apparent from (7.7) that the intensity will display a singularity

at T_c if the spontaneous polarisation has a weaker temperature dependence. To obtain further information we must examine the form of the Devonshire free energy:-

$$F = a + \frac{1}{2}b P_s^2 + \frac{1}{4}c P_s^4 + \frac{1}{6}d P_s^6 + \dots \quad (7.8)$$

Ginzburg [24] has shown that "critical opalescence" is expected near phase transitions when $c = 0$, i.e. in the special case where the transition occurs "near the Curie critical point". The density and temperature are then close to their critical values, and the transition is on the limit between first and second order. In this case, the equilibrium condition $(\frac{\partial F}{\partial P_s}) = 0$ yields $P_s = \left\{ \frac{1}{d}(T_c - T) \right\}^{\frac{1}{4}}$, and the ratio of the temperature gradient of the dielectric susceptibility above and below T_c is exactly $-\frac{1}{4}$. These two quantities are very close to values observed in lead germanate by Iwasaki et al. [2] and Nanamatsu et al. [3] respectively.

Further evidence for the existence of a quasi-elastic component is provided by a lineshape analysis. However, for the reasons mentioned above - but mainly temperature inhomogeneity - the spectra in figure 7.8 are inadequate. We have therefore re-analysed the data in figure 7.1.

7.4.3 Microscopic model

In chapter 6 we have discussed a theory due to Cowley and Coombs [25] which suggests that the spectral response of a zone-centre soft mode may have at low frequency an additional component which is important in piezoelectric crystals. At high frequencies the response

is identical with the damped harmonic oscillator used in (7.3); at low frequency it is modified to include the possibility of dielectric fluctuations coupling to changes in local thermodynamic equilibrium. Their result is:-

$$G^{-1}(\omega) \propto [\hat{\omega}_0^2 - \omega^2 + i\gamma\omega - \frac{\alpha T}{1 + i\omega\tau^*}] \quad (7.9)$$

The form of the scattering then depends sensitively on the values of α and τ^* , and in certain conditions it produces a peak at $\omega = 0$. In pyroelectric crystals the additional loss mechanism is more complicated since the symmetry conditions restricting the values of the coefficients $V(\begin{smallmatrix} 0 & \underline{q} & -\underline{q} \\ j & j_1 & j_1 \end{smallmatrix})$ are not so severe:-

$$\sum_{\underline{q}s} V(\begin{smallmatrix} 0 & \underline{q} & -\underline{q} \\ j & j_1 & j_1 \end{smallmatrix}) \neq 0$$

where $\underline{q}s$ is the "star of $\underline{q}$ " determined by the crystal point group symmetry. This result holds only in the case when $(0j)$ corresponds to a totally symmetric mode in a pyroelectric crystal, and otherwise the summation is identically zero. We have then the possibility of dielectric fluctuations coupling to second-sound [25].

Since the soft mode in the ferroelectric phase fulfils these requirements, the mechanism may be important here. However, we do not expect to observe this effect in the frequency region studied here, and the response function in (7.9) should be sufficient. We have incorporated this expression into (7.3) and obtained a fit to the data over the entire frequency region $5 - 50 \text{ cm}^{-1}$. The parameters

for modes B and C have not been altered, and we have assumed that the additional contribution to the off-diagonal self-energy term, G_{12} , is negligible. The effect of finite instrumental resolution is important in the case of a narrow central component, and should be included in the analysis. However, a detailed analysis is not possible here because, due to lack of data $< 5 \text{ cm}^{-1}$, we find α and γ^* to be highly correlated. The best fit gives the parameters shown in figure 7.10. In the region near T_c , $\hat{\omega}_0^2$ is constrained to be linearly temperature dependent, and γ^* is allowed to vary such that $2 < \gamma^{*-1} < 4 \text{ cm}^{-1}$. We then obtain $\alpha T = 350 \pm 50 \text{ cm}^{-2}$, and it appears to be largely temperature independent. As a result, $(\omega_0^2 - \alpha T) \propto (T_0' - T)$ with $T_0' = 455 \pm 5 \text{ K}$. In addition, the singular behaviour of γ disappears and a simple linear temperature dependence is obtained.

In contrast to SrTiO_3 and KMnF_3 , the quasi-elastic scattering in $5\text{PbO} \cdot 3\text{GeO}_2$ is observed over a wide temperature region. From figure 7.7 we see that it is observed at $T = 295 \text{ K}$; this gives $\xi = \left| \frac{T_c - T}{T} \right| < 0.3$, while Shapiro et al. [21] find $\xi < 0.15$ for the two perovskites. Since the critical region in which deviations from the mean field theory occur is expected to be much closer to the transition temperature in ferroelectric than in non-ferroelectric phase transitions, the quasi-elastic scattering in lead germanate would appear not to arise from critical fluctuations, in agreement with the suggestion of Cowley and Coombs.

Quasi-elastic scattering of light near a structural phase transition has previously been reported. In SbSI [26] the scattering extends over a frequency range $\sim 60 \text{ cm}^{-1}$, which is much larger than that predicted by existing theories. Johnston and Kaminow observed critical Rayleigh scattering in LiTaO_3 [27] but made no attempt to filter out the elastic component. In lead germanate, however, we have observed both inelastic and elastic components. The former is consistent with the classical soft mode picture and the latter has been shown to correspond closely to the microscopic theory proposed by Cowley and Coombs.

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Table 7.1

Oscillator parameters for $5\text{PbO} \cdot 3\text{GeO}_2$ (cm^{-1})

T(K)	P(1)	γ_{11}	$\hat{\omega}_1$	P(2)	γ_{22}	$\hat{\omega}_2$	γ_{12}	$\Delta^{1/2}$	P(3)	γ_{33}	$\hat{\omega}_3$
115	6.8	1.8	37.0	15.0	3.5	43.5	0.0	1.8	10	1.3	46.0
161	6.4	3.0	36.6	14.7	4.3	42.1	0.0	2.5	10	1.7	45.5
210	2.5	4.9	37.0	13.0	5.5	40.4	0.0	3.0	10	2.3	45.0
259	14.0	11.0	36.7	8.0	4.1	38.5	0.0	3.9	10	2.7	44.8
295	14.3	14.4	33.6	7.6	4.1	38.1	0.0	4.5	10	3.0	44.7
330	13.1	18.2	30.9	6.1	4.0	38.1	0.0	5.0	10	3.6	44.8
373	12.7	24.3	27.1	5.0	4.0	38.0	0.0	5.6	10	4.1	44.4
399	11.6	31.7	25.5	3.9	4.0	37.3	0.0	6.0	10	5.0	44.3
418	11.7	45.4	25.9	3.7	4.0	37.8	0.0	6.2	10	5.3	44.7
432	16.8	133	41.0	2.2	3.4	37.0	0.0	6.5	10	6.3	44.0

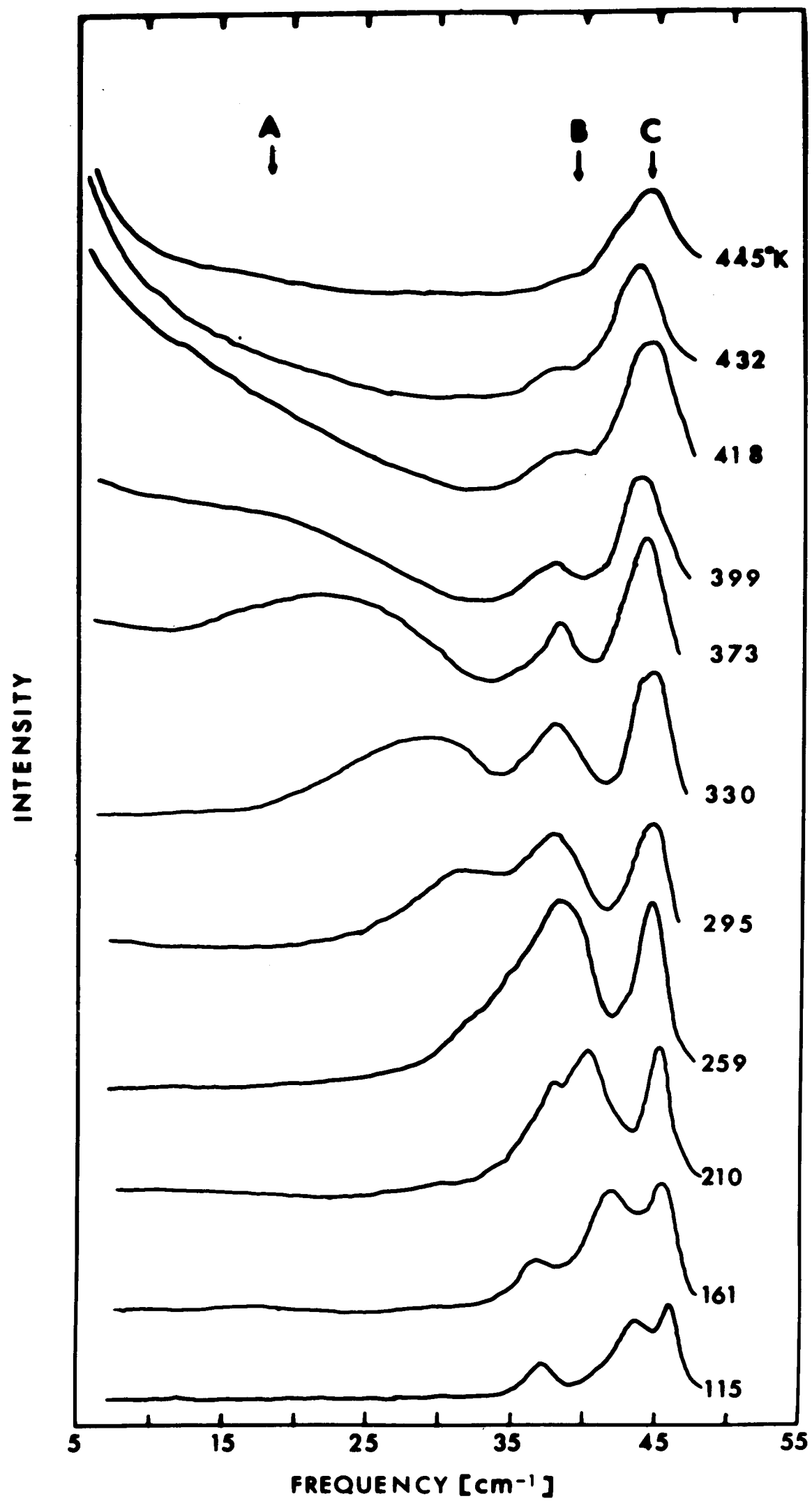


Figure 7.2

Temperature dependence of the characteristic frequencies of the lowest five modes in the $X(ZZ)Y$ spectrum.

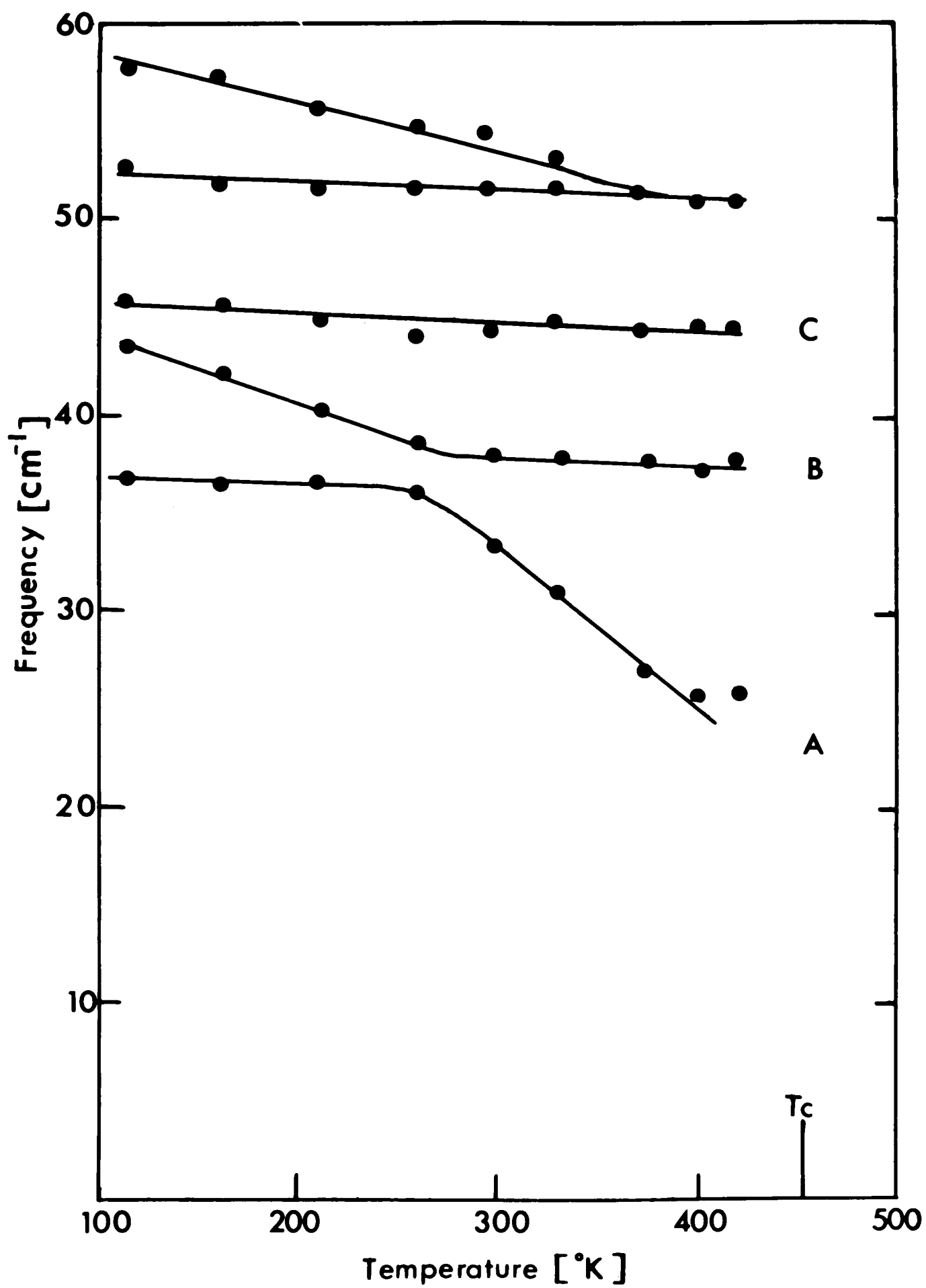


Figure 7.3

Temperature dependence of the product $\prod_j \omega_j^2$
for the five lowest frequency modes

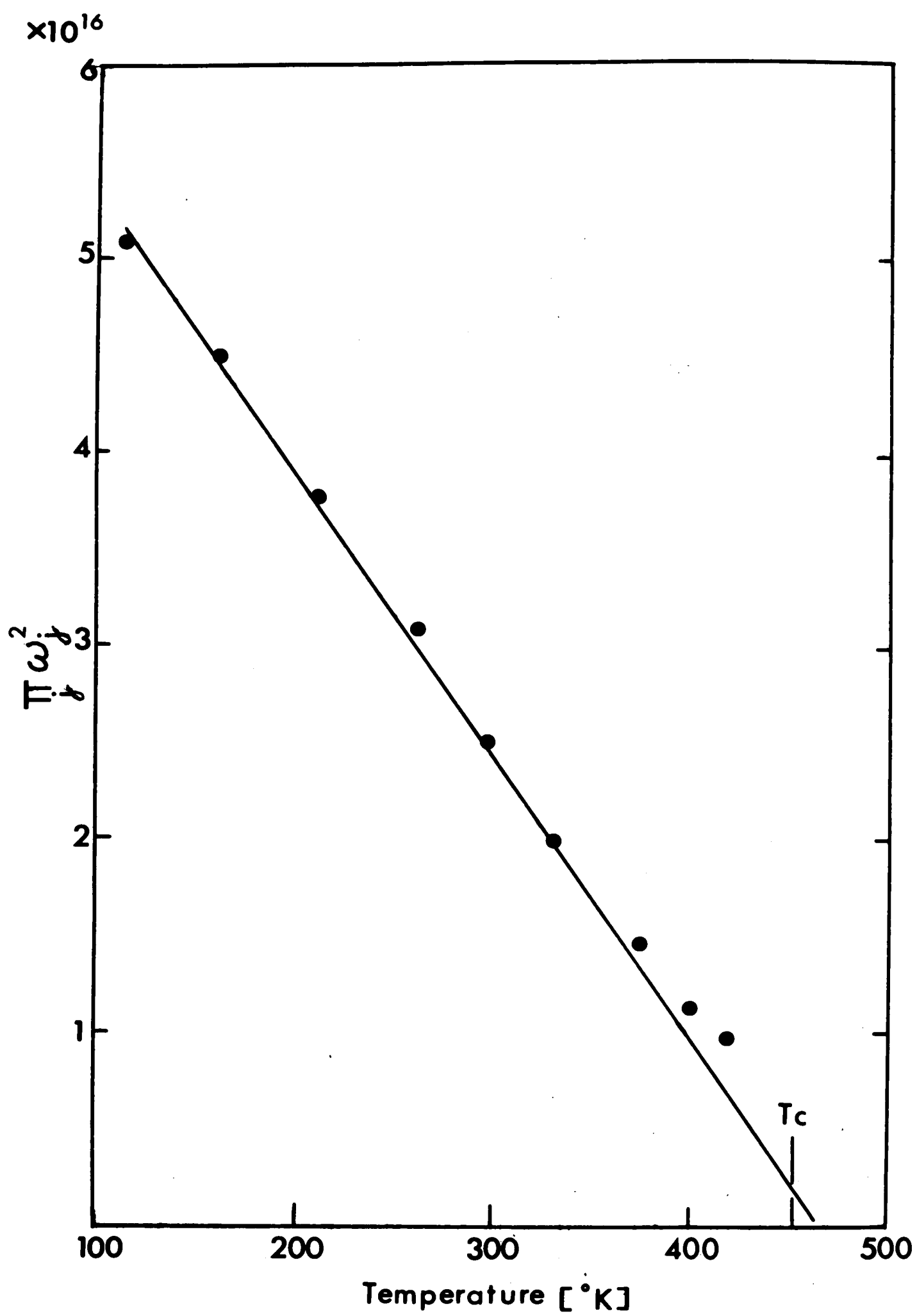


Figure 7.4

**Transfer of Raman intensity between modes
A and B resulting from their interaction.**

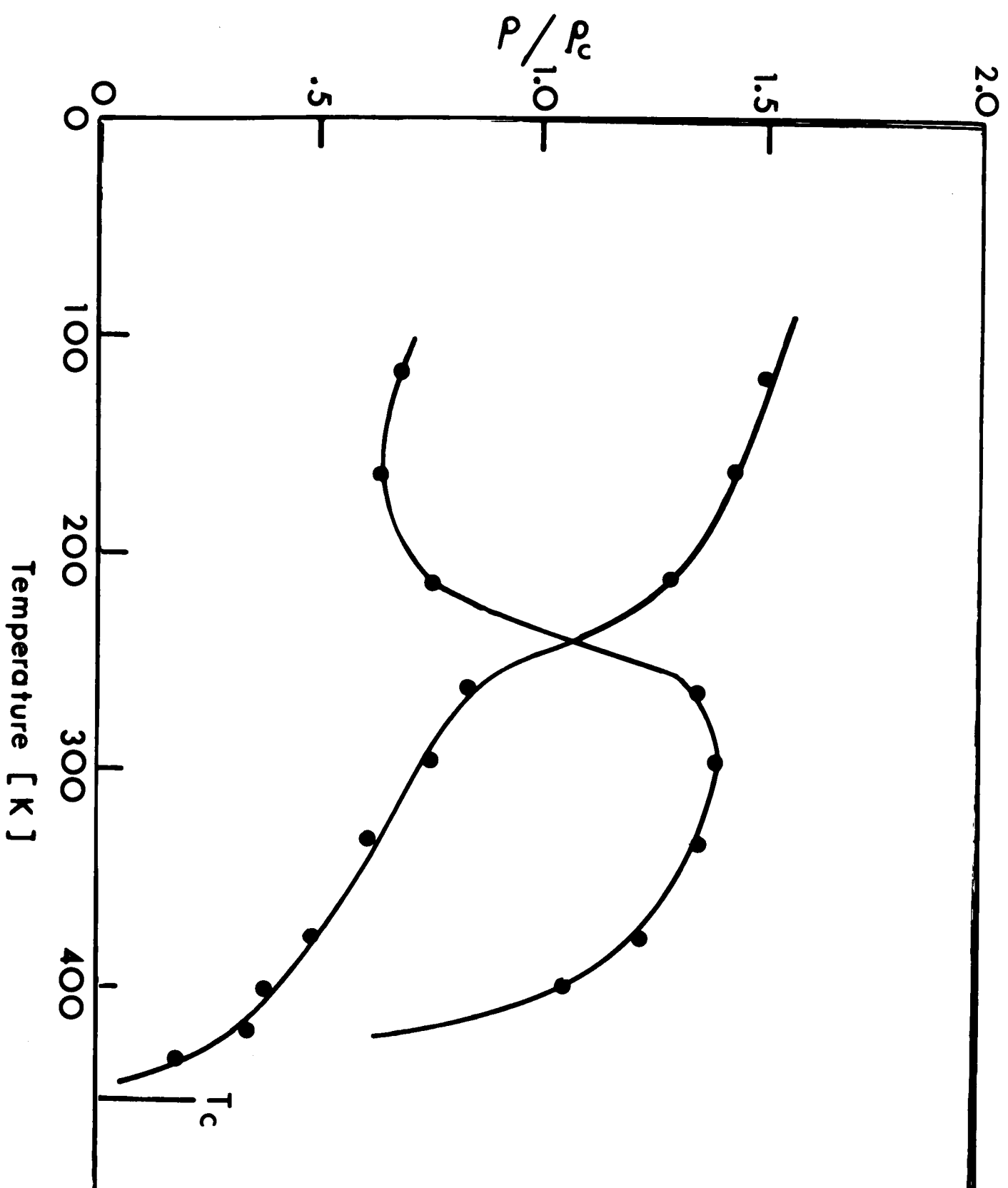


Figure 7.5

Temperature dependence of the soft mode frequency and damping. The broken lines indicate the extrapolation predicted by conventional theory.

