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Long-Wavelength Polarization Fluctuations in Antiferroelectric $NH_4H_2PO_4$

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The low-frequency Raman spectra of crystalline $NH_4H_2PO_4$ are reported for temperatures above the Curie point. Both B_2 and E species are fitted to the model of two coupled harmonic oscillators, which accounts for the strong proton-phonon coupling existing in this type of crystal. The temperature dependence of the equivalent relaxation time is determined for both modes and the results are compared with those of Ryan *et al.*, who have neglected the proton-phonon coupling for the E mode. In addition, the square of the uncoupled overdamped frequency $\omega^2(B_2)$ and the inverse static susceptibility $1/\chi(B_2)$ of the B_2 mode are found to depend on temperature linearly. The temperature dependence of $1/\chi(B_2)$, which compared well with the microwave data of Kaminow, is shown to relate directly to the corresponding long-wavelength polarization fluctuations discussed in this paper.

I. INTRODUCTION

In the past few years, several experimental groups[1-4] have been interested in laser Raman spectroscopy of phonons in ferroelectric KH_2PO_4 (KDP). Except for many interesting line-shape anomalies which deserve further studies,[5,6] there is a qualitative understanding concerning the identification of Raman spectra in KDP. Since the motivation for these intensive interests is related to the ferroelectric phase transition, the low-frequency B_2 spectrum of the ferroelectric mode has been thoroughly studied.[7,8] Recently, the strong proton-phonon coupling in this type of crystal has been accounted for properly[9] and the correct soft-mode parameters have been determined for KDP.[10]

The isomorphic antiferroelectric $NH_4H_2PO_4$ (ADP) has, however, received very little attention. Besides an early report by Chapelle,[11] laser Raman spectra of ADP and mode identifications were discussed only in unpublished works of Wilson[4] and Broberg.[12] Nor has the temperature dependence of the low-frequency Raman spectra associated with polarization fluctuations been much studied. The only investigation so far in this connection is the work of Ryan *et al.*[13] They have reported the temperature dependence of the "Debye" relaxation times for both E and B_2 overdamped modes and have taken into account the proton-phonon coupling for the B_2 mode but not for the E mode. Nor have they determined the temperature dependence of the uncoupled frequency of the overdamped mode and the static susceptibility from Raman spectra. Thus, we report in this paper the temperature dependence of these physical quantities in addition to the equivalent (or Debye) relaxation time of polarization fluctuations in ADP. Unlike Ryan *et al.*, we have considered the mode-interference effect for the E mode as well. As more experimental data points were used, the determination of the relaxation time for the B_2 mode has been further improved.

II. LONG-WAVELENGTH POLARIZATION FLUCTUATIONS

In the high-temperature phase, ADP is isomorphic to KDP and belongs to the space group D_{2d}^{12}. There are four tunneling protons in a primitive cell in this structure and their motions may be decomposed into normal modes of A_2, B_2, and E species.[14] Assuming the simplest linear coupling with a quadratic interaction Hamiltonian,[15] the B_2 and E proton modes which are Raman active are expected to couple with the optical phonons of the same species in both KDP and ADP. The effect of this strong proton-phonon coupling in KDP has been studied by She *et al.*[10] for the B_2 mode and by Scott and Wilson[5] for the E mode. In the case of ferroelectric KDP, the B_2 overdamped mode becomes soft as the transition temperature is approached. Studies of its behavior can yield direct information concerning the phase transition. The long-wavelength fluctuations (either the B_2 or the E mode) in antiferroelectric ADP, however, will not become "soft" as the transition is approached from temperatures above the Curie point. The temperature-dependent low-frequency spectra will nonetheless give rise to the dominant contribution to the dielectric constant of the crystal.

