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PHYSICAL REVIEW B VOLUME 6, NUMBER 5 1 SEPTEMBER 1972

Effect of Proton-Phonon Coupling on the Ferroelectric Mode in KH_2PO_4

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(Received 22 February 1972)

The low-frequency Raman spectra of crystal KH_2PO_4 are reexamined experimentally. For temperatures above the Curie point, the B_2 spectra below 270 cm^{-1} are fitted to the model of two coupled harmonic oscillators. When the proton-phonon-coupling effect is accounted for in this manner, the square of the uncoupled-ferroelectric-mode frequency ω_a^2 and the temperature-weighted inverse equivalent relaxation time T/τ are found to depend on the temperature linearly, contrary to previous interpretation. The extrapolated transition temperature of the uncoupled soft mode (30 °K) is much lower than 116 °K as determined from the $1/\chi(0)$ plot. This discrepancy is attributable to the level repulsion of the proton-phonon coupling which forces the coupled mode to become soft at a higher temperature (116 °K). The evidence presented suggests that the validity of the collective pseudospin model of KH_2PO_4 is questionable.

Kobayashi[1] pointed out the importance of the proton-phonon coupling in relation to the ferroelectric transition in KH_2PO_4-type crystals. The ferroelectric mode in KH_2PO_4 (KDP) was observed in the same year with Raman scattering by Kaminow and Damen.[2] The low-frequency Raman spectrum was fitted to an over-damped simple harmonic oscillator, with a temperature-independent linewidth $\Gamma \simeq 85$ cm^{-1}, and a temperature-dependent soft-mode frequency given by $\omega_0^2 = (99)^2(T-117)/T$ cm^{-2}. Wilson and Cummins[3] recently studied this problem in more detail, and reported their best fit to the data as $\Gamma = 73$ cm^{-1} and $\omega_0^2 = 118.2(T-115.6)^{0.78}$ cm^{-2} for temperatures above the Curie point. These authors have neglected the strong coupling with the optical phonon near 180 cm^{-1} in their analysis of data.

The model of the coupled harmonic oscillators, in one form or another, has been successfully applied many times to explain anomalies in phonon spectra. Noticeably, an interference effect in the infrared absorption of several perovsites was reported by Barker and Hopfield.[4] A similar effect was first reported in Raman spectra by Rousseau and Porto.[5] The Green's-function formalism of the coupled harmonic oscillators was first utilized by Scott[6] and Zawadowski and Ruvalds[7] to explain anomalous interference effects in $AlPO_4$. Katiyar *et al.*[8] have recently applied this analysis to treat the proton-phonon coupling in CsH_2AsO_4 (CsDA) and KH_2AsO_4 (KDA). They reported observation of antiresonance interference in the B_2 spectrum, with the soft-mode linewidth increasing with temperature.

This same anharmonic proton-phonon interaction would undoubtedly alter the interpretation of the low-frequency Raman spectra of KDP as pointed out by Scott and Wilson.[9] Only when the proton-phonon coupling is properly accounted for, can we extract the correct temperature dependence of the uncoupled-soft-mode parameters and disclose the true nature of the long-range order of the proton-tunneling motion. For this reason, we have reexamined experimentally the low-frequency Raman spectra of KDP. For temperatures above the Curie point, we find that the $y(xy)x$ spectra (B_2 mode) below 270 cm^{-1} can be well fitted to the model of two coupled harmonic oscillators. The resultant temperature-dependent parameters of the uncoupled ferroelectric mode ω_a^2 and $1/\tau$ and inverse susceptibility $1/\chi(0)$ have been determined; they will be reported here.