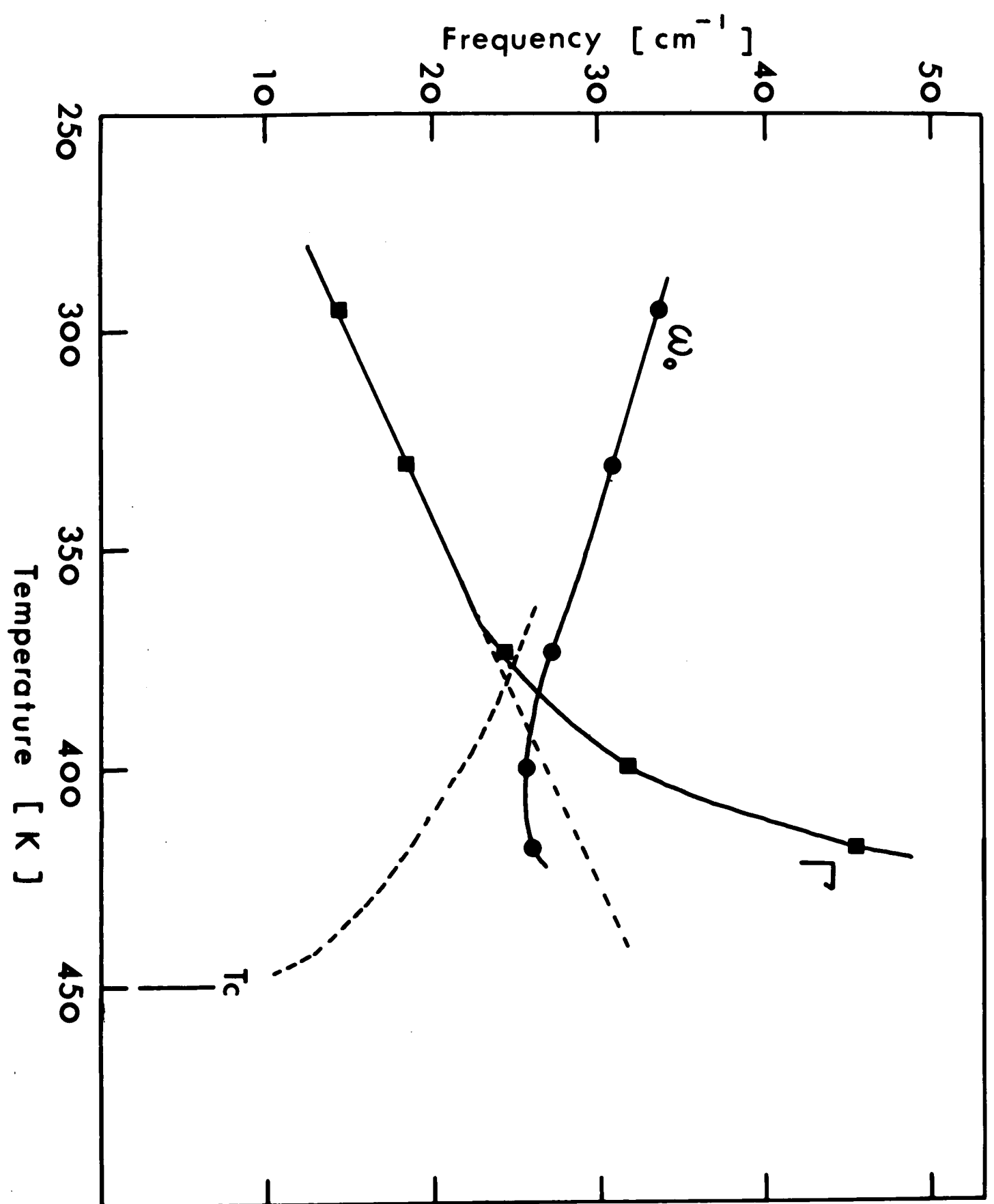


Figure 7.6

Comparison of the observed and calculated spectrum for $T = 373\text{K}$. The circles are a few of the experimental points and the solid line is calculated from equation 7.6 using the parameters listed in Table 7.1. The least squares fit was made to only that part of the spectrum above 15 cm^{-1} . The lower curve shows, on the same scale, the spectrum below 15 cm^{-1} at $T = 115\text{K}$.

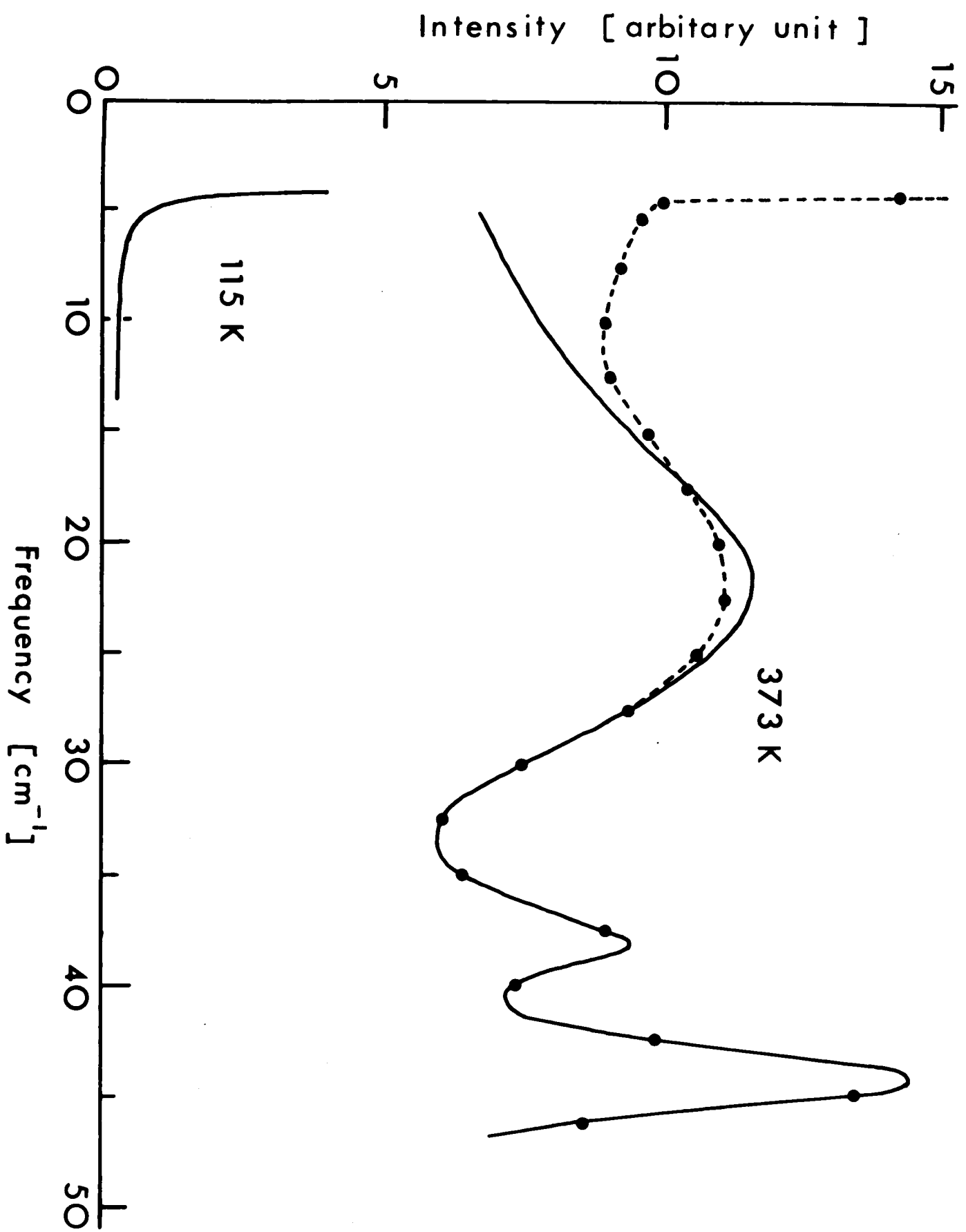


Figure 7.7

The χ_{ZZ} spectrum of lead germanate obtained using the He-Ne 632.8 nm laser excitation. The broken line corresponds to the best fit using coupled classical oscillators, and the solid line is that produced when the soft mode is given by equation (7.9).

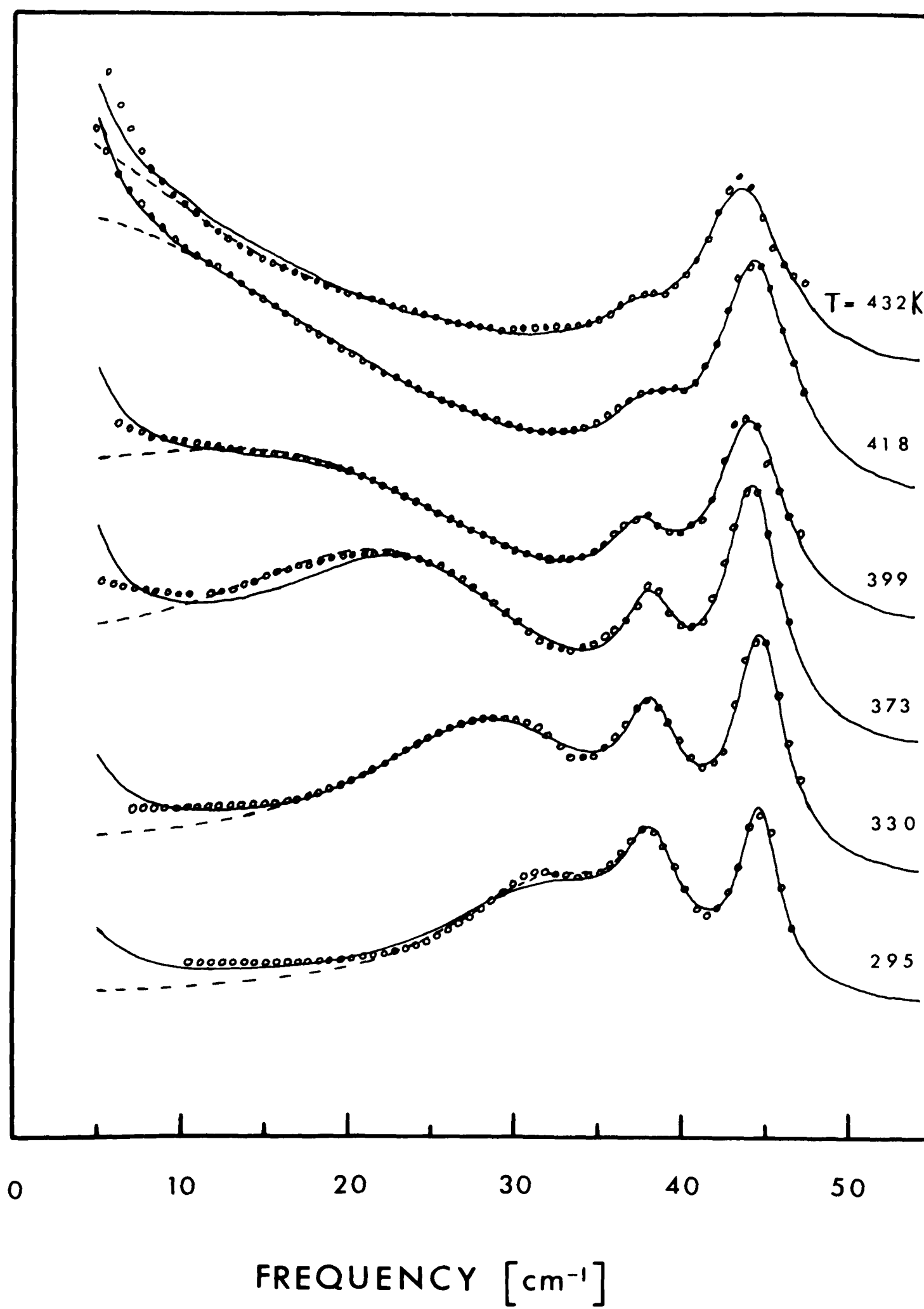


Figure 7.8

The low frequency α_{ZZ} spectrum of lead germanate obtained using the Ar^+ laser. An iodine cell has been used to absorb the elastic scattering at 514.5 nm.

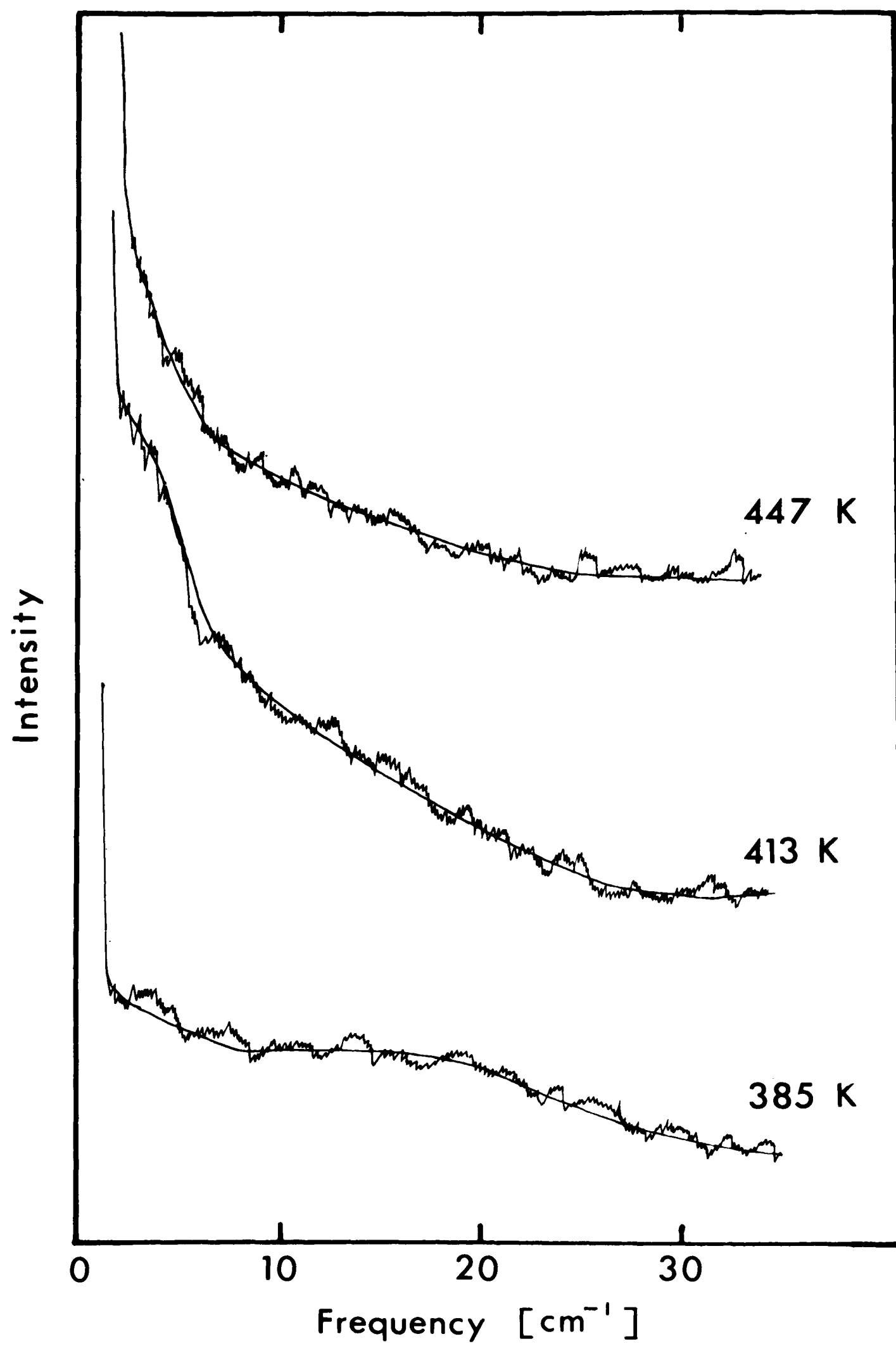


Figure 7.9

The integrated intensity of scattering from the ferroelectric mode, with the temperature corrected for local heating.

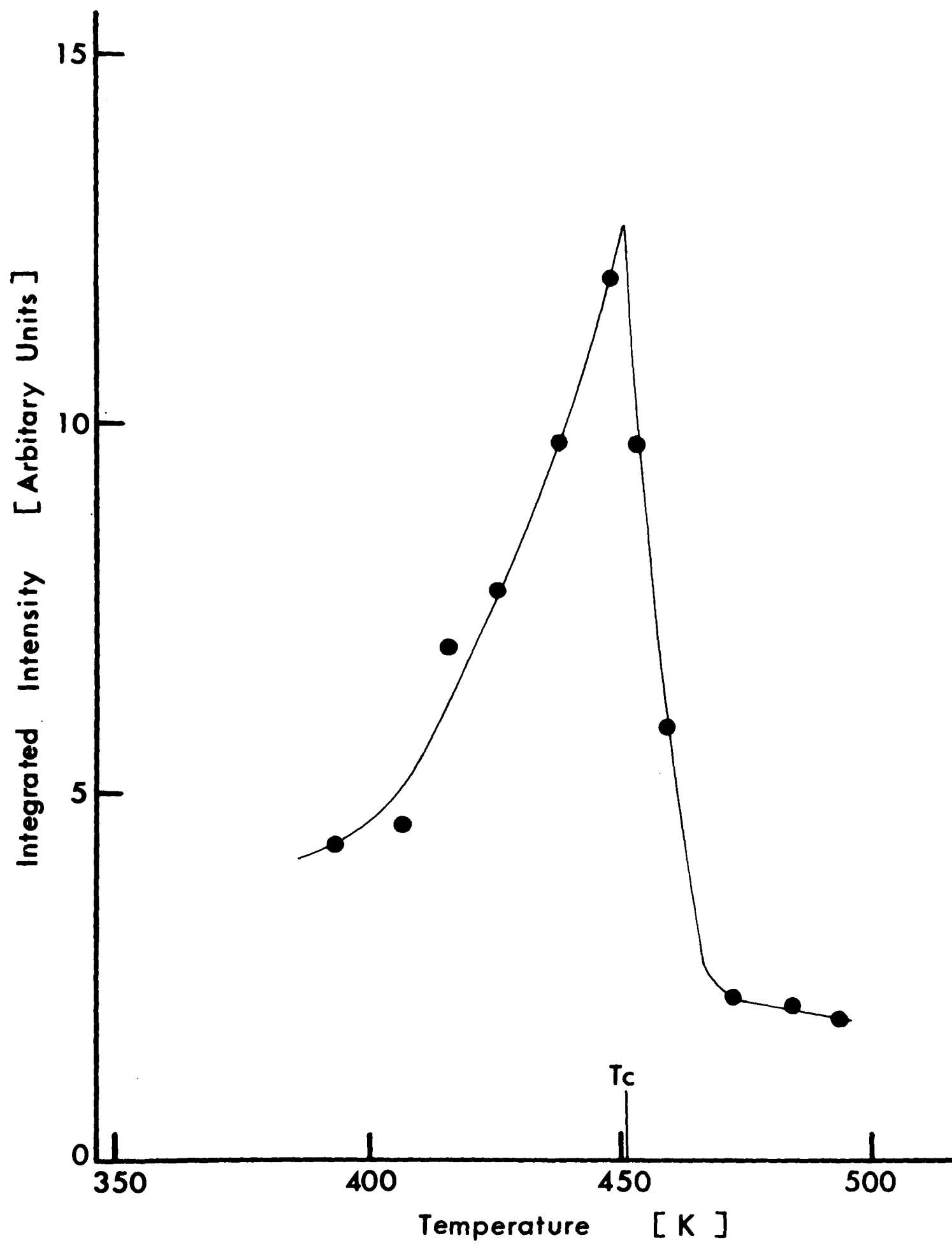
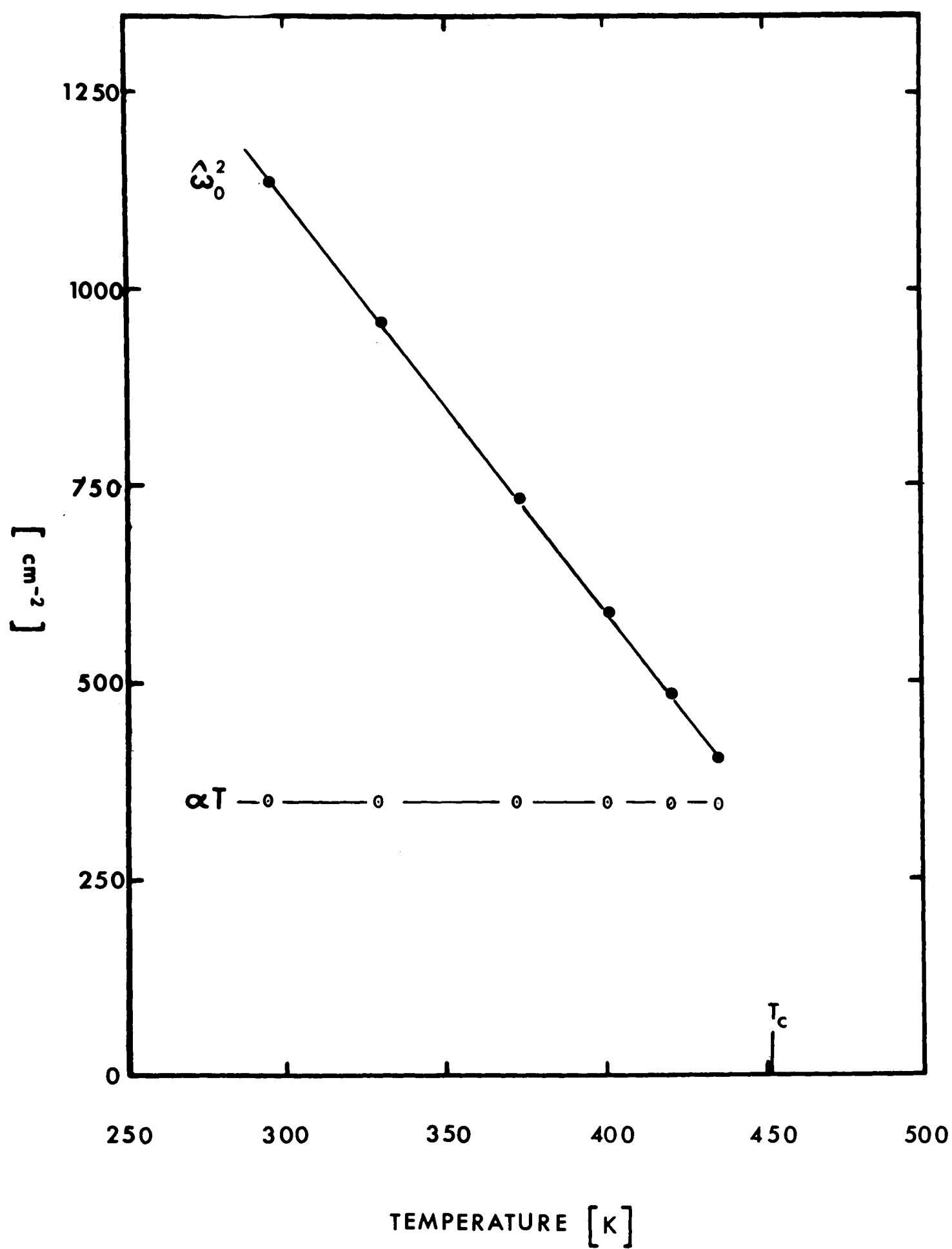


Figure 7.10

The temperature dependence of the soft phonon frequency, $\hat{\omega}_0$, and the anharmonic coupling coefficient α .