Shown in Fig. 1(a) are the low-frequency $y(xy)x$ and $y(xz)x$ spectra near room temperature, which transform as the electric polarizations P_z and P_x (and/or P_y) of KDP and ADP below 300 cm^{-1}. A

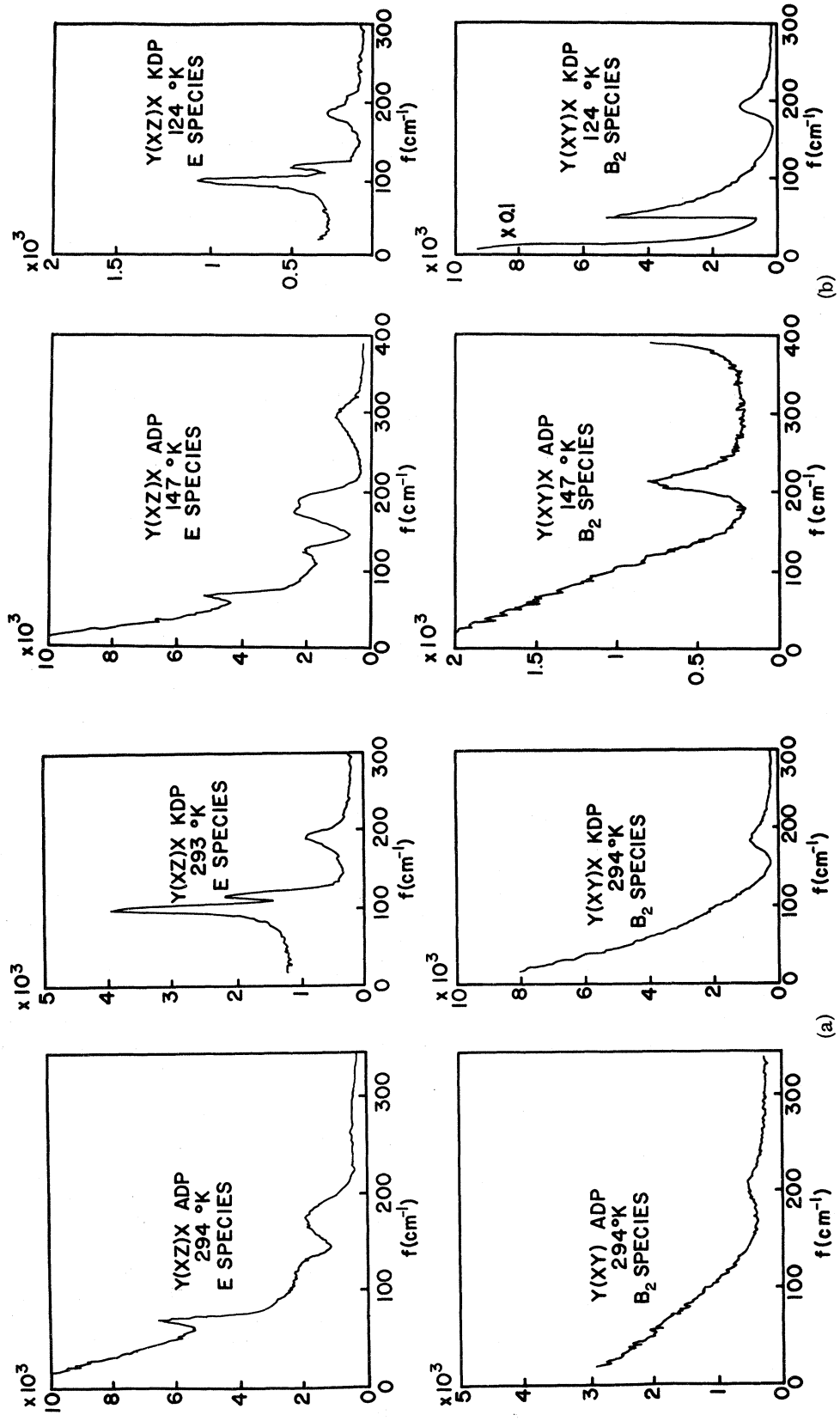

FIG. 1. Low-frequency $y(xy)x$ and $y(xz)x$ spectra of KH_2PO_4 and $NH_4H_2PO_4$, (a) near room temperature and (b) near the transition temperature. Vertical scales are photon counts which represent the relative cross section of these spectra.