It is well known[2,3] that the imaginary part of the susceptibility $\chi''(\omega)$ can be related to the scattered-Stokes-power spectral density $S(\omega)$ by means of the fluctuation-dissipation theorem

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

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

$$\chi''(\omega) = \mathrm{Im}[P_a^2 G_{aa}(\omega) + 2P_a P_b G_{ab}(\omega) + P_b^2 G_{bb}(\omega)] \ , \tag{2}$$

where the Green's functions satisfy the following coupled-mode equation[8]:

$$\begin{bmatrix} \omega_a^2 - \omega^2 + i\omega\Gamma_a & \Delta^2 + i\omega\Gamma_{ab} \\ \Delta^2 + i\omega\Gamma_{ab} & \omega_b^2 - \omega^2 + i\omega\Gamma_b \end{bmatrix} \begin{bmatrix} G_{aa} & G_{ab} \\ G_{ab} & G_{bb} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} . \tag{3}$$

In this model, we assume $\Delta, \Gamma_a, \Gamma_b$, and Γ_{ab} to be frequency independent. Since $\chi''(\omega)$ is invariant with respect to a choice of phase for the interacting modes,[4] we may set the imaginary part of the coupling constant Γ_{ab} zero. This, however, assumes a rather specific form of nondissipative interaction for the coupled modes as described by the coupled-mode equations. With this form of interaction (real coupling constant only), Eq. (3) may be solved to give the following Green's functions:

$$G_{aa} = (\omega_b^2 - \omega^2 + i\omega\Gamma_b)/D \ , \tag{4a}$$

$$G_{ab} = -\Delta^2/D \ , \tag{4b}$$

$$G_{bb} = (\omega_a^2 - \omega^2 + i\omega\omega_a^2\tau)/D \ , \tag{4c}$$

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 relaxation time of the over-damped mode. Raman spectra may therefore be analyzed in terms of a system of two coupled oscillators with seven parameters $\omega_a, \omega_b, \tau, \Gamma_b, \Delta, P_b/P_a$, and R. The choice of τ over Γ_a as an independent fitting parameter following the practice of previous workers,[8,10] is not fundamental.

It should be pointed out that for strongly interacting oscillators of interest here, the Δ^4 terms in Eqs. (4) should not be neglected. Although a good fit to the data is possible whether or not these terms are neglected, the fitting parameters obtained for the two cases would be quite different, and the obtained value for the coupling constant $\Delta(\sim 114\ \mathrm{cm}^{-1})$ is too large to justify dropping the Δ^4 terms.[11] Thus, we have included all the Δ^4 terms in our analysis of experimental data.

Our right-angle Raman-scattering data were obtained from an oriented single crystal, a 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. Temperature in the scattering volume of the crystal is measured to within $\pm 1\ ^\circ\mathrm{K}$.

The observed $y(xy)x$ spectra from 5 to 270 cm^{-1} for temperatures above the Curie point were analyzed in terms of the model discussed above. The results of the analysis are presented in Figs. 1 and 2. Both the square of the "uncoupled" soft mode ω_a^2 and the temperature-weighted inverse equivalent relaxation time T/τ as shown in Fig. 1, and the inverse susceptibility $1/\chi(0)$ as shown in Fig. 2, can be fitted to straight lines with good accuracy. The function $1/\chi(0)$ is plotted in arbitrary units, similar to the original work of Kaminow and Damen.[2] These functions may be expressed analytically as

$$\frac{1}{\chi(0)} \propto (T - 116) \ , \tag{5a}$$

$$\omega_a^2 = 67.7(T - 30)\ \mathrm{cm}^{-2} \ , \tag{5b}$$

$$\frac{1}{\tau} = 2.69 \times 10^{12} \frac{T - 71}{T}\ \mathrm{sec}^{-1} \ . \tag{5c}$$

The inverse susceptibility $1/\chi(0)$, where $\chi(0) = P_a^2 G_{aa}(0) + 2P_a P_b G_{ab}(0) + P_b^2 G_{bb}(0)$, including the contributions of the coupled modes, agrees approximately with the previously reported results.[2,3] On the other hand, the uncoupled-soft-mode parameters ω_a^2 (to be compared with ω_0^2) and $\Gamma_a = \omega_a^2\tau$ (to be compared with 2Γ), show quite different temperature dependence. The square of the uncoupled-soft-mode frequency ω_a^2 depends linearly on temperature, contrary to the prediction of the collective pseudospin model[12] of KDP which gives a $(T - T_c)/T$ dependence. The uncoupled-soft-mode linewidth Γ_a now depends on temperature. Approximately it increases linearly with temperature as one might expect.