Appendix 1

Green's Function Methods

In order to determine the dielectric and scattering properties of a crystal we require a knowledge of the excitation spectrum, which in principle must be obtained from the crystal wave functions using perturbation theory. The complication involved in this is enormous and so some alternative simplified approach is desirable. One would prefer to work with dynamical quantities which are more closely related to experiment and the physical properties of the crystal, and which are much less detailed than the full crystal wave functions. Quantities which satisfy these conditions are the Green's function of quantum field theory. A one-particle Green's function describes the motion of one particle added to a many-particle system, while a two-particle Green's function describes the motion of two added particles. This technique has the advantage of great directness and has been applied successfully to many problems. An excellent account is given by Abrikosov et al. [1]; the description by Maradudin and Fein [2] and Cowley [3] are particularly useful.

The one-phonon Green's function is defined by:-

$$G(\underline{q} j, \underline{q}' j', t) = P[A_H(\underline{q} j, t), A_H^*(\underline{q}' j', 0)] \quad (A1.1a)$$

where P is a time-ordering operator such that

$$\begin{aligned} &= \langle A_H(\underline{q} j, t) A_H^*(\underline{q}' j', 0) \rangle, t > 0 \\ &= \langle A_H^*(\underline{q}' j', 0) A_H(\underline{q} j, t) \rangle, t < 0 \end{aligned} \quad (A1.1b)$$

$A_H(\underline{q}j, t)$ is the phonon coordinate operator, written in the Heisenberg picture, which depends on the phonon wave-vector $\underline{q}$ in the j^{th} branch of the dispersion curve; $\langle \quad \rangle$ denotes thermodynamic averaging. Since the crystal is assumed translationally invariant, this expectation value is zero unless $\underline{q} = \underline{q}'$. In this representation the wave function is written:-

$$\psi_H = \exp\left(\frac{iHt}{\hbar}\right) \psi \quad (\text{A1.2})$$

and therefore:-

$$A_H(\underline{q}j, t) = \exp\left(\frac{iHt}{\hbar}\right) \{ a(\underline{q}j) + a^*(-\underline{q}j) \} \exp\left(-\frac{iHt}{\hbar}\right) \quad (\text{A1.3})$$

where H is the crystal vibrational Hamiltonian and $a(\underline{q}j)$, $a^*(-\underline{q}j)$ are the phonon creation and destruction operators. Using the statistical mechanical result that

$$\langle \hat{O} \rangle = \frac{1}{Z} \text{Tr}[e^{-\beta H} \hat{O}], \text{ we obtain:-}$$

$$\begin{aligned} G(\underline{q}jj', t) &= \frac{1}{Z} \text{Tr}[\exp(-\beta H + \frac{\tau H}{\hbar}) A(\underline{q}j) \exp(-\frac{\tau H}{\hbar}) A^*(\underline{q}j')], t > 0 \\ &= \frac{1}{Z} \text{Tr}[\exp(-\beta H) A^*(\underline{q}j') \exp(\frac{\tau H}{\hbar}) A(\underline{q}j) \exp(-\frac{\tau H}{\hbar})], t < 0 \end{aligned} \quad (\text{A1.4})$$

where we have introduced the imaginary time $\tau = it$.

Comparing these two equations, and using the cyclic property of the trace operation, we obtain:-

$$G(\underline{q}jj', \tau) = G(\underline{q}, jj', \tau + \beta\hbar), \quad 0 < \tau < -\beta\hbar \quad (\text{A1.5})$$

The Green's functions are therefore periodic functions of τ and so we may expand them in a Fourier series:-

$$G(\underline{q}jj', \tau) = \sum_{n=-\infty}^{+\infty} G(\underline{q}jj', i\omega_n) \exp(i\omega_n \tau) \quad (\text{A1.6})$$

where $\omega_n = \frac{2\pi n}{\beta\hbar}$, $n = 0, \pm 1, 2, \dots$ and so

$$G(\underline{q}jj', i\omega_n) = \frac{1}{2\beta\hbar} \int_{-\beta\hbar}^{+\beta\hbar} G(\underline{q}jj', \tau) \exp(-i\omega_n \tau) d\tau \quad (\text{A1.7})$$

For a harmonic crystal $G(\underline{q}j j', \gamma)$ is zero unless $j = j'$ since phonon interactions are not permitted; using the commutation properties of the creation and destruction operators, we obtain from (A1.4):-

$$G(\underline{q}j, \gamma) = [n(\underline{q}j)\exp(|\gamma|\omega(\underline{q}j)) + (n(\underline{q}j) + 1)\exp(-|\gamma|\omega(\underline{q}j))]$$

where $n(\underline{q}j)$ is the occupation number of the mode $(\underline{q}j)$ whose frequency is $\omega(\underline{q}j)$. Substitution into (A1.7) yields

$$\begin{aligned} G(\underline{q}j, i\omega_n) &= \frac{1}{\beta\hbar} \left\{ \frac{1}{\omega(\underline{q}j) + i\omega_n} + \frac{1}{\omega(\underline{q}j) - i\omega_n} \right\} \\ &= \frac{2\omega(\underline{q}j)}{\beta\hbar(\omega^2(\underline{q}j) + \omega_n^2)} \end{aligned} \quad (A1.8)$$

To determine anharmonic effects we must include an anharmonic perturbation in the Hamiltonian and use perturbation theory to obtain $G(\underline{q}j j', i\omega_n)$. This then becomes the sum of an infinite series, each term of which may be represented as a Feynman diagram. It is convenient to work in the interaction representation where the crystal wave function is chosen to be independent of time under the unperturbed Hamiltonian H_0 and to vary with the perturbation H_A . Thus:-

$$\tilde{\psi}(t) = \exp\left(\frac{iH_0 t}{\hbar}\right) \psi(t) \quad (A1.9)$$

An operator $\hat{O}$ is then written:-

$$\tilde{\hat{O}} = \exp\left(\frac{iH_0 t}{\hbar}\right) \hat{O} \exp\left(\frac{-iH_0 t}{\hbar}\right)$$

We introduce a time development operator $S(t_1, t_2)$ such that when it operates on a wave function at t_2 (in the interaction representation) it generates the wave function

at t_1 in the interaction representation. Therefore

$$\tilde{\psi}(t_1) = S(t_1, t_2) \tilde{\psi}(t_2) \quad (A1.10)$$

Comparing now equations (A1.2) and (A1.9), we obtain the relation

$$\tilde{\psi}(t_2) = \exp\left(\frac{iH_0 t_2}{\hbar}\right) \exp\left(\frac{-iH t_2}{\hbar}\right) \psi_H$$

Similarly

$$\tilde{\psi}(t_1) = \exp\left(\frac{iH_0 t_1}{\hbar}\right) \exp\left(\frac{-iH t_1}{\hbar}\right) \psi_H$$

and so:-

$$S(t_1, t_2) = \exp\left\{\frac{iH_0(t_1 - t_2)}{\hbar}\right\} \exp\left\{\frac{-iH(t_1 - t_2)}{\hbar}\right\} \quad (A1.11)$$

We can re-write this with the complex time variable

$$S(\tau, 0) = \exp\left(\frac{iH_0 \tau}{\hbar}\right) \exp\left(\frac{-iH \tau}{\hbar}\right) \quad (A1.12)$$

and differentiation yields:-

$$\frac{dS(\tau, 0)}{d\tau} = -\frac{\tilde{H}_A}{\hbar} S(\tau, 0)$$

Since $\tilde{H}_A$ is a function of τ , this equation must be solved by iteration. The result is [3]

$$S(\tau, 0) = 1 + \sum_{n=1}^{\infty} \frac{1}{n!} \left(-\frac{1}{\hbar}\right)^n \int_0^{\tau_1} \dots \int_0^{\tau_n} P[\tilde{H}_A(\tau_1) \dots \tilde{H}_A(\tau_n) \dots] d\tau_1 \dots d\tau_n \dots \quad (A1.13)$$

Substituting this result in equation (A1.4), performing the time ordering, and using an extension of (A1.11) which gives

$S(t_1, t_3) \cdot S(t_3, t_2) = S(t_1, t_2)$ for $t_1 > t_3 > t_2$, we obtain for the form of the Green's function:-

$$G(qj j', \tau) = \frac{1}{Z} \text{Tr}[\exp(-\beta H) P[\tilde{A}(qj, \tau) \tilde{A}^*(qj', 0) S(\beta \hbar, 0)]] \quad (A1.14)$$

The anharmonic effects are included entirely within $S(\beta \hbar, 0)$.

Each term in the series may be represented by a Feynman diagram, and the time ordering corresponds to the time ordering of the interaction vertices. The rules for the summation of this series have been explained in detail by Maradudin and Fein [2]: the result obtained is the Dyson equation:-

$$\sum_{j''} [(\omega(\underline{qj})^2 + \omega_n^2) \delta_{jj''} + 2\omega(\underline{qj}) \pi(\underline{qjj''}, i\omega_n)] G(\underline{qj''j'}, \omega) = \frac{2\omega(\underline{qj})}{\beta\hbar} \delta_{jj'} \quad (\text{A1.15})$$

If we re-define the Green's function in terms of normalised phonon coordinates, i.e.:-

$$G'(\underline{qjj'}, t) = \langle Q(\underline{qj}, t) Q^*(\underline{qj'}, 0) \rangle$$

where $Q(\underline{qj}, t) = \left(\frac{\hbar}{2\omega(\underline{qj})}\right)^{\frac{1}{2}} A(\underline{qj}, t)$, then the Dyson equation becomes:-

$$\sum_{j''} [(\omega(\underline{qj})^2 + \omega_n^2) \delta_{jj''} + \pi'(\underline{qjj''}, i\omega_n)] G'(\underline{qj''j'}, i\omega_n) = \delta_{jj'} \quad (\text{A1.16})$$

$$\text{where } \pi'(\underline{qj}, j'', i\omega_n) = 2 \sqrt{\omega(\underline{qj})\omega(\underline{qj''})} \pi(\underline{qjj''}, i\omega_n)$$

This is the form used in the coupled mode analyses in chapters 5, 6 and 7.

This is the basic equation describing the effects of anharmonicity on the one-phonon properties of the crystal; however, as will be shown later, the physical properties depend on the analytic continuation to the real frequency axis, i.e. $i\omega_n \rightarrow \Omega + i\varepsilon$. The term $\pi(\underline{qjj'}, i\omega_n)$ is the proper self-energy which includes all the anharmonic contributions which we expect to give rise to finite lifetime effects and frequency shifts of the normal modes. It may be expressed:-

$$\pi(\underline{qjj'}, i\omega_n) \rightarrow \Delta(\underline{qjj'}, \Omega) + i\Gamma(\underline{qjj'}, \Omega)$$

In the case where phonon interactions do not appreciably intermix the different normal modes, the pseudo-harmonic modification of the harmonic Green's function of equation (A1.8) becomes

$$G^{-1}(\underline{q}j, \Omega) = \left(\frac{\beta \hbar}{2\omega(\underline{q}j)} \right) [(\omega(\underline{q}j)^2 - \Omega^2) + 2\omega(\underline{q}j) \{ \Delta(\underline{q}j, \Omega) + i\Gamma(\underline{q}j, \Omega) \}] \quad (A1.17)$$

so that for $\Delta, \Gamma \ll \omega(\underline{q}j)$, we can interpret Δ as the frequency shift, while Γ gives rise to broadening. However, when the normal modes are strongly interacting the life-times become short and equation (A1.17) no longer holds; the full form of (A1.15) must then be considered.

We can write the anharmonic perturbation as a power series in the displacements of atoms from their equilibrium positions in the form:-

$$\begin{aligned} H_A = & \sum_{\substack{\underline{q}_1 \underline{q}_2 \underline{q}_3 \\ j_1 j_2 j_3}} V(\substack{\underline{q}_1 \underline{q}_2 \underline{q}_3 \\ j_1 j_2 j_3}) A(\underline{q}_1 j_1) A(\underline{q}_2 j_2) A(\underline{q}_3 j_3) + \\ & \sum_{\substack{\underline{q}_1 \underline{q}_2 \underline{q}_3 \underline{q}_4 \\ j_1 j_2 j_3 j_4}} V(\substack{\underline{q}_1 \underline{q}_2 \underline{q}_3 \underline{q}_4 \\ j_1 j_2 j_3 j_4}) A(\underline{q}_1 j_1) A(\underline{q}_2 j_2) A(\underline{q}_3 j_3) A(\underline{q}_4 j_4) \\ & + \dots \end{aligned} \quad (A1.18)$$

where the wave vectors of the phonons in the coefficients obey the momentum conservation, e.g. $\underline{q}_1 + \underline{q}_2 + \underline{q}_3 = \underline{K}$, $\underline{K}$ being a reciprocal lattice vector. The contributions to the frequency shift and width are then found to be [3]:-

$$\begin{aligned} \Delta(\underline{q}j, \Omega) = & \frac{2}{\hbar} \sum_{\alpha\beta} V_{\alpha\beta}(\substack{\underline{q} & -\underline{q} \\ j & j'}) U_{\alpha\beta}^T + \frac{12}{\hbar} \sum_{\underline{q}_1 j_1} V(\substack{\underline{q} & -\underline{q} & \underline{q}_1 & -\underline{q}_1 \\ j & j' & j_1 & j_1}) \\ (2n(\underline{q}_1 j_1) + 1) - & \frac{18}{\hbar^2} \sum_{\underline{q}_1 \underline{q}_2 j_1 j_2} V(\substack{\underline{q} & -\underline{q}_1 & -\underline{q}_2 \\ j & j_1 & j_2}) V(\substack{-\underline{q} & \underline{q}_1 & \underline{q}_2 \\ j' & j_1 & j_2}) X(\Omega) \end{aligned} \quad (A1.19)$$

where U^T is the thermal strain parameter and

$$\begin{aligned} X(\Omega) = & (n_1 + n_2 + 1) \left[\frac{1}{(\omega_1 + \omega_2 + \Omega)_p} + \frac{1}{(\omega_1 + \omega_2 - \Omega)_p} \right] \\ & + (n_2 - n_1) \left[\frac{1}{(\omega_1 - \omega_2 + \Omega)_p} + \frac{1}{(\omega_1 - \omega_2 - \Omega)_p} \right] \end{aligned} \quad (A1.20)$$

Also:-

$$\Gamma(qjj', \Omega) = \frac{18\pi}{\hbar^2} \sum_{q_1 q_2 j_1 j_2} v \begin{pmatrix} q & -q_1 & -q_2 \\ j & j_1 & j_2 \end{pmatrix} v \begin{pmatrix} -q & q_1 & q_2 \\ j' & j_1 & j_2 \end{pmatrix} Y(\Omega) \quad (A1.21)$$

where

$$\begin{aligned} Y(\Omega) = & (n_1 + n_2 + 1) [\delta(\omega_1 + \omega_2 - \Omega) - \delta(\omega_1 + \omega_2 + \Omega)] \\ & + (n_2 - n_1) [\delta(\omega_2 - \omega_1 + \Omega) - \delta(\omega_1 - \omega_2 + \Omega)] \end{aligned} \quad (A1.22)$$

Therefore, both Δ and Γ are functions of temperature and probe frequency. In the high temperature limit the Bose factors can be approximated $\frac{k_B T}{\hbar \Omega}$ and Δ and Γ are proportional to temperature. In the low frequency limit we may approximate Δ to be constant and Γ to be linearly dependent on Ω . However, the full frequency dependence is much more complicated, as shown by neutron inelastic scattering experiments [4] and infra-red reflection studies [5].

Using the results of this section we can now determine the form of the Raman scattering cross-section since the problem is basically that of obtaining a measure of the correlations in fluctuations of the optical polarisability of the material. In the first Born approximation the inelastic scattering cross-section is given by

$$\sigma(\Omega) = \langle P_i P_j \rangle \delta(E_f - E_i - \hbar \Omega)$$

where P is a polarisability operator, E_i and E_f are the initial and final states of the crystal, $\hbar \Omega$ is the energy transfer to the photon, and the δ -function

expresses energy conservation. If we introduce complete sets of eigenstates of the Hamiltonian:-

$$\sigma(\Omega) = \sum_{nm} \frac{\exp(-\beta E_n)}{Z} \langle n | P_i | m \rangle \langle m | P_j | n \rangle \delta(\hbar\omega_{mn} - \hbar\Omega) \quad (A1.23)$$

This same operation can be performed on the Green's function defined in equation (A1.4), and we obtain:-

$$G(P_i P_j, \Omega) = \sum_{nm} \frac{\exp(-\beta E_n - \omega_{mn} \tau)}{Z} \langle n | P_i | m \rangle \langle m | P_j | n \rangle \quad (A1.24)$$

We define also a spectral function:-

$$\mathcal{S}(P_i P_j, \Omega) = \sum_{nm} \frac{\exp(-\beta E_n)}{Z} \langle n | P_i | m \rangle \langle m | P_j | n \rangle \delta(\Omega - \omega_{mn}) \quad (A1.25)$$

such that :-

$$G(P_i P_j, \tau) = \int_{-\infty}^{+\infty} \mathcal{S}(P_i P_j, \Omega) \exp(-\Omega \tau) d\Omega.$$

$\mathcal{S}(P_i P_j, \Omega)$ and σ are therefore closely related. The spectral function can then be obtained by analytically continuing $G(P_i P_j, i\omega_n)$ over the whole frequency plane:-

$$\mathcal{S}(P_i P_j, \Omega) = \frac{i\beta H}{2\pi} [1 - \exp(-\beta \hbar \Omega)]^{-1} \left\{ G(P_i P_j, \Omega + i\varepsilon) - G(P_i P_j, \Omega - i\varepsilon) \right\} \varepsilon \rightarrow 0^+ \quad (A1.26)$$

The cross-section is therefore related to the discontinuity of the Green's function across the real frequency axis.

The advantage of this method is that it allows us to describe the scattering in terms of the same functions as the susceptibility. In addition, the coupled mode analysis in chapter 5 is presented very conveniently in terms of the one-phonon Green's function.

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Appendix 2

The Far Infra-red Spectrum of CsDA

The far infra-red spectrum of CsDA has been measured in the range $20 - 400 \text{ cm}^{-1}$ at 295K. Since Barker and Tinkham [1] first measured the far infra-red spectrum of KDP and identified the ferroelectric mode, there have been several experiments verifying their conclusions [2,3]. However, since we have observed in the Raman spectrum a strong interaction between the ferroelectric mode and another optical mode, a similar effect is expected in the i-r spectrum.