distinct difference between the low-frequency wings of B_2 and E species is seen in KDP while this anisotropy in polarization fluctuations is less pronounced in ADP. The ratio of the scattered intensities of these low-frequency wings, as seen in Fig. 1(a), is roughly $I(B_2)/I(E) = 7.5$ for KDP and $I(E)/I(B_2) = 3.5$ for ADP. Examining the corresponding low-frequency spectra as shown in Fig. 1(b) one finds that these same ratios increase to approximately 110 and 5.0 near their respective phase transitions. This reflects the fact that the long-wavelength (near the center of the Brillouin zone) B_2 proton-tunneling mode in KDP becomes soft as the transition temperature is approached. The B_2 mode accordingly scatters 110 times more light than the E mode in KDP. In the antiferroelectric ADP for temperatures above the transition, only the mode at the corner of the Brillouin zone which cannot be observed by the first-order Raman scattering, will become soft. Thus, one does not expect much anisotropy between the long-wavelength B_2 and E wings in ADP. Similar wave-vector dependence of the static susceptibilities is quite common in the magnetic phase transitions, [16] where Raman scattering can be used to probe the antiferromagnetic[17] soft mode only from below the transition temperature because the crystal primitive cell doubles in the low-temperature phase. The doubling of the primitive cell in the low-temperature phase is also well known in $SrTiO_3$ below 110 °K. [18] Unfortunately, ADP crystals shatter at the transition making Raman study of ADP in the antiferroelectric phase so far impossible. The anisotropy between the B_2 and E overdamped modes and the knowledge of the temperature-dependent parameters of the long-wavelength low-frequency spectra for temperatures above the Curie point are the only information obtainable by light scattering, but they reveal very little about the nature of the antiferroelectric phase transition in ADP.

The broad line near 290 cm^{-1} in the $y(xz)x$ spectrum of Fig. 1(a) is a feature existing only in ADP and we attribute it to the E librational (torsional) mode of the $(NH_4)^+$ ion. This selection was made because the 290-cm^{-1} line appeared in the $y(xz)x$ spectrum belonging to the E species in agreement with the decomposition of the rotational F_2 modes of the $(NH_4)^+$ ions into $B_2 + E$ species in ADP, and its location (290 cm^{-1}) falls in the range of librational frequencies of the other ammonium salts. [19] As the temperature is lowered, this feature becomes much more evident as can be seen in Fig. 1(b).

III. EXPERIMENTAL

Our right-angle Raman data for both B_2 and E modes were obtained from an oriented single crystal, a 1-m double spectrometer, a cooled S-20 phototube, and an argon-ion laser (500 mW) at 4880 Å. A multichannel analyzer was used to permit total digital data processing. [20] The crystal was cooled by a cold tip. Different parts of the crystal were monitored and the temperature in the scattering volume was then determined to within ±1 °K. The resolution of our Raman spectra is 4 cm^{-1}. Unlike the corresponding spectra of Ryan *et al.* (Fig. 3 of Ref. 13), a slight dip near 110 cm^{-1} was developed in our $y(xz)x$ E-mode spectra as the crystal is cooled. This indicates that their temperature reading was perhaps lower than the true temperature in the scattering volume of the crystal.

IV. ANALYSIS OF SPECTRA

Our Raman spectrum $S(\omega)$ is related to the imaginary part of the susceptibility $\chi''(\omega)$ by the fluctuation-dissipation theorem

$$S(\omega) = R[n(\omega)+1]\chi''(\omega) , \tag{1}$$

where $n(\omega) = (e^{\hbar\omega/kT} - 1)^{-1}$ and R is a normalization constant. For the model of two coupled harmonic oscillators, $\chi''(\omega)$ is expressed in terms of the Green's functions $G_{ij}(\omega)$ and the mode strengths P_i, P_j as

$$\chi''(\omega) = \mathrm{Im} \sum_{i,j=a,b} P_i P_j G_{ij}(\omega) . \tag{2}$$

Following Katiyar *et al.*, [9] the Green's functions may be expressed as[10]

$$G_{aa} = (\omega_b^2 - \omega^2 + i\omega\Gamma_b)/D , \tag{3a}$$

$$G_{ab} = -\Delta^2/D , \tag{3b}$$

$$G_{bb} = (\omega_a^2 - \omega^2 + i\omega\omega_a^2\tau)/D , \tag{3c}$$

where $D = (\omega_a^2 - \omega^2 + i\omega\omega_a^2\tau)\,(\omega_b^2 - \omega^2 + i\omega\Gamma_b) - \Delta^4$; ω_a and Γ_a are, respectively, the uncoupled frequency and linewidth of the over-damped mode; and $\tau = \Gamma_a/\omega_a^2$ is the equivalent (or Debye) relaxation time of the over-damped mode. ω_b and Γ_b are the uncoupled frequency and linewidth of the optical-phonon mode. Δ is the mode-coupling strength. Raman spectra may therefore be analyzed in terms of a system of two coupled oscillators with seven parameters ω_a, ω_b, τ, Γ_b, Δ, P_b/P_a, and R. The choice of τ over Γ_a as an independent fitting parameter, following the practice of previous workers, [9,13] is not fundamental.