A2.1 Experimental

The reflection spectrum at 10° to normal incidence was measured for a bulk specimen - an optically polished 1 cm cubic single crystal. A Beckman R.I.I.C. FS-720 Fourier spectrophotometer with analogue computation was used. The beam is collimated, then polarised using an A.I.M. aluminium grid on polythene, which gives a degree of polarisation greater than 99%.

The spectra obtained for $E \parallel C$ and $E \perp C$ are shown in figure A2.1. Measurements extend only to 20 cm^{-1} , but an extrapolation to $\omega = 0$ may be made using equation (A2.7) and the static dielectric constants, $\epsilon_{33}(0) = 34$ and $\epsilon_{11}(0) = 58$. This gives a reflectivity of 50% for $E \parallel C$ and 59% for $E \perp C$ respectively at $\omega = 0$. Since the ferroelectric mode has polarisation fluctuations parallel to the c-axis, we are primarily interested in the $E \parallel C$ spectrum. This

has been analysed using both Kramers-Kronig and classical oscillator models.

A2.2.1 Coupled oscillator model

The polarisation observed when an electric field is applied to a crystal is a measure of the dielectric response. An adiabatic perturbation $H_E = -\underline{M} \cdot \underline{E} \exp(-i\Omega t)$ is applied, and the expectation value of the dipole moment,

$\langle M(t) \rangle$, gives the response. Using linear response theory and the Green's function methods described in Appendix 1, we can express the dielectric susceptibility as:-

$$\chi_{\alpha\beta}(\Omega) = \beta G(M_\beta M_\alpha, \Omega) \quad (A2.1)$$

The dipole moment may be expanded in a phonon series (as was the polarisability in chapter 2):-

$$M = \sum_{Oj} M(Oj) A(Oj) + \sum_{\underline{q}jj'} M\left(\frac{\underline{q}}{j} - \frac{\underline{q}}{j'}\right) A(\underline{q}j) A(-\underline{q}j') + \dots \quad (A2.2)$$

so that the one-phonon contribution to the dielectric susceptibility is:-

$$\chi_{\alpha\beta}(\Omega) = \beta \sum_{jj'} M_\alpha(Oj) M_\beta(Oj') G(Ojj', \Omega) \quad (A2.3)$$

where $G(Ojj', \Omega)$ is given by equation (A1.15). The form of $G(Ojj', \Omega)$ has been described in chapter 5 for the special case of two coupled modes: since we are studying the same two modes in CsDA as discussed in chapter 6, the approximations and constraints applied there will also be valid here.

The frequency dependent dielectric constant may be written:-

$$\epsilon(\omega) = \epsilon(\infty) + 4\pi \sum_{i,j=1}^2 M_i M_j G_{ij}(\omega) + \epsilon(\omega) \quad (A2.4)$$

where $\xi(\infty)$ is the optical frequency dielectric constant and $\Sigma(\omega)$ represents the contribution from all modes other than the two coupled modes. The static value is then:-

$$\xi(0) = \xi(\infty) + 4\pi \sum_{i,j=1}^2 M_i M_j G_{ij}(0) + \Sigma(0) \quad (A2.5)$$

Since the dielectric behaviour of the crystal is dominated by the ferroelectric mode, we expect only small temperature independent contributions from the other modes. In addition, we expect the contribution from $\Sigma(\omega)$ to be constant in the region $0 - 200 \text{ cm}^{-1}$, and therefore we assume it to be approximately $\Sigma(0)$. Then:-

$$\xi(\omega) = \xi(0) + 4\pi \sum_{i,j=1}^2 M_i M_j [G_{ij}(\omega) - G_{ij}(0)] \quad (A2.6)$$

The frequency dependent dielectric constant may then be described for a system of two coupled modes in terms of the nine parameters, $\xi(0)$, M_1 , M_2 , $\hat{\omega}_1$, $\hat{\omega}_2$, γ_{11} , γ_{22} , γ_{12} and Δ .

A2.2.2 Reflectivity analysis

The reflectivity is given by Fresnel's equation:-

$$R(\omega) = \left| \frac{\sqrt{\xi(\omega)} - 1}{\sqrt{\xi(\omega)} + 1} \right|^2 \quad (A2.7)$$

Using the form of $\xi(\omega)$ given above we can obtain a least-squares fit of this expression to the reflectivity spectrum with $E \parallel C$ in figure A2.1. The values of the parameters obtained are given in Table A2.1 for the three models discussed in chapter 5. Comparison with Table 6.6, which gives the corresponding results for the analysis of the

Raman spectrum of CsDA, shows that there is a good correspondence.

In the fitting process only the data between $20 - 200 \text{ cm}^{-1}$ was used and the low frequency extrapolation was not employed. We see from Table A2.1 that the value obtained for $\epsilon(0)$, is ≈ 25 , whereas the measured value is ≈ 34 . The reflectivity at $\omega = 0$ is then $\approx 44\%$. In figure A2.2 the observed spectrum is compared with the best fit, and we see that this indeed is the result. This difference can be accounted for quite well by the theory of Cowley and Coombs, as discussed in chapter 6. At low frequency, they predict an additional contribution to the response which increases the static dielectric constant to a value greater than that obtained by an extrapolation from higher frequencies. This would mean, therefore, that extrapolation to $\omega = 0$ should be to 44%, but that in a small frequency region near $\omega = 0$ the reflectivity rises to 50%. This difference may be sufficient to show up in a Kramers-Kronig analysis of the spectrum, and this is discussed in detail in section A2.3.

Considering now the fit to the Barker-Hopfield model, we see that for the overdamped mode $T/\tau = 6.25 \times 10^{14} \text{ deg. sec.}^{-1}$ for $T = 295^\circ\text{K}$. This agrees well with the value $6.0 \times 10^{14} \text{ deg. sec.}^{-1}$ obtained in the Raman analysis. The underdamped mode frequency at 106 cm^{-1} is displaced from the Raman value of 96 cm^{-1} , but this is just within experimental uncertainty. However, the damping constant of this mode is much smaller; this may indicate that the anti-resonance between the modes is stronger than

indicated by the Raman measurements. There is also the possibility that the difference arises from the nature of the surface properties of the material. The Raman experiment samples the bulk properties whereas this experiment studies only a small region at the surface. The surface properties of materials have become the subject of great interest quite recently and obviously, to obtain further information here would require such a specially detailed study.

A2.2.3 Kramers-Kronig analysis

If we write the reflectivity as $re^{i\theta}$ with $r = R^{\frac{1}{2}}$, then the Kramers-Kronig relation [4] gives:-

$$\theta(\omega) = \frac{2\omega}{\pi} \int_0^{\infty} \frac{\ln r(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (\text{A2.8})$$

From this relation we can obtain the real and imaginary dielectric constants. In the computer program used to calculate $\epsilon'(\omega)$ and $\epsilon''(\omega)$, this infinite integral is approximated by a finite integral over the range of available data, and correction terms are included which result from the low and high frequency extrapolations of $R(\omega)$. Between data points, $\ln r(\omega)$ is represented by straight line segments; in addition to avoid the singularities which occur at $\omega = \omega'$, the function

$\ln \{r(\omega)/r(\omega')\}$ is calculated.

The results of the analysis are shown in figures A2.3 and A2.4, corresponding to the two different low frequency extrapolations discussed above; it is evident that the shape of $\epsilon''(\omega)$ is dependent on the choice of $R(0)$.

The minimum of the antiresonance drops to zero when we chose $\epsilon(0) = 25$, and the strength of the overdamped mode appears to increase. To investigate further the detailed dependence, we have also been able to fit $\epsilon''(\omega)$ using the coupled oscillator expression in (A2.6) with $\epsilon(0)$ fixed. The results of the fit are given in Tables A2.2 and A2.3. The values of the parameters obtained compare favourably with those in Table A2.1, which describe the reflectivity directly. We obtain $T/\tau = 6.17 \times 10^{14}$ deg. sec⁻¹ with $\epsilon(0) = 25$ which again agrees well with the previous results. However, with $\epsilon(0) = 34$ we find $T/\tau = 5.45 \times 10^{14}$ deg. sec⁻¹; the additional low frequency response therefore has the effect of increasing the relaxation time of the overdamped mode. This is consistent with our picture where the quasi-elastic scattering diverges at T_c whereas the overdamped mode frequency is zero at $T_0 < T_c$.

Another feature is that now $\gamma_{22} = 0.5$ cm⁻¹ for $\epsilon(0) = 25$: this situation is almost exactly that of the Barker-Hopfield model. In order to describe the zero in the response between the modes, all the damping must be associated with the ferroelectric mode. On the other hand, in the model with $\gamma_{12} = 0$, there is no apparent important difference in the parameters.

A2.3 Discussion

The conclusions reached on the basis of the Raman data appear now to be consistent with the infra-red data. In both cases, the results indicate an additional scattering process at low frequency, but this has not

been observed directly.

From a mode coupling viewpoint, it is interesting that the reflection data indicates a much sharper anti-resonance, with the intensity going to zero. This differs from the Raman data, but can be explained by two factors. Firstly, the slitwidth is $\lesssim 10 \text{ cm}^{-1}$ in the Raman experiment, and $\approx 3 \text{ cm}^{-1}$ in the infra-red; in the former case, the poorer resolution effectively smooths the spectrum. In addition, no background has been subtracted from the Raman data, so that some of the signal at the minimum in the response may be due to parasitic scattering. These indications suggest that the Raman experiments should be repeated with higher resolution and that an attempt should be made to take account of the background. As we have seen in chapter 7, the iodine cell technique may therefore prove useful in studying the low frequency quasielastic scattering in CsDA and the isomorphous crystals.

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Table A2.1

Oscillator Parameters for CsDA : reflectivity fit

Parameter	Model 1 (Kobayashi)	Model 2 (Barker-Hopfield)	Model 3 ($\Delta = 0$)
M_1	0	369	371
γ_1	37.8	1523	1412
$\hat{\omega}_1$	69.1	337	350
M_2	373	56.9	44.9
γ_2	1488	2.5	1148
$\hat{\omega}_2$	347	108	55.2
γ_{12}	-229	0	396
$\Delta^{1/2}$	119	176	0

Table A2.2

Oscillator parameters for CsDA: $\epsilon''(\omega)$ fit with $\epsilon(0) = 25$

Parameter	Model 1 (Kobayashi)	Model 2 (Barker-Hopfield)	Model 3 ($\Delta = 0$)
M_1	0.0	885	153
γ_1	30.6	772	101
ω_1	69.8	233	56.5
M_2	903	178	890
γ_2	742	0.6	671
ω_2	245	104	248
γ_{12}	-149	0.0	259
$\Delta^{1/2}$	99	140	0

Table A2.3

Oscillator parameters for CsDA: $\epsilon''(\omega)$ fit with $\epsilon(0) = 34$

Parameter	Model 1 (Kobayashi)	Model 2 (Barker-Hopfield)	Model 3 ($\Delta = 0$)
M_1	0.0	876	189
γ_1	30.8	754	119
ω_1	68.0	216	48.0
M_2	892	169	872
γ_2	727	3.8	539
ω_2	229	102	234
γ_{12}	-139	0.0	271
$\Delta^{1/2}$	104	138	0.0

Figure A2.1

The far infra-red spectrum of CsDA. The low frequency extrapolation in the region $0 - 20 \text{ cm}^{-1}$ is made with $\epsilon_{11}(0) = 58$ and $\epsilon_{33}(0) = 34$

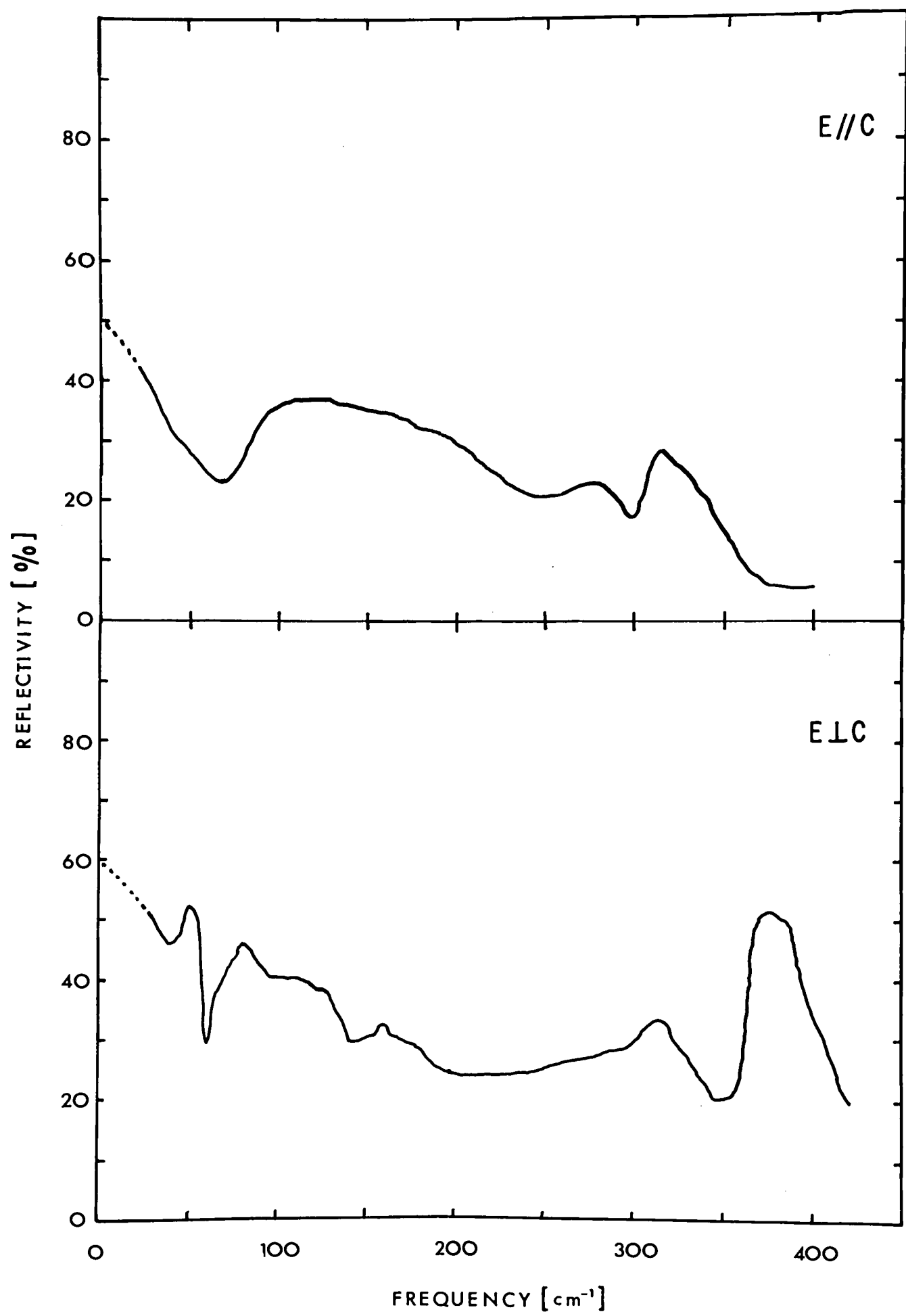


Figure A2.2

Coupled oscillator fit to the i-r spectrum of CsDA in the region $20 - 200 \text{ cm}^{-1}$. In the low frequency region ($< 20 \text{ cm}^{-1}$) there is a discrepancy between the extrapolated experimental and calculated reflectivity

COUPLED OSCILLATOR FIT

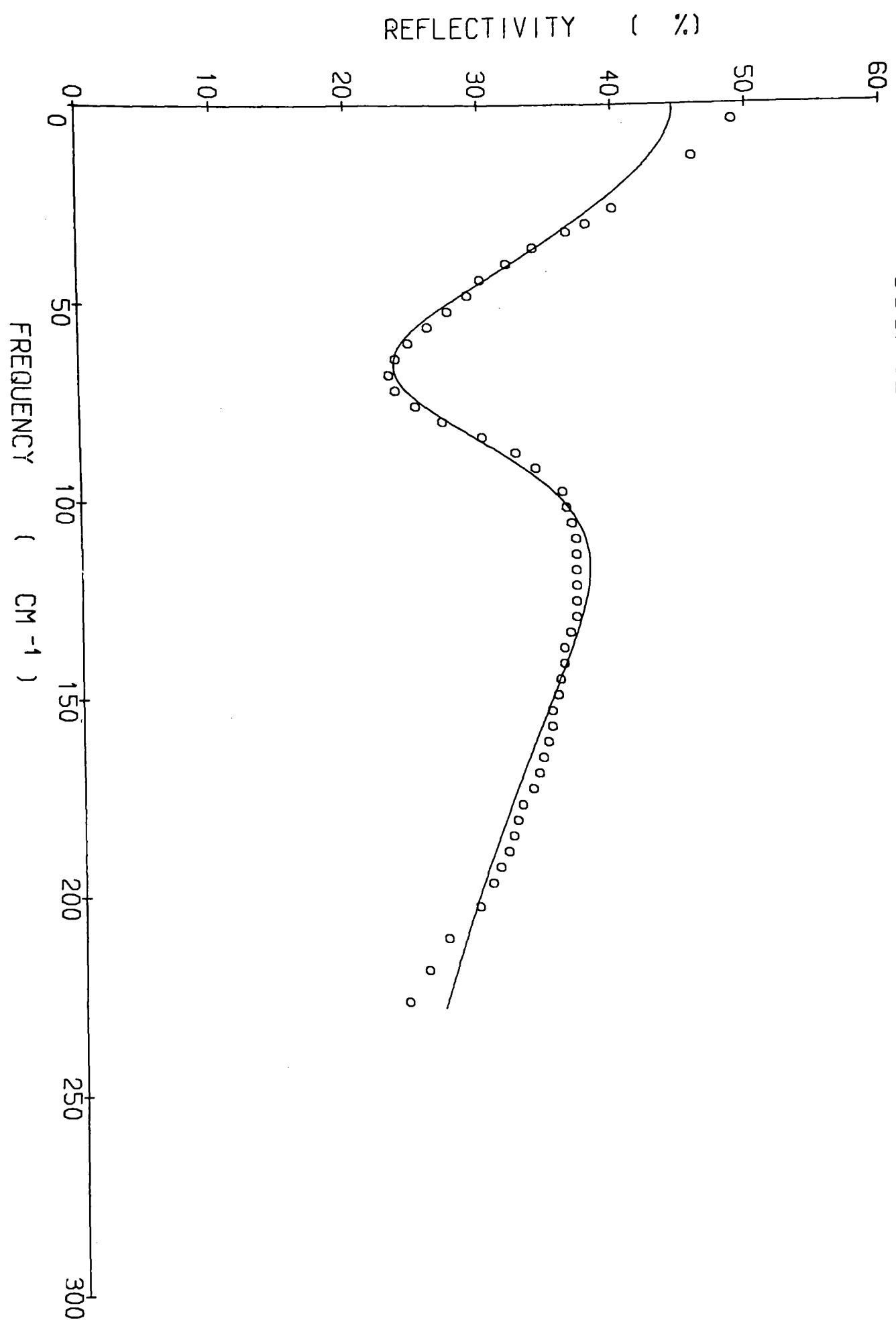


Figure A2.3

Kramers-Kronig analysis of the E || C i.r.
reflectivity of CsDA with $\epsilon_{33}(0) = 34$

K - K ANALYSIS OF CSDA

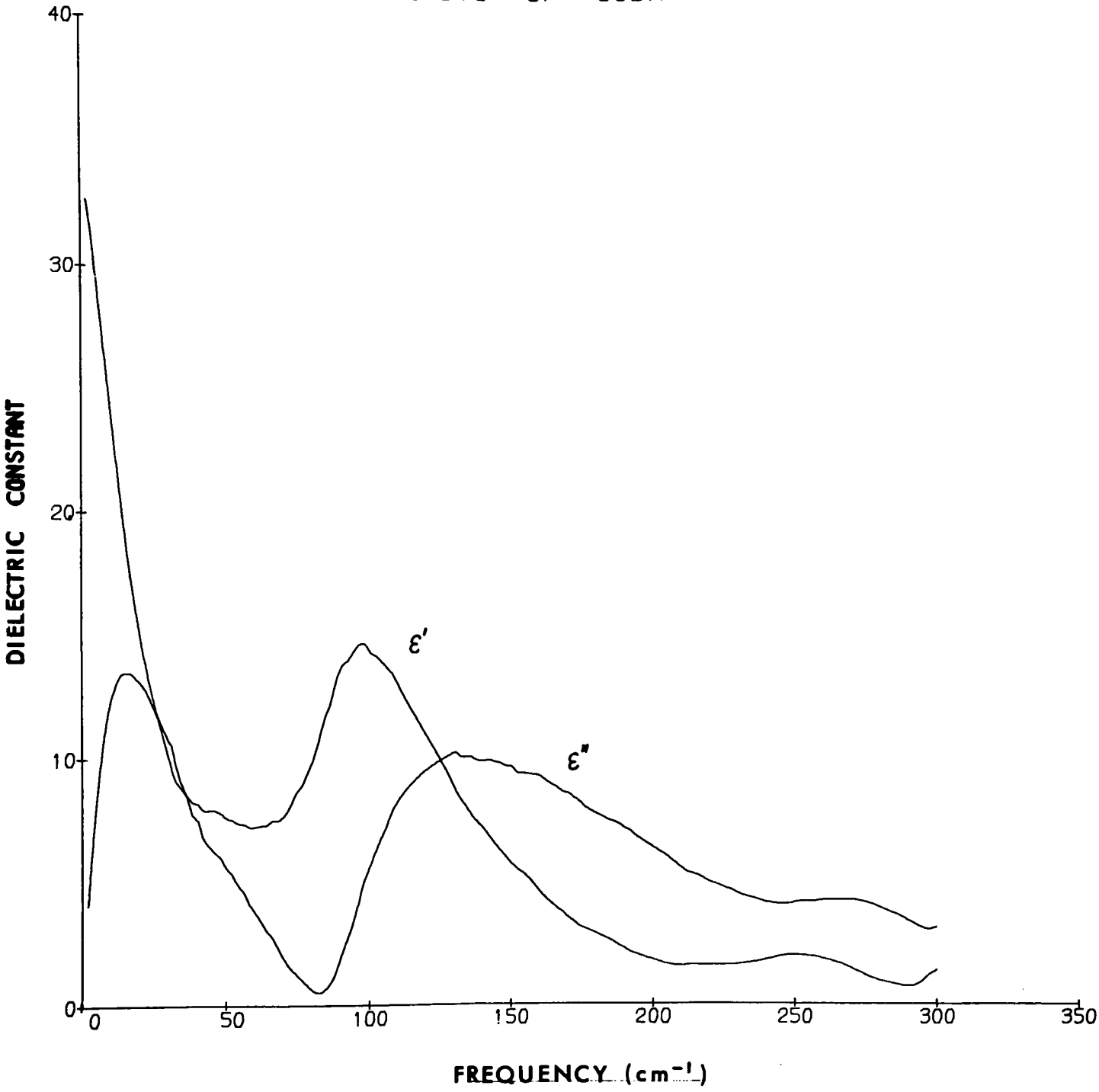
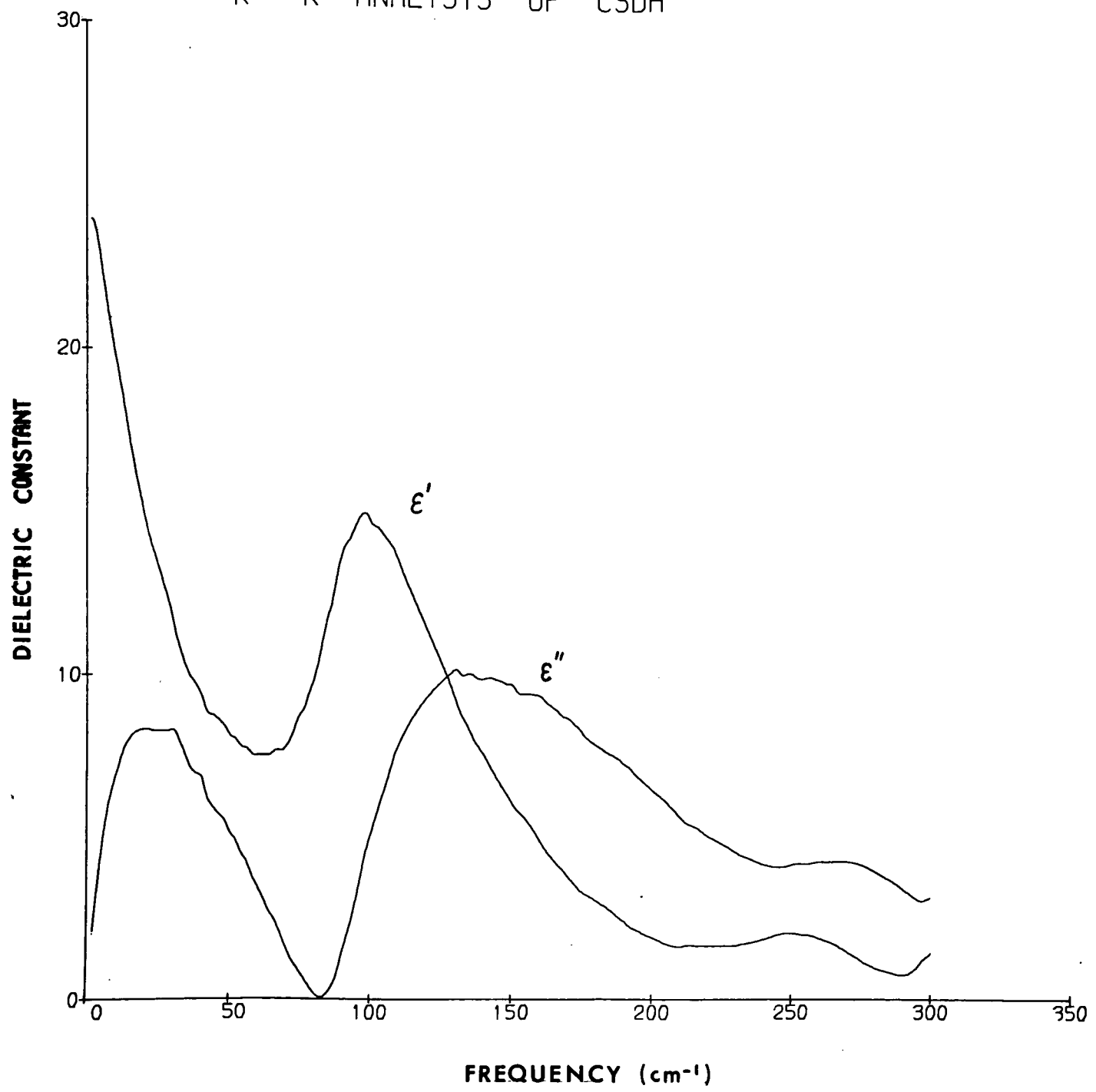


Figure A2.4

Kramers-Kronig analysis of the E || C i.r.
reflectivity of CsDA with $\epsilon_{33}(0) = 25$

K - K ANALYSIS OF CSDA



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$\Gamma = 35 \pm 10 \text{ cm}^{-1}$ in reasonable agreement with Kaminow et al.'s data and our polarized infrared reflectivity measurements. The damping factor for KDP tends to reduce on cooling down to Curie temperature. This result is not in agreement with Kaminow's data, but it is supported by ESR relaxation measurements by Blinc and Sumer²², which indicate that damping decreases in vicinity of T_c .

At 300°K in case of KH_2AsO_4 the observed Raman scattered intensity can be fitted with $\omega_0 = 70 \pm 10 \text{ cm}^{-1}$, $\Gamma = 45 \pm 10 \text{ cm}^{-1}$ while in ADP a heavily overdamped mode around 80 cm^{-1} is present for both B_2 and E symmetries. The temperature dependence of these modes is being analyzed and will be published elsewhere.

Proton Tunneling

The evidence of proton tunneling in KDP from our Raman data in the nonpolar phase comes from the temperature dependence of the intensity of some of the $[\text{PO}_4]$ bands in the ferroelectric phase. The intensity of such bands increases by almost a factor of two as the transition is approached from the paraelectric phase into the ferroelectric phase. The corresponding line widths in the ferroelectric phase decrease by a factor of two. Also in the ferroelectric phase, on lowering the temperature below T_c , the intensity increase of the bands can be directly related to the increase in the spontaneous polarization. The large half-widths in the paraelectric phase are due to strong coupling of the $[\text{PO}_4]^+$ internal vibrations to the collective hydrogen motions. At the transition in the ferroelectric phase the reduction in half-width corresponds to a large drop in the hydrogen tunneling probability. The corresponding changes in KD^*P are much smaller because of the reduced deuterium motion in both phases.

The temperature dependence of the lattice modes (in the region $0\text{--}250 \text{ cm}^{-1}$) has been observed in both KDP and KD^*P . The evidence that these lattice modes are coupled to the proton tunneling can be seen from their temperature dependence. The softening of the ferroelectric mode in the paraelectric phase as the transition is approached is the result of the coupling of an optical mode of vibration of $[\text{K-PO}_4]$ complex to the proton tunneling; it is the mode ω_- discussed by Kobayashi¹³. Another higher frequency mode ω_+ which also results from such a coupling is due to 180° out of phase motion of $[\text{K-PO}_4]$ complex. We can assign the 175 cm^{-1} band in KDP and KD^*P to ω_+ . In KDP the intensity of this mode reduces dramatically as the Curie temperature is crossed from above, and is due to sudden

reduction in the H tunneling motion. In KD^*P this mode is relatively much weaker at 300°K. Its intensity decreases as the transition is approached and it finally disappears below the Curie temperature.

Isotopic Effect of Deuteration

The deuteration results in some additional Raman bands which could not be identified in KDP, KDA or ADP. This indicates significant distortion of both the lattice and the $[\text{PO}_4]$ tetrahedra. Thus the large isotopic shift of the Curie temperature on deuteration is both due to the large change of tunneling motion and due to distortion of the crystal structure caused by deuteration.

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PROTON-PHONON COUPLING IN CsH_2AsO_4 AND KH_2AsO_4

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ABSTRACT

We have observed strong anharmonic coupling between the pseudospin « tunneling » mode and an optical mode of B_2 symmetry in the paraelectric phase of caesium dihydrogen arsenate and potassium dihydrogen arsenate. At temperatures above T_c this interaction is manifest as an antiresonance interference shape in the Raman spectrum, similar to that in AlPO_4 ; however, the interacting modes in CsH_2AsO_4 and KH_2AsO_4 are heavily damped, in contrast to AlPO_4 . The observed spectra are in good agreement with a spectral distribution function obtained from a Green's function calculation. The temperature dependences of the Debye relaxation times for the tunneling mode in each crystal obey a functional dependence of form $\tau^{-1}(T) = \tau_\infty^{-1} \frac{T - T'_c}{T}$ with T'_c significantly less than the actual transition temperature T_c .

It is known that in the hydrogen-bonded ferroelectric KDP (KH_2PO_4) the onset of ferroelectricity involves both proton displacements (tunneling) and some optical phonon instability involving the other ions¹. This is a necessary deduction from the fact that the proton displacements are at right angles to the spontaneous polarization. The coupled proton-phonon excitation has been discussed in detail by Kobayashi² using a pseudo-spin formalism to represent the two proton tunnelling positions³. On the basis of the Raman study of Kaminow and Damen⁴ on the paraelectric phase of KDP and of Levstek and Lavrencic⁵ on the ferroelectric phase it is known that the coupled proton-phonon mode which « softens » in KDP and induces ferroelectricity is overdamped, and can be described as an anharmonic oscillator with a width of approximately 100 cm^{-1} and a temperature dependent frequency ω_0 . The present knowledge of the dynamics of the KDP phase transition has been summarised by Cochran⁶ recently, and some further study of the pseudo-spin formalism has been given by Silverman⁷.

In the series of Raman experiments on ferroelectrics isomorphous with KDP we have found evidence of a very strong optical mode coupling of protons and phonons manifest in a way not previously considered in such crystals. We observe very asymmetric spectral features in the low frequency spectra of CsH_2AsO_4 and KH_2AsO_4 . These arsenates manifest the same heavily damped temperature-dependent mode observed in KDP⁴ (which we shall call the « tunneling mode » with the qualifications on that description in the preceding paragraph); however, the tunneling mode has an unusual spectral shape and cannot be described as a single anharmonic oscillator, nor as a Debye relaxation spectrum.

We have been able to fit our observed spectra extremely well, however, in terms of coupling between the « tunneling » mode and a transverse optical phonon of B_2 symmetry. The

present communication contains spectra for CsH_2AsO_4 and for KH_2AsO_4 in the paraelectric phase.

THEORY

We write the imaginary part of the complex susceptibility $\chi(\omega)$ for the coupled modes in terms of the Green function $G_{ij}(\omega)$ and the mode strengths P_i, P_j as

$$\chi''(\omega) = \text{Im} \sum_{ij} P_i P_j G_{ij}(\omega) \quad (1)$$

The imaginary part of the susceptibility $\chi(\omega)$ can be related to the Raman (Stokes) scattering intensity $S(\omega)$ by means of the fluctuation-dissipation theorem.

$$S(\omega) = R \chi''(\omega) (n(\omega) + 1) \quad (2)$$

$$\text{where } n(\omega) = [e^{\hbar\omega/kT} - 1]^{-1} \quad (3)$$

and R is a constant.

We can determine the expressions for $G_{ij}(\omega)$ by means of the coupled mode equation :

$$\begin{bmatrix} (\omega_a^2 - \omega^2 + i\omega\Gamma_a) & (i\omega\Gamma_{ab} + \Delta^2) \\ (\Delta^2 + i\omega\Gamma_{ab}) & (\omega_b^2 - \omega^2 + i\omega\Gamma_b) \end{bmatrix} \begin{bmatrix} G_{11} & G_{12} \\ G_{12} & G_{22} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad (4)$$

Here we approximate $\Delta, \Gamma_a, \Gamma_b$ and Γ_{ab} as constants. This is the form of eqn. (4) expected in the low frequency limit ($\omega \rightarrow 0$); however, the Δ and Γ 's we evaluate will be average values over the range 0 - 200 cm^{-1} and not the low frequency values.

Raman spectra may therefore be calculated for a system of two coupled modes in terms of the seven parameters $\omega_a, \omega_b, \Gamma_a, \Gamma_b, \Delta, \Gamma_{ab}$ and P_a/P_b (the normalization constant R is of course required for absolute cross sections). The related problem of phonon couplings and anharmonicity in inelastic neutron scattering spectra has been treated theoretically by

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Maradudin and Fein⁸ and applied to several crystals by Cowley⁹.

EXPERIMENTAL

The Raman data were obtained from a large ($1 \times 1 \times 1.2$ cm), orientated single crystal. Right-angle scattering was detected by means of a 0.75 m double monochromator and a cooled S-20 phototube. Excitation was approximately 50 mW at 4880 Å from an argon ion laser. For CsDA the observed $x(yx)y$ 295°K spectrum from 10–250 cm^{-1} is shown as a solid line in Fig. 1.

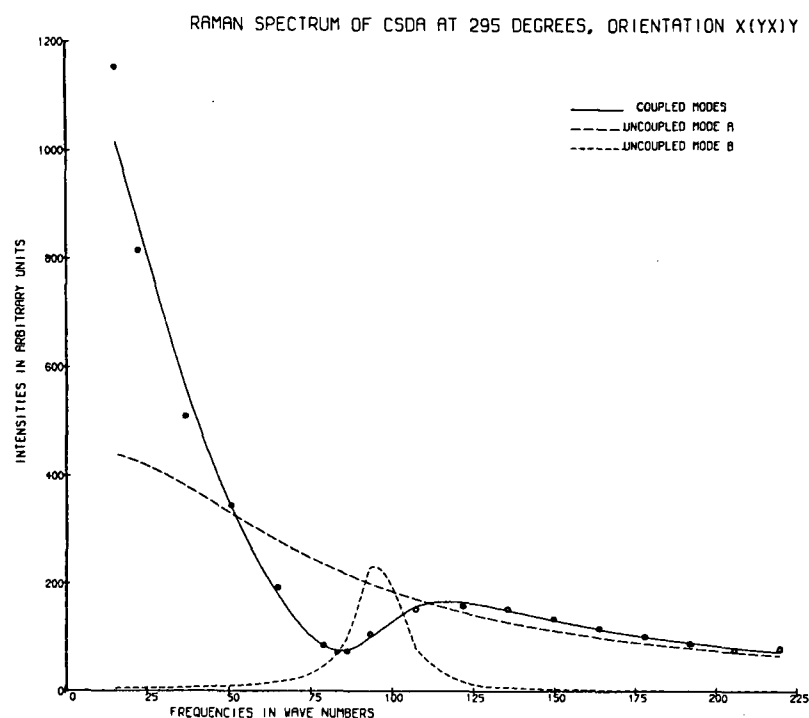


FIG. 1. — Raman spectrum of CsH_2AsO_4 at 293°K with $x(yx)y$ orientation. Spectral slitwidth is 10 cm^{-1} . Other experimental details as described in the text. The calculated spectrum corresponds to the parameters listed under calculation 1 in Table 1. Model 2 is equivalent to 1 and can be obtained by a unitary transformation of the basis states in 1.

ANALYSIS OF CsDA DATA

The calculated spectrum in Fig. 1 is obtained from a least square fit of equ. (2) to the observed spectrum, using expressions for $\chi''(\omega)$ and $G_{ij}(\omega)$ given in eqns. (1) and (4). The parameters determined from the fit are listed in Table 1. These parameters have been used to determine the shape of the uncoupled modes and are represented as Mode A and Mode B in the figure. Mode A is very heavily damped and resembles the tunneling mode in KDP. Mode B is a transverse optic phonon having B_2 symmetry. Because of the strong interaction between the tunneling and phonon modes there is a dip in the spectrum around 86 cm^{-1} . The interaction is similar to that in AlPO_4 ¹⁰ where a Green's function treatment by Zawadowski and Ruvalds¹¹ yielded very good agreement with the observed spectrum. Their expressions can be recovered from our equ. (4) by making approximations $\Gamma_{ab}^2 = \Gamma_a \Gamma_b$, $\Delta = 0$, $\omega_a \approx \omega_b \approx \omega$ and $\omega_a, \omega_b \gg \Gamma_a, \Gamma_b$. The latter approximations are not valid in CsH_2AsO_4 .

As discussed by Barker and Hopfield¹² there are an infinite number of solutions to the diagonalization in eqn. (4); we

may always diagonalize the real part of the matrix ($\Delta = 0$) or the imaginary part ($\Gamma_{ab} = 0$). The choice is equivalent to a choice of phase for the interacting modes.

In Table 1 we summarise two physically plausible choices. One is analogous to that of Barker and Hopfield¹² and has $\Gamma_b \approx 0$, i.e. all the damping is due to one oscillator — in our case, the proton tunneling mode. Note that this model yields a phonon frequency ω_b very near the peak in our spectrum.

The second model we present is analogous to the Kobayashi theory for KDP—structure, hydrogen—bonded ferroelectrics. In this model the pseudo-spin tunneling mode is viewed as having no direct contribution to the dielectric function, only indirect through phonon coupling. Hence $P_a = 0$.

While we obtain algebraic solutions to this model, they are physically different from Kobayashi's theory. The data can be fitted by two modes, one having zero polarizability and underdamped (this corresponds to the tunneling mode which is overdamped in the prevailing view of KDP-structures), and the other having non-zero polarizability and overdamped (this corresponds to the phonon mode). We conclude that the coupled mode in CsH_2AsO_4 does not correspond closely to the Kobayashi theory, and that it will be necessary to associate greater polarization with the tunneling mode than with the phonon in order to obtain a physically realistic model.

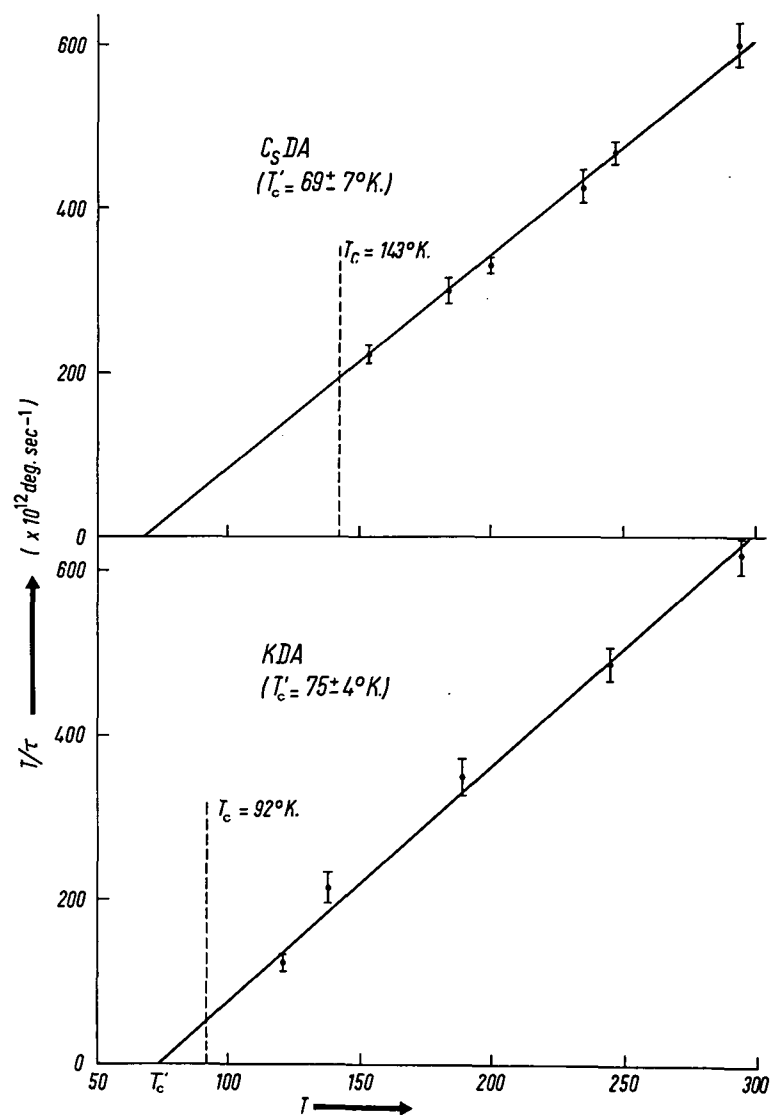


FIG. 2. — Temperature dependence of the Debye relaxation times in CsDA and KDA.

We are thus led to a preference for Model *A* in Table 1.

It is not possible on the basis of the 295°K data to obtain a definitive choice of basis states. However, work at other temperatures enables us to do so, for only one choice of phase yields simple temperature dependences for ω_a and ω_b .