It should be pointed out that for strongly interacting oscillators of interest here, the Δ^4 term in Eqs. (3) should not be neglected. Although good fit to the data is possible whether or not these terms are neglected, the value of the coupling parameter Δ obtained in the cases of ADP and KDP does not justify dropping the Δ^4 term, which is comparable or larger than $\omega_a^2\omega_b^2$. Therefore, if Δ^4 is dropped, the resulting model function no longer

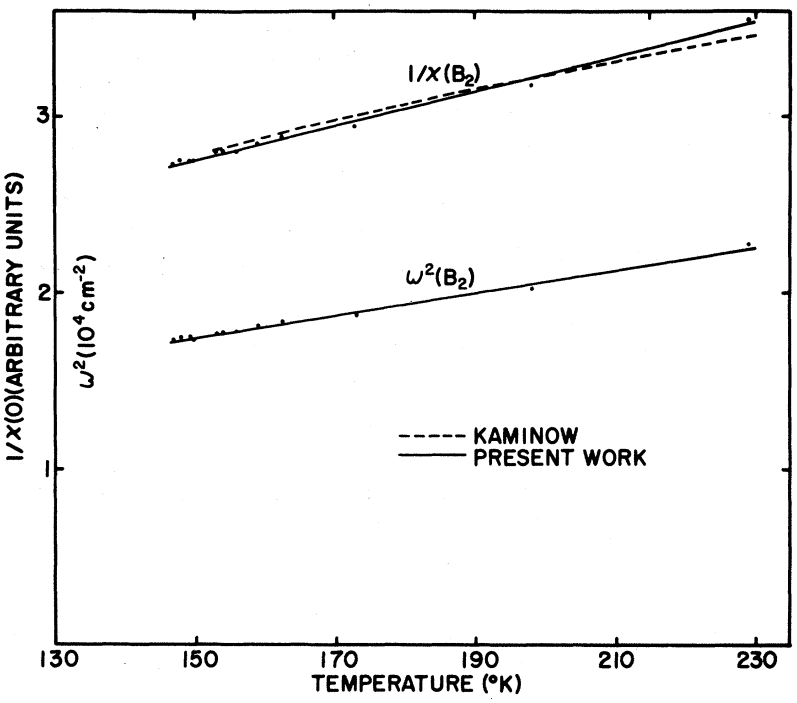

FIG. 2. Temperature dependence of the uncoupled overdamped frequency square $\omega^2(B_2)$ and the inverse susceptibility $1/\chi(B_2)$ of the B_2 mode in $NH_4H_2PO_4$ above the Curie point.

corresponds to the coupled-harmonic-oscillator problem.

Numerically, the effect of the Δ^4 term can be seen in Table I, in which the least-square-fitted parameters obtained by either neglecting the Δ^4 terms or including them in Eqs. (3) are compared. The spectrum analyzed was the B_2 spectrum of ADP at 147 °K. Depending on whether the Δ^4 terms were included in the fitting program, different sets of parameters were obtained. The quality of fit is about the same in two cases, but only the parameters fit to the exact expression (i.e., keeping the Δ^4 terms) are meaningful on physical grounds. It is interesting to note that in Table I the parameters ω_a and $\tau = \Gamma_a/\omega_a^2$ are not too different in the two cases. However, the obtained values for the coupling strength Δ, whose temperature dependence is essential in determining the correct model to describe the long-range ordering of the system, [10] and the obtained values P_b/P_a are very much different. Katiyar *et al.* [9] have noted that in their case, the fitted parameters ω_a^2 and Γ_a are correlated while τ is quite accurate.