Due to the very large damping present in CsDA, we cannot extract reliable values of ω_a and Γ_a from a least squares fit to the data; these two parameters are correlated in the fitting procedure. Since the overdamped spectrum approximates that of a Debye relaxation, only the ratio $\tau_a(T) = \frac{\Gamma_a(T)}{\omega_a^2(T)}$ can be accurately evaluated. In the anharmonic oscillator approximation, we expect $\Gamma_a(T)$ to be linear in T and $\omega_a^2(T)$ to vary as $(T - T_c)$. Hence $\tau_a(T)$ should have a temperature dependence of form

$$\tau^{-1}(T) = \tau_{\infty}^{-1} \frac{(T - T_c)}{T} \quad (5)$$

where τ_{∞} is the asymptotic relaxation time in the high-temperature limit. Fig. 2 shows that $\tau^{-1}(T)$ does have the temperature dependence predicted in equ. (5).

More important, we note that the value T_c determined in Fig. 2 is about 69°K and differs quite considerably from the actual phase transition temperature in CsDA (143°K). This is not an uncommon situation: in crystals with first-order phase transitions, such as PbTiO_3 , T_c as extrapolated from soft-mode frequencies can be as much as 30-40°K or more from the actual transition temperature T_c . However, the transition in CsDA is nearly second-order, as determined from measurement of the dielectric constant $\epsilon(T)$ in the paraelectric phase (B. Lavrencic, private communication). That is, in contrast to non-hydrogen-bonded ferroelectrics such as the perovskite titanates $\epsilon(T)$ is *not* proportional to $\omega_a^{-2}(T)$, where ω_a is the soft-mode frequency. R. A. Cowley has interpreted¹³ this anomalous behaviour in terms of the anomalous self-energies of the soft-mode excitations in CsDA.

TABLE I. CsDA Parameters at 295°K (cm^{-1}).

Parameter	Model 1 (« Barker-Hopfield »)	Model 2 (« Kobayashi »)
P_a	4887	0
Γ_a	2375*	29.2
ω_a	403*	76.6
P_b	379	4902
Γ_b	15.1	2361
ω_b	96.3	407
Γ_{ab}	0	-182
Δ	167.3	126.0

* Other choices of Γ_a and ω_a consistent with $\tau_a = \Gamma_a/\omega_a^2 = 5 \times 10^{-13}$ sec. give nearly as good a fit.

ANALYSIS OF KDA DATA

The KDA data are similar in all respects to those of CsDA, except that the damping is not as large. Typical data are shown in Fig. 3, and the temperature dependence of the relaxation time is plotted in Fig. 2. Because the relaxation

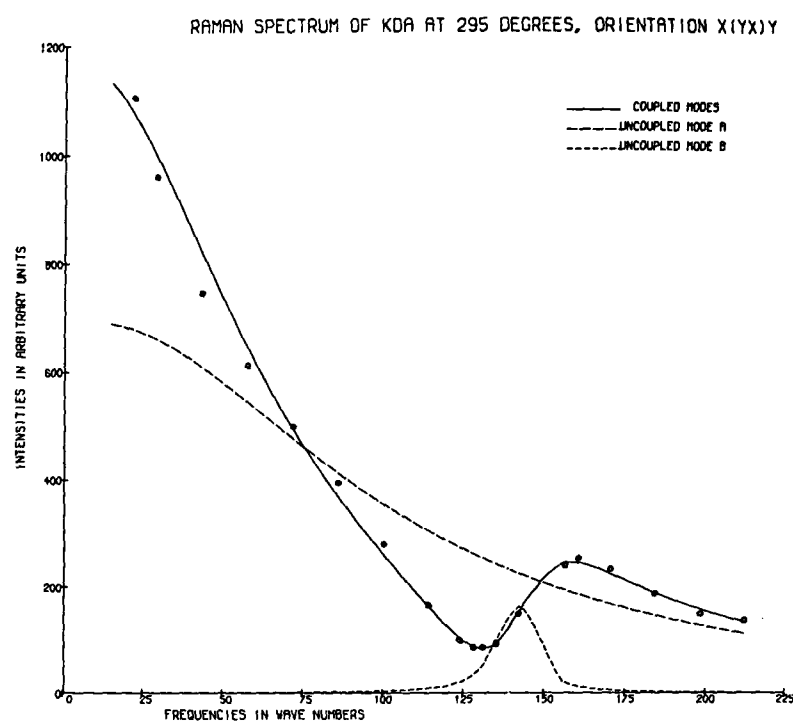


FIG. 3. — Raman spectrum of KH_2AsO_4 at 295°K for $x(yx)y$ orientation.

times are longer, we can reliably extract Γ_a and ω_a as independent parameters in KDA. Values are summarized in Table II.

TABLE II. KDA Parameters (cm^{-1}).

	295°K	245°K	189°K	137°K
P_a	2440	2393	2385	2060
Γ_a	372	372	292	247
ω_a	161	158	134	112
P_b	380	403	431	391
Γ_b	11.8	14.5	14.7	12.9
ω_b	140	145	147	148
Γ_{ab}	0	0	0	0
Δ	112	116	112	107
$\tau_a(\text{sec})$	4.8 $\times 10^{-13}$	5.0 $\times 10^{-13}$	5.4 $\times 10^{-13}$	6.6 $\times 10^{-13}$

Note that there is some evidence for a maximum in the phonon width Γ_b near the temperature at which ω_a crosses ω_b ($\sim 217^\circ\text{K}$).

CONCLUSION

We have found evidence in CsH_2AsO_4 and KH_2AsO_4 for very strong anharmonic interactions. These involve the overdamped « soft » mode analogous to that observed⁴ in isomorphic KH_2PO_4 , and a B_2 symmetry TO phonon. The observed data are accurately described by a Green function calculation. Although the mode couplings involve the « pseudo-spin proton tunneling mode » described by Kobayashi and others, the analysis we give is fundamentally different from those previously presented from such proton-phonon systems. The spectral line shapes are very similar to those analysed by Scott¹⁰, Zawadowski and Ruvalds¹¹ in AlPO_4 . The extension of this kind of anharmonic analysis to the proton-tunneling pseudo-spin systems provides a new

way of measuring proton-phonon interactions in hydrogen-bonded ferroelectrics. Indeed, this is the first direct observation of proton-phonon coupling.

It should be of interest for readers to compare the coupled anharmonic phonon analysis presented here with the pseudo-spin model of coupled modes in KDP structures presented at this conference by Blinc, Lavrencic, et al.

ACKNOWLEDGMENT

It is a pleasure to acknowledge many enlightening discussions with Professor R. A. Cowley. The cooperation of Dr. W. Taylor during early phases of the experimental work is also appreciated.

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$$\Gamma_{ab} = 0 \quad \text{and} \quad \Gamma_a, \Gamma_b \ll \omega_a, \omega_b;$$

however, this leads to a trivial level repulsion with no lineshape anomalies.

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STUDY OF THE PHASE TRANSITION OF TGS BY SECOND HARMONIC SCATTERING

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INTRODUCTION

In recent years second harmonic generation (SHG) of light has been extensively studied, but far less attention has been paid to the phenomena of nonlinear scattering¹. We have previously observed this phenomena in TGS at room temperature². Here, we present some results obtained by second harmonic (SH) scattering near the Curie temperature ($T_c = 49^\circ\text{C}$).

In most ferroelectric crystals the nonlinear susceptibility tensor d depends upon the order parameter, which is the polarisation P . When the paraelectric phase is centrosymmetric (as in TGS) one can often take d to be proportional³ to P . In the ferroelectric phase, the polarisation is not uniform and has a spatial dependence $P(\vec{r})$, due to the domain structure which produces inhomogeneities in the nonlinear properties, which give rise to SH scattering. One can show

that the SH intensity $I_{2\omega}$ produced in a direction with wave vector $\vec{k}_2$, by a light beam of wave vector $\vec{k}_1$ is given by²:

$$I_{2\omega} \sim |P(\Delta\vec{k})|^2 \quad (1)$$

where

$$P(\Delta\vec{k}) = \int_{\text{crystal}} P(\vec{r}) \exp i \Delta\vec{k} \cdot \vec{r} d^3r \quad (2)$$

and

$$\Delta\vec{k} = \vec{k}_2 - 2\vec{k}_1 \quad (3)$$

If the crystal is a single domain plane parallel slab, $P(\vec{r})$ would be uniform and $P(\Delta\vec{k})$ would be different from zero only for $\Delta\vec{k}$ perpendicular to the surface. But as the crystal contains domains the Fourier transform of the polarization is different from zero for other directions of $\Delta\vec{k}$.

In TGS, there are only 180° domains⁴ which are in form of cylinders parallel to the ferroelectric axis, with a polarisation $P(r) = \pm P_s$, the spontaneous polarization. So, $P(\Delta\vec{k})$ is now different from zero not only for $\Delta\vec{k}$ perpendicular to the surface but also for $\Delta\vec{k}$ perpendicular to the axis of these cylinders, i.e. to the ferroelectric axis OY . If the domain structure is quite regular one can define a period $2a$ and the intensity of scattered light has a maximum for $|\Delta\vec{k}| = 2\pi/2a$.

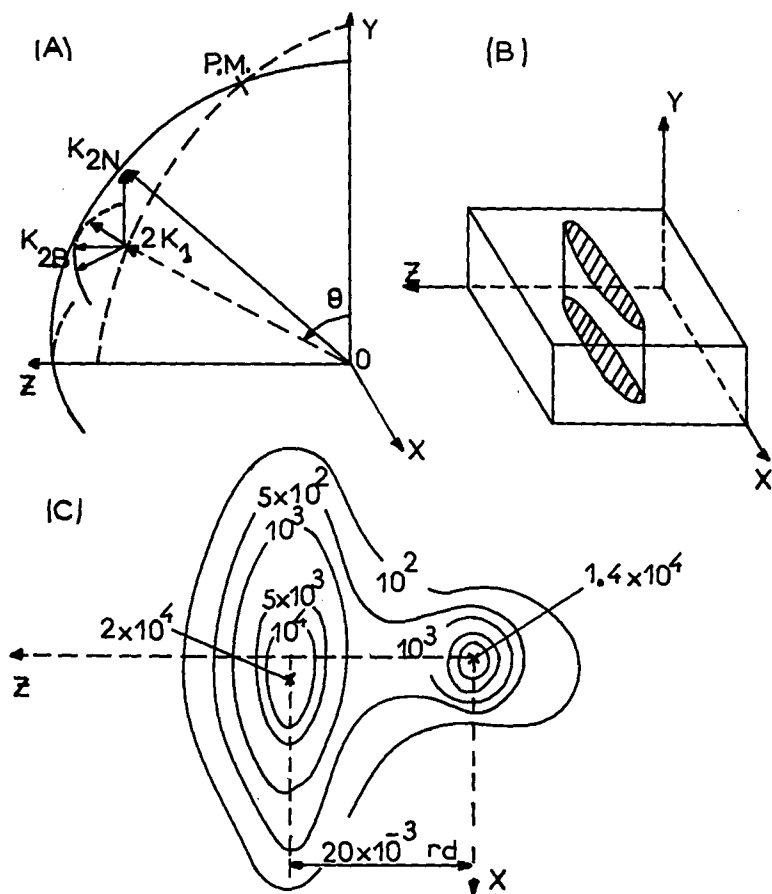


FIG. 1. — a) Schematic representation of scattering vectors in SH scattering in TGS; b) Usual form of domains in a TGS crystal; c) Typical angular dependence of equi-intensity curves of scattered SH.

Fig. 1A is a schematic representation of the wave vectors of light inside a slab perpendicular to OY and shows these two kinds of $\Delta\vec{k}$. Actually the crystal is optically anisotropic, and has several refractive index surfaces, which lead to several scattered lines, but here only one labeled B in² will be considered. Another consequence of the anisotropy is the existence of phase matching directions, one with $\vec{k}_2 = 2\vec{k}_{10}$ (type I), the other with $\vec{k}_2 = \vec{k}_{10} + \vec{k}_{1e}$ (type II) where the subscripts 0 and e refer respectively to ordinary and extraordinary light. When the incidence angle of the fundamental beam is changed from a phase matching direction, the magnitude of the scattering vector $\Delta\vec{k}$ varies continuously from 0 to a finite value. So one can obtain the Fourier transform of the domain structure by measuring the angular dependence of the SH near a phase matching direction and examine its temperature variation, particularly around T_c , where the spontaneous polarization vanishes.

SECOND HARMONIC SCATTERING NEAR T_c

The experimental results, reported here, were obtained on a plane parallel slab of TGS of $1 \times 1 \times 0.2$ cm, cut perpendicular to the ferroelectric axis OY . Gold electrodes were evaporated on parts of the faces in order to measure the dielectric constant. The sample was immersed in a paraffin oil bath regulated with an accuracy of $5 \times 10^{-3}^\circ\text{C}$. This experimental apparatus is described with greater detail in references^{2,5}. The cross sections of TGS domains are irregular but often elongated parallel to the optic plane (XOY) (Fig. 1B). The incident plane is YOZ and the incidence angle can be changed by rotating the crystal. A typical angular distribution of SH light is shown in Fig. 1C, where we have kept only the B scattered line, with extraordinary polarisation produced by a nonlinear polarisation wave of wave vector $\vec{k}_{10} + \vec{k}_{1e}$. Henceforth, only the intensity of the maximum of line B will be plotted, this maximum is obtained when $\Delta\vec{k}_B$ is perpendicular to the large dimension of domains.

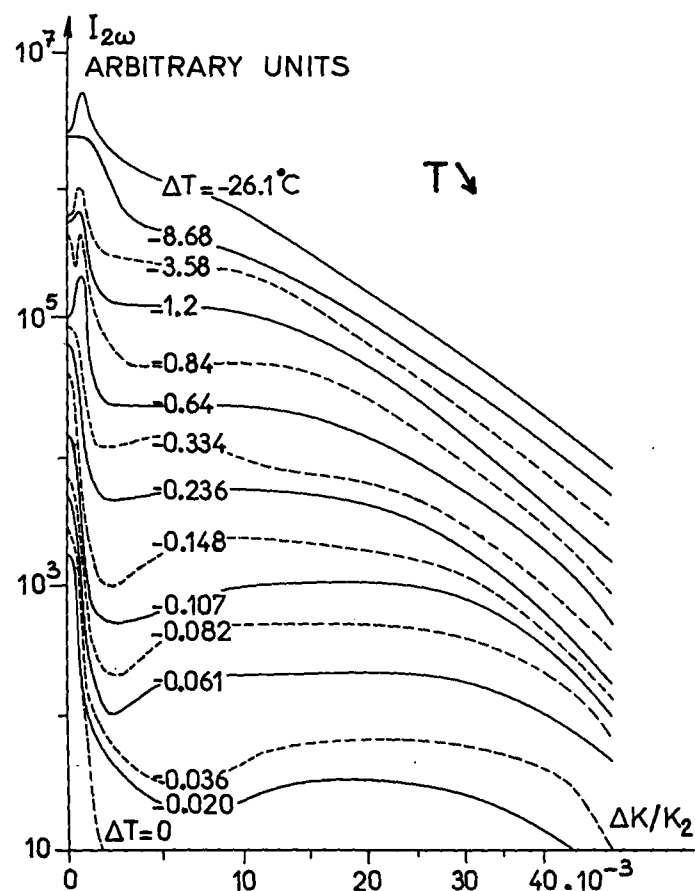


FIG. 2. — SH intensity as a function of the modulus of the scattering vector $\Delta\vec{k}$ for different temperatures.

On Fig. 2 are plotted scattering curves $I_{2\omega}(|\Delta\vec{k}|)$, obtained in cooling the crystal from $T > T_c$ to room temperature. The intensity of the maximum of the scattered B line is given as a function of $|\Delta\vec{k}_B|$ for different temperatures. This variation of $\Delta\vec{k}_B$ was obtained by varying the incidence angle between 44.5° (direction of phase matching) and 20° , in the YOZ plane. In the paraelectric phase, one observes only a narrow peak, the origin of which will be discussed farther. Just below T_c , at the maximum of the dielectric constant, broad domain scattering appears. As the temperature is lowered the intensity increases and the maximum

RAMAN SCATTERING FROM FERROELECTRIC MODES IN THE KDP ISOMORPHOUS PHOSPHATES AND ARSENATES

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Résumé. — Nous avons étudié les spectres Raman à basse fréquence pour un certain nombre d'isomorphes à KH_2PO_4 (KDP) dans la phase paraélectrique pour une certaine gamme de températures.

Nous avons prolongé les mesures jusqu'à des fréquences de 250 cm^{-1} et fait coïncider avec notre modèle l'interférence caractéristique entre les phonons optiques à fortement amortis et ceux à basse fréquence ayant la même symétrie.

Nous avons donné la première observation d'un mode amorti de symétrie B_2 dans le spectre Raman pour $(\text{NH}_4)\text{H}_2\text{PO}_4$. La variation du temps de relaxation de Debye en fonction de la température à la fois pour les modes E et B_2 dans $(\text{NH}_4)\text{H}_2\text{PO}_4$ est comparée aux mesures diélectriques.

Abstract. — The low frequency Raman spectra of a number of KH_2PO_4 (KDP) isomorphs have been recorded over a range of temperatures in the paraelectric phase. We have extended the measurements to frequencies of 250 cm^{-1} and have included in our model fitting the characteristic interference between the overdamped and the low frequency optical phonon of the same symmetry. We report the first observation of an overdamped mode of B_2 symmetry in the Raman spectrum of $(\text{NH}_4)\text{H}_2\text{PO}_4$. The temperature dependence of the Debye relaxation times for both E and B_2 modes in $(\text{NH}_4)\text{H}_2\text{PO}_4$ are compared with dielectric measurements.

Since the first observation of an overdamped mode in the Raman spectrum of KH_2PO_4 by Kaminow and Damen [1], there have been several reports of similar experiments. The most extensive of these is that of Wilson [2]. In each case, a temperature dependent overdamped mode of B_2 symmetry, appearing as wings on the Rayleigh line, is observed, and has been fitted with the spectral response function

$$S(\omega) = R(n(\omega) + 1) \text{Im} [G(\omega)] \quad (1)$$

where

$$G(\omega) = (\omega_1^2 - \omega^2 + i\Gamma_1 \omega)^{-1} \quad (2)$$

and

$$n(\omega) = (e^{\hbar\omega/kT} - 1)^{-1} \quad (3)$$

to give a mode frequency ω_1 and damping constant Γ_1 . When the damping is very large most of the scattered intensity from this mode occurs at low frequency, i. e. $\omega < \omega_1$, and so

$$G(\omega) = \omega_1^{-2} \left(1 + i \frac{\Gamma_1}{\omega_1^2} \omega \right)^{-1}. \quad (4)$$

The quantity (Γ_1/ω_1^2) is the Debye relaxation time, τ , for the overdamped mode. This is equivalent to saying that for large damping, the quality of the fit is insensitive to absolute values of Γ_1 and ω_1 and that these two parameters are highly correlated.