V. ADP RESULTS AND DISCUSSIONS

The observed $y(xy)x$ spectra of ADP from 5 to 270 cm^{-1} for temperatures above the Curie point were analyzed in terms of the model discussed above. Both the square of the frequency $\omega^2(B_2)$, and the static inverse susceptibility $1/\chi(B_2)$, where $\chi(B_2) = \sum_{i,j} P_i P_j G_{ij}(0)$ of the B_2 spectrum are found to depend linearly on temperature as shown in Fig. 2. These data, so far as we know, have not been previously investigated. The inverse static susceptibility, with its value at 193 °K properly adjusted, compares reasonably well with the temperature-dependent microwave data of Kaminow. [14] The temperature-weighted inverse equivalent relaxation time T/τ also varies linearly in temperature as shown in Fig. 3, in qualitative agreement with Ryan *et al.* [13] Our accuracy in temperature measurement and our analysis of many more data points could account for the difference in detailed results.

The $y(xz)x$ spectrum (E mode) is much more complex as can be seen in Fig. 1. The apparent coupling of the protonic overdamped E mode with several optical-phonon modes would make our model of two coupled oscillators, strictly speaking,

TABLE I. Comparison of least-squares-fit parameters obtained by including Δ^4 (in top row) and neglecting it (in bottom row) in the coupled-mode problem. The sample is ADP at about 147 °K. Parameter values for ω_a, $1/\tau$ ω_b, Γ_b, and Δ can be converted to cm^{-1} by multiplying by $\frac{5}{3}$.

R	P_b/P_a	ω_a	τ	ω_b	Γ_b	Δ
-6.06×10^6	0.248	78.7	0.0215	117.8	9.89	66.9
-1.37×10^6	0.0206	68.3	0.0298	117.6	17.3	270

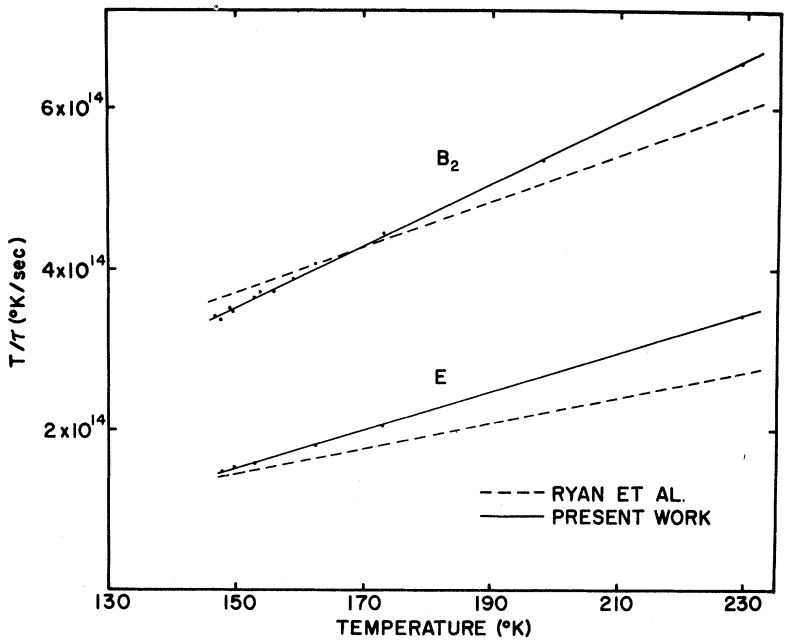

FIG. 3. Temperature dependence of the weighted equivalent inverse relaxation time T/τ of $NH_4H_2PO_4$ for both B_2 and E overdamped modes above the Curie point.

invalid for analyzing these spectra. The exact analysis in terms of four coupled oscillators would be too complicated, if not impossible. Therefore, Ryan *et al.* have neglected the proton-phonon coupling completely. While the protonic motion couples with all three optical phonons, its coupling with the lowest phonon near 70 cm^{-1} would be strongest. Hence, we analyze the E spectrum from 5 to 85 cm^{-1} in terms of the two coupled oscillators described above. The equivalent relaxation time $\tau = \Gamma_a/\omega_a^2$ for the E mode obtained in this way should be quite accurate. The result of the temperature-weighted inverse equivalent relaxation time T/τ is also shown in Fig. 3. When the overdamped mode is coupled to other modes, the relaxation time τ is expected to become shorter in agreement with the discrepancy between the solid (with coupling) and dashed (without coupling) curves for the E mode in Fig. 3. The mild anisotropy of T/τ between B_2 and E modes are evident as can be seen in Fig. 3.

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