We have observed these overdamped modes in the various phosphates and arsenates isomorphous with KH_2PO_4 and have extended the measurements to 250 cm^{-1} , so as to include the nearest underdamped

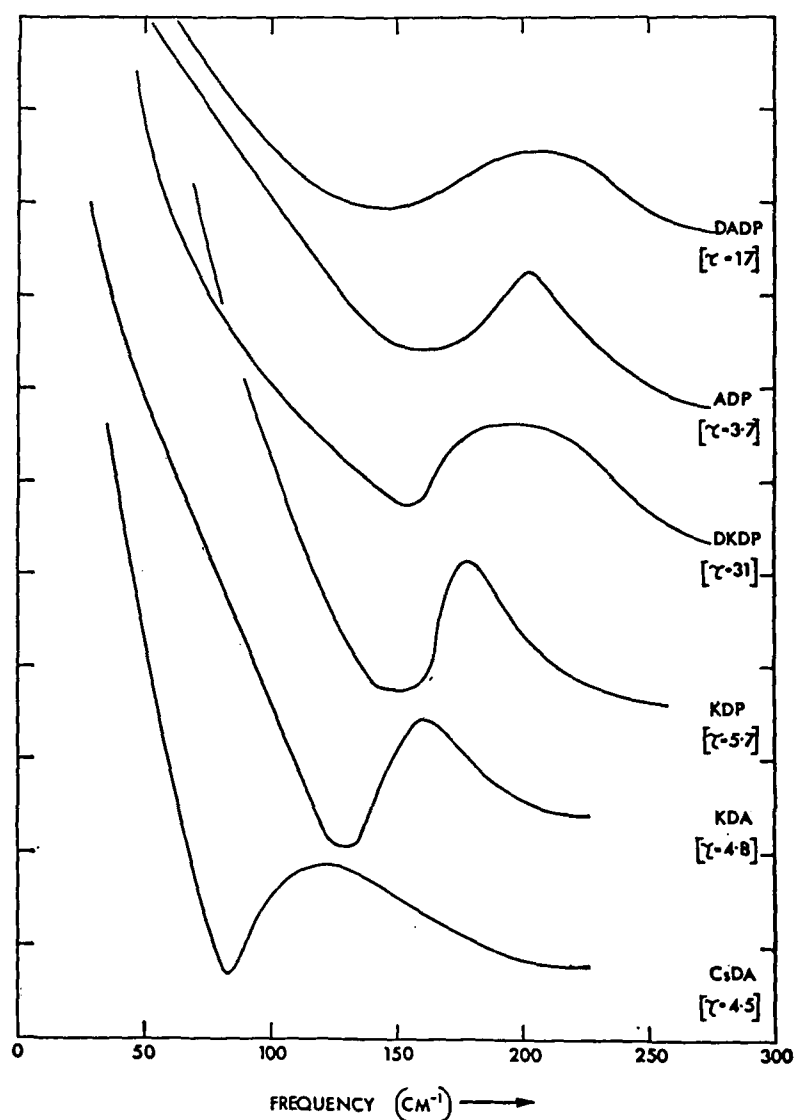


FIG. 1. — The Raman spectra of $\text{ND}_4\text{D}_2\text{PO}_4$ (DADP), $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP), KD_2PO_4 (DKDP), KH_2PO_4 (KDP), KH_2AsO_4 (KDA) and CsH_2AsO_4 (CsDA) at $T = 295^\circ\text{K}$, orientation $X(YX)Y$. The incident laser intensity is different in each case. The Debye relaxation time for the overdamped mode in each spectrum is shown in parenthesis (Units are 10^{-13} s) Slitwidth equals 10 cm^{-1} .

transverse optical mode of B₂ symmetry. The spectra are shown in figure 1. The asymmetry in this TO phonon lineshape suggests that there is strong anharmonic coupling between it and the overdamped mode. The spectral response may then be expressed in terms of the Green function $G_{ij}(\omega)$ and the two mode strengths P_1, P_2 .

$$\chi(\omega) = \sum_{i,j=1}^2 P_i P_j G_{ij}(\omega) \tag{5}$$

where

$$G_{ij}(\omega) = \begin{bmatrix} \omega_1^2 - \omega^2 + i\Gamma_1 \omega & \Delta^2 + i\Gamma_{12} \omega \\ \Delta^2 + i\Gamma_{12} \omega & \omega_2^2 - \omega^2 + i\Gamma_2 \omega \end{bmatrix}^{-1} \tag{6}$$

Simple soft mode theory predicts that $\omega_1^2/\Gamma_1 = 1/\tau$, varies as $(T - T_c)/T$ where T_c is the temperature of the dielectric anomaly of the free crystal. Kaminow and Damen [1] have verified this in KH₂PO₄, but they have not taken into account the coupling between the overdamped mode and the transverse optic mode. They used the simple damped harmonic oscillator

model of eq. (2) to fit their data at all temperatures whereas Wilson [2] has found that as the crystal temperature is lowered towards the transition, the

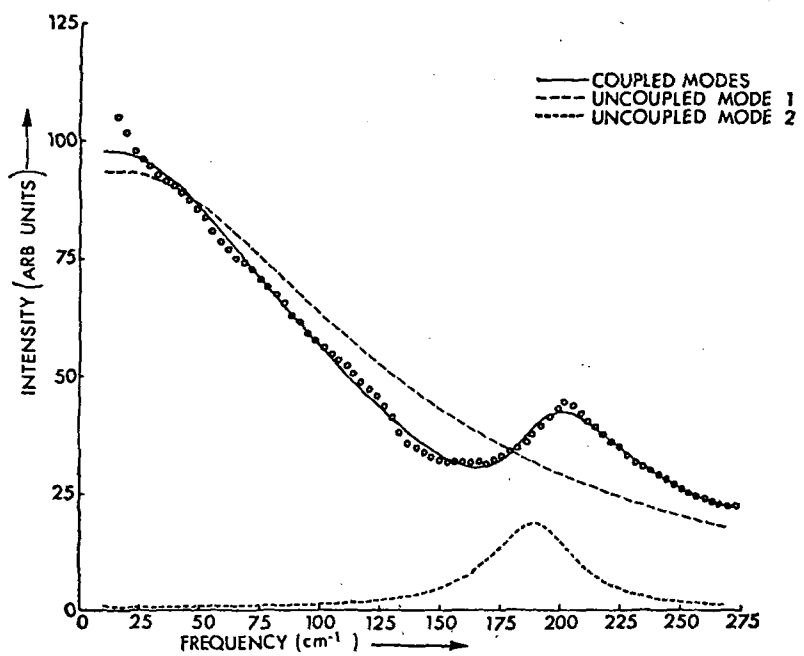


FIG. 2. — The Raman spectrum of NH₄H₂PO₄ at $T = 295$ °K orientation $X(YX)Y$. Open circles are experimental data. The solid line is the lineshape obtained when the two uncoupled modes (dotted lines) interact as described in the text.

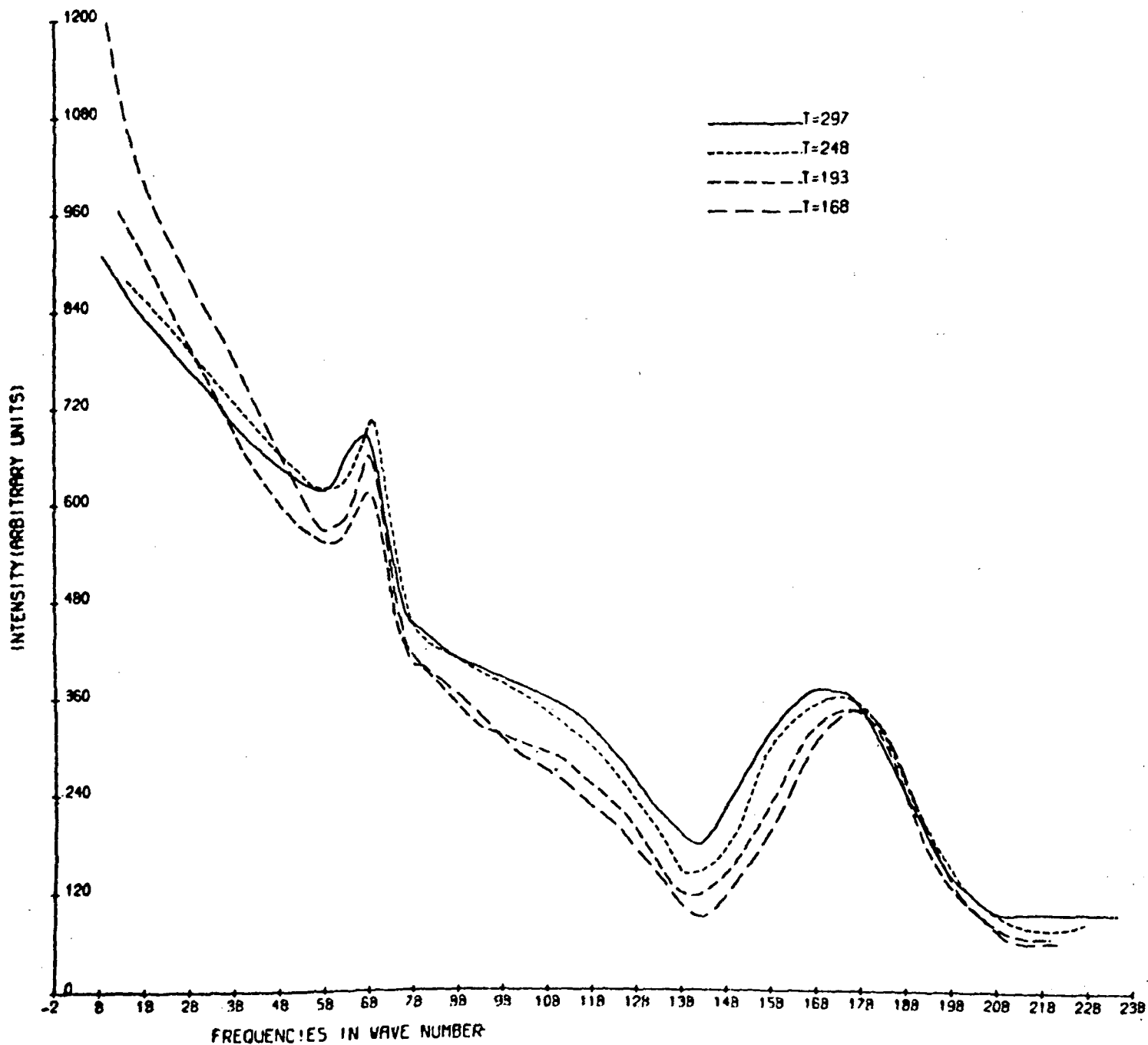


FIG. 3. — The Raman spectrum of NH₄H₂PO₄ at various temperatures orientation $Z(XZ)X$. Slitwidth equals 10 cm⁻¹.

shape of the spectrum becomes more like the Debye oscillator of eq. (4). This suggests that there is an additional temperature dependent factor present which is not included in the simple model. When the coupled mode eq. (6) is used to fit the room temperature spectrum of KH_2PO_4 we find that the Debye model is the most suitable with a relaxation time

$$\tau = 5.7 \times 10^{-13} \text{ s.}$$

We are proceeding with this type of analysis at various temperatures for KH_2PO_4 and KD_2PO_4 and our results will be published elsewhere.

This analysis has already been carried out for KH_2AsO_4 and CsH_2AsO_4 [3] where it was found that $1/\tau$ varied as $(T - T_0)/T$, with T_0 considerably different from T_c . Cowley *et al.* [4] have proposed that this difference is due to an anomaly in the response of the soft mode at low frequencies. This will be explained in detail by Coombs and Cowley later in this session.

$(\text{NH}_4)\text{H}_2\text{PO}_4$ is isomorphous with KH_2PO_4 but undergoes an antiferroelectric transition at 148 °K with a large dielectric anomaly occurring in the a -direction and a small anomaly in the c -direction. We report here the first observation by Raman spectroscopy, of the overdamped mode of B_2 symmetry. Earlier infra-red experiments have already indicated its presence [5]. The results of the coupled mode analysis are shown in figure 2. A value for the relaxation time, τ_B , is found and its temperature dependence studied. In figure 3 we show the Raman spectrum of the E symmetry modes in $(\text{NH}_4)\text{H}_2\text{PO}_4$. Since there are three optical modes in the spectrum any model taking account of coupling between the modes would contain a prohibitive number of parameters. We have fitted this spectrum with four uncoupled oscillators and studied the temperature dependence of τ_E for the overdamped mode.

In figure 4 we compare our results for $(\text{NH}_4)\text{H}_2\text{PO}_4$ with the earlier dielectric data of Mason [6] and microwave data of Kaminow [7]. We have found

$$\frac{1}{\tau_B} = 3.1 \left(\frac{T - 29}{T} \right) \times 10^{13} \text{ s}^{-1}$$

$$\frac{1}{\tau_E} = 1.6 \left(\frac{T - 54}{T} \right) \times 10^{13} \text{ s}^{-1}$$

where the extrapolated transition temperatures are

$$T_{0B} = 29 \pm 3 \text{ °K}$$

$$T_{0E} = 54 \pm 5 \text{ °K.}$$

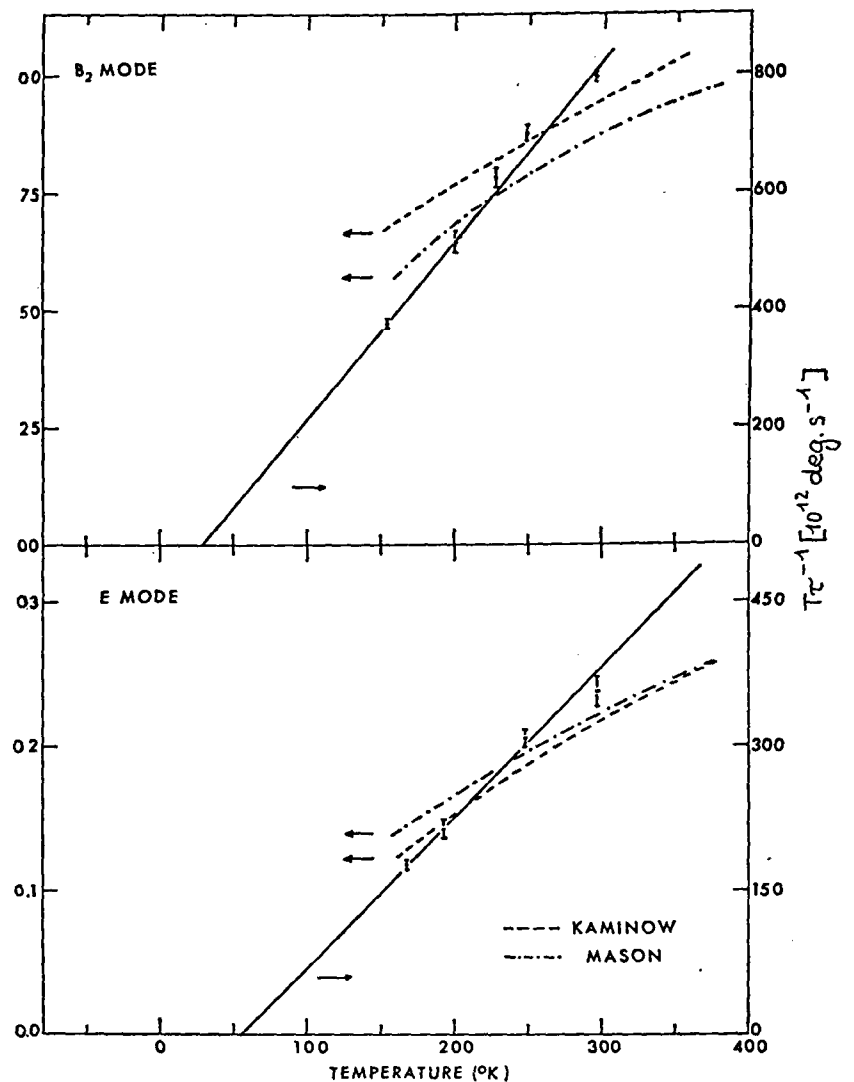


FIG. 4. — Solid line is $1/\tau = 1/\tau_\infty(T - T_0)/T$ as obtained from Raman data. The dotted lines correspond to the inverse dielectric susceptibility $\frac{1}{\eta} = \frac{4\pi}{\epsilon(0, T) - 1}$ of $\text{NH}_4\text{H}_2\text{PO}_4$.

The static dielectric constant has a Curie-Weiss temperature dependence

$$\epsilon(0, T) = A + \frac{B}{T - T_c}$$

but because in this case the antiferroelectric transition occurs at a temperature much higher than the projected ferroelectric transition, it is difficult to extrapolate accurately and extract a value for T_c . It is therefore, not possible to compare the Raman and dielectric measurements in $(\text{NH}_4)\text{H}_2\text{PO}_4$ in the manner in which it was done for KH_2AsO_4 and CsH_2AsO_4 .

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Proton-Phonon Coupling in CsH_2AsO_4 and KH_2AsO_4

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We have observed strong anharmonic coupling between the pseudospin "tunneling" mode and an optical mode of B_2 symmetry in the paraelectric phase of cesium dihydrogen arsenate. At temperatures above $T_c = 143^\circ\text{K}$ this interaction is manifest as an antiresonance interference shape in the Raman spectrum, similar to that in AlPO_4 ; however, the interacting modes in CsH_2AsO_4 are heavily damped, in contrast to AlPO_4 . The observed spectra are in good agreement with a spectral distribution function obtained from a Green's-function calculation. Very similar results are obtained for KH_2AsO_4 .

INTRODUCTION

It is known that in the hydrogen-bonded ferroelectric KDP (KH_2PO_4) the onset of ferroelectricity involves both proton displacements (tunneling) and some optical-phonon instability involving the other ions.¹ This is a necessary deduction from the fact that the proton displacements are at right angles to the spontaneous polarization. The coupled proton-phonon excitation has been discussed in detail by Kobayashi² using a pseudospin formalism to represent the two proton tunneling positions.³ On the basis of the Raman study of Kaminow and Damen⁴ on the paraelectric phase of KDP and of Levstek and Lavrencic⁵ on the ferroelectric phase, it is known that the coupled proton-phonon mode which "softens" in KDP and induces ferroelectricity is overdamped, and can be described as an anharmonic oscillator with a width of approximately 100 cm^{-1} and a temperature-dependent frequency ω_0 . The present knowledge of the dynamics of the KDP phase transition has been summarized by Cochran⁶ recently, and some further study of the pseudospin formalism has been given by Silverman.⁷

In a series of Raman experiments on ferroelectrics isomorphic with KDP we have found evidence of a very strong optical mode coupling of protons and phonons manifest in a way not previously considered in such crystals. We observe very asymmetric spectral features in the low-frequency spectra of CsH_2AsO_4 and KH_2AsO_4 . These arsenates manifest the same heavily damped temperature-dependent mode observed in KDP⁴ (which we shall call the "tunneling mode" with the qualifications on that description given in the preceding paragraph); however, the tunneling mode has an unusual spectral shape and cannot be described as a single anharmonic oscillator, nor as a Debye relaxation spectrum.

We have been able to fit our observed spectra extremely well, however, in terms of coupling between the "tunneling" mode and a transverse optical

(TO) phonon of B_2 symmetry. The present communication contains the room-temperature spectrum for CsH_2AsO_4 in the paraelectric phase ($T_c = 143^\circ\text{K}$). Analyses at other temperatures in CsH_2AsO_4 and KH_2AsO_4 will be given in a subsequent paper.

THEORY

We write the imaginary part of the complex susceptibility $\chi(\omega)$ for the coupled modes in terms of the Green's function $G_{ij}(\omega)$ and the mode strengths P_i , P_j as

$$\chi''(\omega) = \text{Im} \sum_{ij} P_i P_j G_{ij}(\omega). \quad (1)$$

The imaginary part of the susceptibility $\chi''(\omega)$ can be related to the Raman (Stokes) scattering intensity $S(\omega)$ by means of the fluctuation-dissipation theorem,

$$S(\omega) = R\chi''(\omega)[\bar{n}(\omega) + 1], \quad (2)$$

where

$$\bar{n}(\omega) = (e^{\hbar\omega/kT} - 1)^{-1} \quad (3)$$

and R is a constant.

We can determine the expressions for $G_{ij}(\omega)$ by means of the coupled mode equation:

$$\begin{bmatrix} \omega_a^2 - \omega^2 + i\omega\Gamma_a & \Delta^2 + i\omega\Gamma_{ab} \\ \Delta^2 + i\omega\Gamma_{ab} & \omega_b^2 - \omega^2 + i\omega\Gamma_b \end{bmatrix} \begin{bmatrix} G_{11} & G_{12} \\ G_{12} & G_{22} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}. \quad (4)$$

Here we approximate Δ , Γ_a , Γ_b , and Γ_{ab} as constants. This is the form of Eq. (4) expected in the low-frequency limit ($\omega \rightarrow 0$); however, the Δ and Γ 's we evaluate will be average values over the range $0-200\text{ cm}^{-1}$ and not the low-frequency values.

Raman spectra may therefore be calculated for a system of two coupled modes in terms of the seven parameters ω_a , ω_b , Γ_a , Γ_b , Δ , Γ_{ab} , and P_a/P_b (the normalization constant R is of course required for absolute cross sections). The related problem of phonon couplings and anharmonicity in inelastic neutron scattering spectra has been treated theoret-

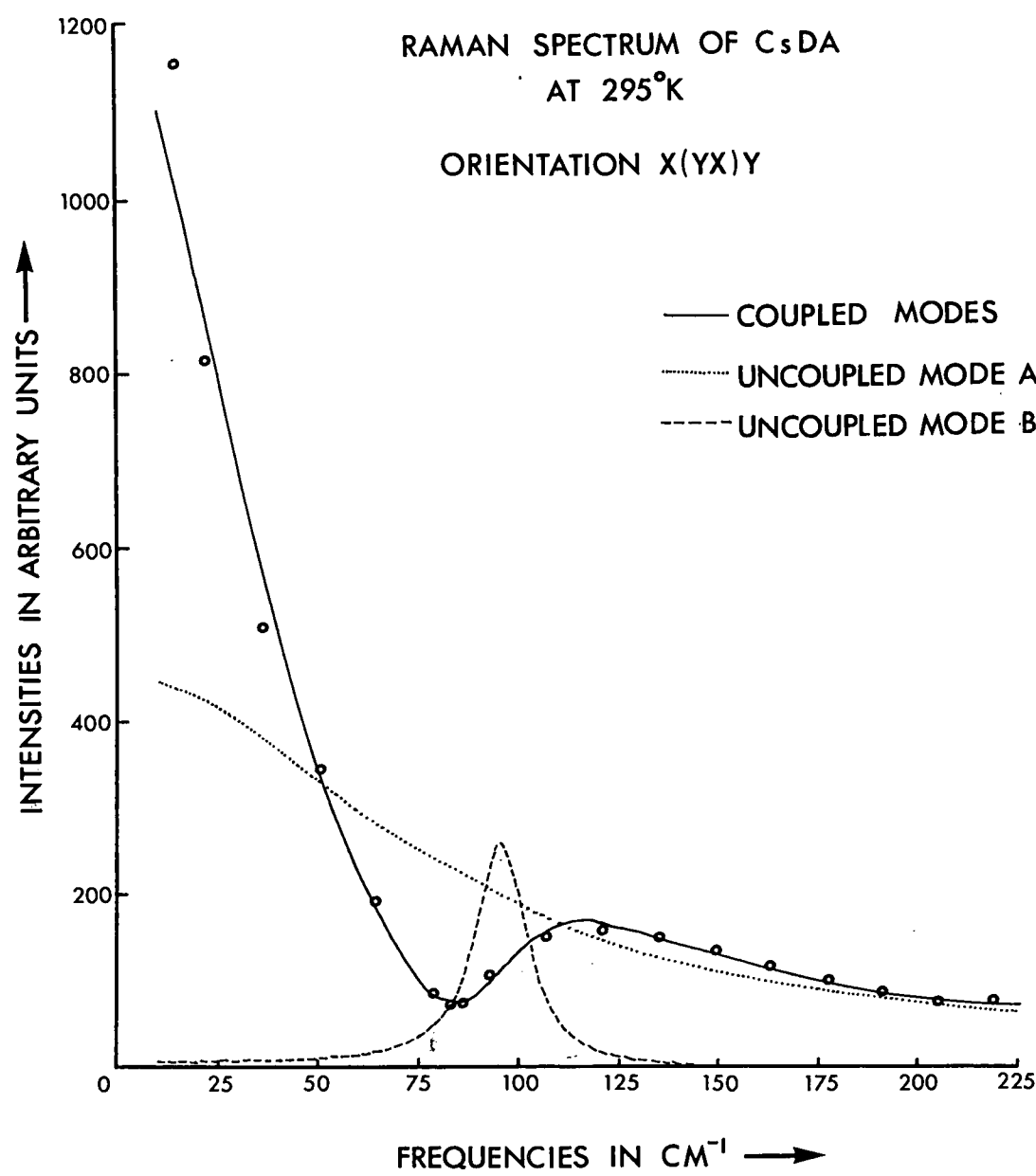


FIG. 1. Raman spectrum of CsH₂AsO₄ at 153 °K with *x(yx)y* orientation. Spectral slit width is 10 cm⁻¹. Other experimental details as described in the text. The calculated spectrum corresponds to the parameters listed under Model 1 in Table I.

ically by Maradudin and Fein⁸ and applied to several crystals by Cowley.⁹

EXPERIMENTAL

The Raman data were obtained from a large (1×1×1.2 cm) oriented single crystal. Right angle scattering was detected by means of a 0.75-m double monochromator and a cooled S-20 phototube. Excitation was approximately 50 mW at 4880 Å from an argon ion laser. The observed *x(yx)y* spectrum from 10–250 cm⁻¹ is shown as circles in Fig. 1.

ANALYSIS

The calculated spectrum in Fig. 1 is obtained from a least-squares fit of Eq. (2) to the observed spectrum, using expressions for $\chi''(\omega)$ and $G_{ij}(\omega)$ given in Eqs. (1) and (4). The parameters determined from the fit are listed in Table I. These parameters have been used to determine the shape of the uncoupled modes and are represented as Mode A and Mode B in the figure. Mode A is very heavily damped and resembles the tunneling mode in KDP.

Mode B is a TO phonon having *B*₂ symmetry. Because of the strong interaction between the tunneling and phonon modes there is a dip in the spectrum around 86 cm⁻¹. The interaction is similar to that in AlPO₄,¹⁰ where a Green's-function treatment by Zawadowski and Ruvalds¹¹ yielded very good agreement with the observed spectrum. Their expressions can be recovered from our Eq. (4) by making approximations $\Gamma_{ab}^2 = \Gamma_a \Gamma_b$, $\Delta = 0$, $\omega_a \approx \omega_b \approx \omega$, and $\omega_a, \omega_b \gg \Gamma_a, \Gamma_b$. The latter approximations are not valid

TABLE I. CsDA parameters at 295 °K (cm⁻¹).

Parameter	Model 1 (Barker-Hopfield)	Model 2 (Kobayashi)
<i>P</i> _{<i>a</i>}	4887	0
Γ _{<i>a</i>}	2375 ^a	29.0
ω _{<i>a</i>}	403 ^a	76.6
<i>P</i> _{<i>b</i>}	379	4902
Γ _{<i>b</i>}	15.1	2361
ω _{<i>b</i>}	96.3	407
Γ _{<i>ab</i>}	0	-182
Δ	167.3	126.0

^aOther choices of Γ_{*a*} and ω_{*a*} consistent with τ_{*a*} = Γ_{*a*}/ω_{*a*}² = 5×10⁻³ sec give nearly as good a fit.

TABLE II. KDA parameters (cm^{-1}). Note that there is some evidence for a maximum in the phonon width Γ_b near the temperature at which ω_a crosses ω_b ($\sim 217^\circ\text{K}$).

	295°K	245°K	189°K	137°K
P_a	2440	2393	2385	2060
Γ_a	372	372	292	247
ω_a	161	158	134	112
P_b	380	403	431	391
Γ_b	11.8	14.5	14.7	12.9
ω_b	140	145	147	148
Γ_{ab}	0	0	0	0
Δ	112	116	112	107
$\tau_a(10^{-13} \text{ sec})$	4.8	5.0	5.4	6.6

in CsH_2AsO_4 .

As discussed by Barker and Hopfield¹² there are an infinite number of solutions to the diagonalization in Eq. (4); we may always diagonalize the real part of the matrix ($\Delta=0$) or the imaginary part ($\Gamma_{ab}=0$). The choice is equivalent to a choice of phase for the interacting modes.

In Table I we summarize two physically plausible choices. One is analogous to that of Barker and Hopfield¹² and has $\Gamma_b \approx 0$, i.e., all the damping is due to one oscillator—in our case, the proton tunneling mode. Note that this model yields a phonon frequency ω_b very near the peak in our spectrum.

The second model we present is analogous to the Kobayashi theory for KDP-structure hydrogen-bonded ferroelectrics. In this model the pseudospin tunneling mode is viewed as having no direct contribution to the dielectric function, only indirect through phonon coupling. Hence $P_a=0$. While we obtain algebraic solutions to this model, they are physically different from Kobayashi's theory. The data can be fitted by two modes, one having zero polarizability and *underdamped* (this corresponds to the tunneling mode which is *overdamped* in the prevailing view of KDP structures), and the other having nonzero polarizability and *overdamped* (this corresponds to the phonon mode). We conclude that the coupled modes in CsH_2AsO_4 do not correspond closely to the Kobayashi theory, and that it will be necessary to associate greater polarization with the tunneling mode than with the phonon in order to obtain a physically realistic model.

We are thus led to a preference for Model 1 in Table I.

It is not possible on the basis of the 293°K data to obtain a definitive choice of basis states. However, work at other temperatures enables us to do so, for only one choice of phase yields simple temperature dependences for ω_a and ω_b . We would expect that $\omega_a = A(T - T_c)^{1/2}$ or $\omega_a = A[(T - T_c)/T]^{1/2}$, with other parameters (ω_b , Γ_a , etc.) slowly and monotonically varying with T . The analyses of data at lower temperatures and in KH_2AsO_4 will be given in a subsequent paper.¹³ KDA parameters are given in Table II, however, and confirm our choice of $\Gamma_{ab}=0$ phase.

We conclude this paper by pointing out that the simplest choice of basis states ($P_a=0$; $\Gamma_b=0$ —all the damping due to proton tunneling and all the polarization due to the phonon) does not describe the real situation in CsH_2AsO_4 .

CONCLUSION

We have found evidence in CsH_2AsO_4 for very strong anharmonic interactions. These involve the overdamped "soft" mode analogous to that observed⁴ in isomorphic KH_2PO_4 , and a B_2 -symmetry TO phonon. The observed data are accurately described by a Green's-function calculation. Although the mode couplings involve the "pseudospin proton-tunneling mode" described by Kobayashi and others, the analysis we give is fundamentally different from those previously presented for such proton-phonon systems. The spectral line shapes are very similar to those analyzed by Scott¹⁰ and by Zawadowski and Ruvalds¹¹ in AlPO_4 . The extension of this kind of anharmonic analysis to the proton-tunneling pseudospin systems provides a new way of measuring proton-phonon interactions in hydrogen-bonded ferroelectrics.

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Dielectric response in piezoelectric crystals

Abstract. Raman scattering measurements in KDA and CsDA are used to show that the soft mode in a piezoelectric ferroelectric may not be described as a classical damped oscillator. The discrepancy arises because of a contribution to the selfenergy of the mode at low frequencies which arises from the coupling of the mode with fluctuations in the phonon density.

The temperature dependence of the dielectric constant of a ferroelectric material is known to be associated with the temperature dependence of a long wavelength normal mode of vibration (Cochran 1960, and Anderson 1960). The relationship

$$\omega_0^2 \propto \frac{1}{\epsilon}$$

has been especially well verified for the near ferroelectrics SrTiO_3 and KTaO_3 by Fleury and Worlock (1968) using Raman scattering techniques. In other materials it has been found that the damping of the 'soft' mode is of importance, when the response of the soft mode to an applied frequency, ω , may be written as for a classical damped harmonic oscillator

$$G(\omega) = (\omega_0^2 - \omega^2 + i\omega\gamma)^{-1}. \quad (1)$$

This relationship has been shown to give a satisfactory description of the soft mode in many ferroelectrics, for example, BaTiO_3 (Yamada *et al.* 1969). This response function

may also be obtained from the theory of a weakly anharmonic crystal (Maradudin and Fein 1962) when

$$\omega_0^2 \propto (T - T_c)$$

and

$$\gamma \propto T.$$

We have measured the Raman spectra from single crystals of CsDA (CsH_2AsO_4) and KDA (KH_2AsO_4). The measurements were performed with an argon ion laser and a double grating spectrometer and the $B_2(X(YX)Y)$ spectra recorded at several temperatures above the ferroelectric transition temperatures T_T of 143 K and 92 K respectively.

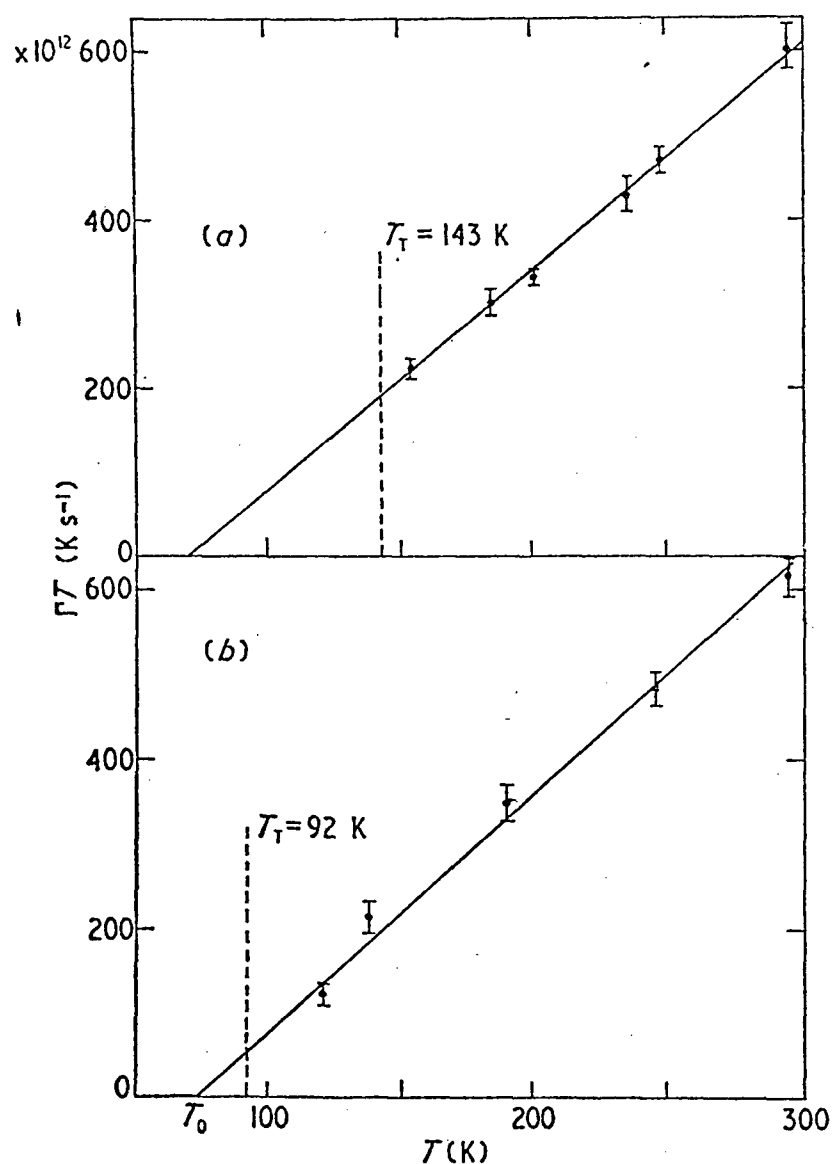


Figure 1. The temperature dependence of the width of the ferroelectric mode multiplied by temperature, ΓT . (a) CsDA ($T_0 = 69 \pm 7$ K), (b) KDA ($T_0 = 75 \pm 4$ K).

The results showed scattering characteristic of an overdamped mode which is associated with the ferroelectric properties and also scattering from other modes at higher frequencies. We have analysed these spectra to find the parameters of the overdamped mode ω_0 and γ as functions of temperature. Since in fact the lowest of the phonon modes gave a characteristic interference with the wing of the overdamped mode the analysis was performed with two interfering modes as will be reported in detail elsewhere (Katiyar *et al.* 1971). The results for the parameters of the overdamped mode, ω_0 and γ were highly correlated but, in common with other overdamped mode situations, the width $\Gamma = \omega_0^2/\gamma$ was little correlated

with the other parameters. Since we might expect $\Gamma \propto (T - T_c)/T$ we show in figure 1 ΓT plotted against T . The results give a reasonably straight line but the intercept with the temperature axis, T_0 , is not the transition temperature, T_T , but considerably below. For CsDa, $T_0 = (0.48 \pm 0.05)T_c$ and for KDA, $T_0 = (0.81 \pm 0.04)T_c$.

These results cannot arise because of the difference between the clamped and free Curie temperatures. In this class of materials this difference is only 1 or 2 K. Likewise the difference between T_0 and T_T is not because the transitions are first order instead of second order. In both materials the transitions are believed to be very close to second order as shown particularly well by Kaminow (1965) for KDA. He finds that the dielectric constant at 9 GHz follows a Curie law temperature dependence with $T_c = T_T \pm 2$ K. We are unfortunately unaware of dielectric measurements on CsDA but Blinc *et al.* (1970) quote $T_c = T_T$ for CsDA. Furthermore it is possibly of interest that they observe the temperature dependence of the inverse quadrupole coupling coefficient of ^{75}As and find that it obeys a temperature dependence given by $(T - T_0)/T$ with $T_0 = 0.43T_c$. The simple soft mode theory gives a temperature dependence of $(T - T_c)/T$.

We conclude from our results that the damped simple harmonic oscillator model is not an adequate description of the soft mode in these materials. We believe that the origin of the difficulty lies in an anomaly in the response of the soft mode at low frequencies as discussed qualitatively before (Cowley 1970).

In the anharmonic theory of lattice dynamics the damping of the modes arises in lowest order from the decay of the phonon into pairs of other modes. The selfenergy diagram is shown in figure 2(a). In ferroelectric materials we are interested in the behaviour of the

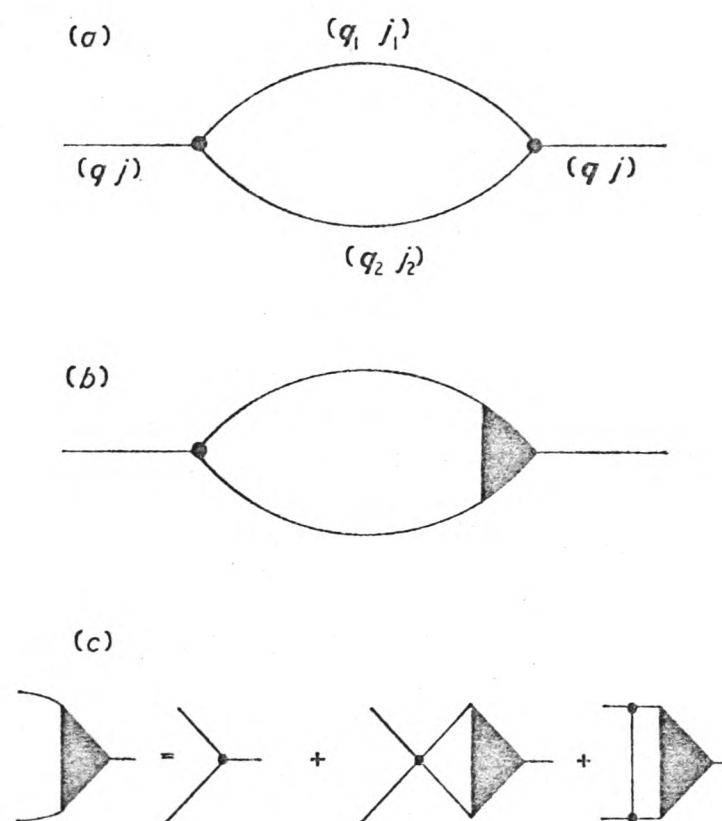


Figure 2. The selfenergy diagram applicable for the width of modes in low order perturbation theory (a). The selfenergy diagram modified to be correct as $q \rightarrow 0$ and $\omega \rightarrow 0$ (b). The equation for the renormalized vertex of (b) is shown in part (c).

selfenergy as $\omega \rightarrow 0$ and $q \rightarrow 0$. Most of the terms in the selfenergy are uniquely defined in this limit but the term in which the phonon (q, j) decays by absorbing a phonon (q_1, j_1) and emitting a phonon (q_2, j_2) is not well defined. In fact for this term the lowest order of

perturbation theory, figure 2(a) is inadequate and it is necessary to obtain the selfenergy from the selfenergy diagram, figure 2(b), containing the renormalized vertex given by the equation of figure 2(c). In the case of materials which are not piezoelectric the matrix elements for scattering

$$V \begin{pmatrix} 0 & q_1 & -p_1 \\ j & j_1 & j_1 \end{pmatrix}$$

are identically zero. In nonpiezoelectric materials the damped harmonic oscillator expression, equation (1), is therefore expected to be adequate as found experimentally.

For materials which are piezoelectric these matrix elements are finite and we expect there to be an anomaly in the selfenergy of the soft mode at low frequencies. We have calculated the form of the response given by the selfenergy of figures 2(b) and 2(c), by use of the techniques developed by Sham (1967) and by Klein and Wehner (1969) for the analogous problem in ultrasonics. The theory as applied to ferroelectrics differs from that for ultrasonics in that the effects may be larger and also that the fluctuations in the phonon distribution couple to neither the temperature nor the heat current fluctuations. The details of the calculations will be reported elsewhere but the final result for the response function of a ferroelectric mode is

$$G(\omega) = \left(\omega_0^2 - \omega^2 + i\omega\gamma - \frac{\alpha T}{1 + i\omega\tau} \right)^{-1}$$

where α is a positive constant and τ is the lifetime of the modulations introduced into the phonon distribution by the fluctuations in the ferroelectric mode. At high frequencies, $\omega\tau \gg 1$, the response function is identical with that of a damped harmonic oscillator with

$$\omega_0^2 = K(T - T_0).$$

At low frequencies the response is however determined by $\omega_0^2 - \alpha T$ which is proportional to $T - T_C$ with

$$T_0 = \frac{(K - \alpha)T_C}{K}$$

The difference between the high frequency response, $\omega\tau \gg 1$, and the low frequency response $\omega\tau \ll 1$, arises because at low frequencies the fluctuations in the phonon distribution function caused by the ferroelectric mode have time to decay within each period of the wave, whereas at high frequencies there is not sufficient time for this to occur.

The ratio of T_0/T_C determines the ratio of the anomalous contribution to the selfenergy to that of the regular term, α/K . This ratio is about 0.8 in KDA and 0.5 in CsDA, both results being very similar in magnitude to those found in calculations of the ultrasonic properties of KBr (Cowley 1967). The lifetimes of the fluctuations, τ , may be estimated by a comparison of the frequencies in Kaminow's experiment (1965) and those involved in ours. This suggests that $\tau \simeq 10^{-10} - 10^{-11}$ s which agrees quite reasonably with typical phonon lifetimes.

The theory should also be applicable to the two similar materials KDP (KH_2PO_4) and DKDP (KD_2PO_4). In KDP the Raman spectra shows an overdamped mode whose width decreases as T_C is approached. Kaminow and Damen (1968) give $T_0 = 0.98T_C$ showing that α must be small in KDP. In DKDP the situation is still unclear. Hill and Ichiki (1963) have measured the dielectric properties while White *et al.* (1970) have observed the Raman spectra. Both sets of authors agree that the results cannot be fitted by a simple damped oscillator model but further work is needed to test our model. The lifetime, τ , for DKDP must certainly be considerably longer than that for KDA.

In conclusion we have shown that the damped single harmonic oscillator does not give an adequate description of the soft mode in piezoelectric ferroelectrics. The selfenergy has

an additional contribution at low frequencies which arises from fluctuations in the phonon distribution caused by the ferroelectric mode. Although the anharmonic oscillator model is almost certainly not an adequate model for these hydrogen bonded materials, the effects discussed here depend primarily on symmetry so that the same concepts should be equally applicable in an analysis of the response of other models.

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Mobility of an impurity in a Fermi liquid: analogy with a phase transition

Abstract. The equations of Josephson and Lekner describing the mobility of an impurity in a Fermi liquid admit three solutions for the mobility over a certain temperature range.

A model for the mobility of ionic impurities in a Fermi liquid has been proposed by Josephson and Lekner (1969). They calculate the force on an ion when it moves with a constant drift velocity through a gas of quasiparticles. The recoil of the ion, due to the scattering of the quasiparticles, is given by the scattering function $S(q, \omega)$, which Josephson and Lekner calculate in a Gaussian approximation.

The mobility, according to Josephson and Lekner, is given by the following set of equations. (We use units of unit volume and $\hbar = 1$.)

$$\mu(0)^{-1} = \frac{1}{12} \int_0^{2k_F} dq q^3 \sigma(q) \int_{-\infty}^{\infty} dt \exp \left\{ -\frac{q^2 \gamma(t)}{2} \right\} / \beta \cosh^2 \left(\frac{\pi t}{2\beta} \right) \quad (1)$$