The fact that ω_a^2 and $1/\chi(0)$ extrapolate to different transition temperatures is quite disturbing at first sight and implies a violation of the Lyddane-Sachs-Teller relationship.[13] That this discrepancy is actually a natural consequence of the proton-phonon coupling discussed above can be inferred when the square of the lower coupled-mode frequency[9] (with damping neglected)

$$\omega_c^2 = \tfrac{1}{2}(\omega_a^2 + \omega_b^2) - \{[\tfrac{1}{2}(\omega_a^2 - \omega_b^2)]^2 + \Delta^4\}^{1/2} \tag{6}$$

is plotted as a function of temperature in Fig. 2. The fact that ω_c^2 and $1/\chi(0)$ extrapolate to the same phase transition temperature (116 °K) means that the coupled mode (a true normal mode of the system), forced by the level-repulsion of the strong proton-phonon coupling, becomes soft long before the extrapolated transition temperature of the uncoupled soft mode is reached. The difference between 116 °K and the true phase transition at 122

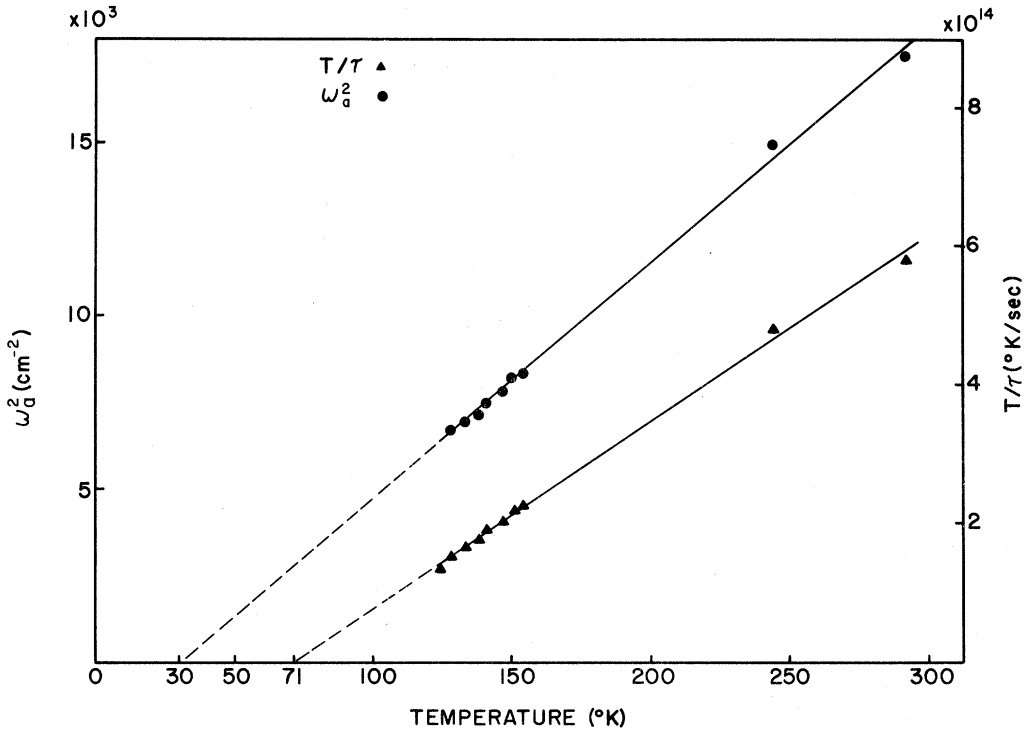

FIG. 1. Temperature dependence of the square of the uncoupled-soft-mode frequency ω_a^2 and the temperature-weighted inverse equivalent relaxation time T/τ above the Curie point in KH_2PO_4.

°K has been explained by Brody and Cummins[14] in terms of the coupled ferroelectric and acoustic modes.

Our $y(xy)x$ Raman data for temperatures below the Curie point are not analyzed. Scott and Wilson[9] have shown that the simpler Breit-Wigner single-level expression is sufficient to account for some aspects of the proton-phonon coupling in this

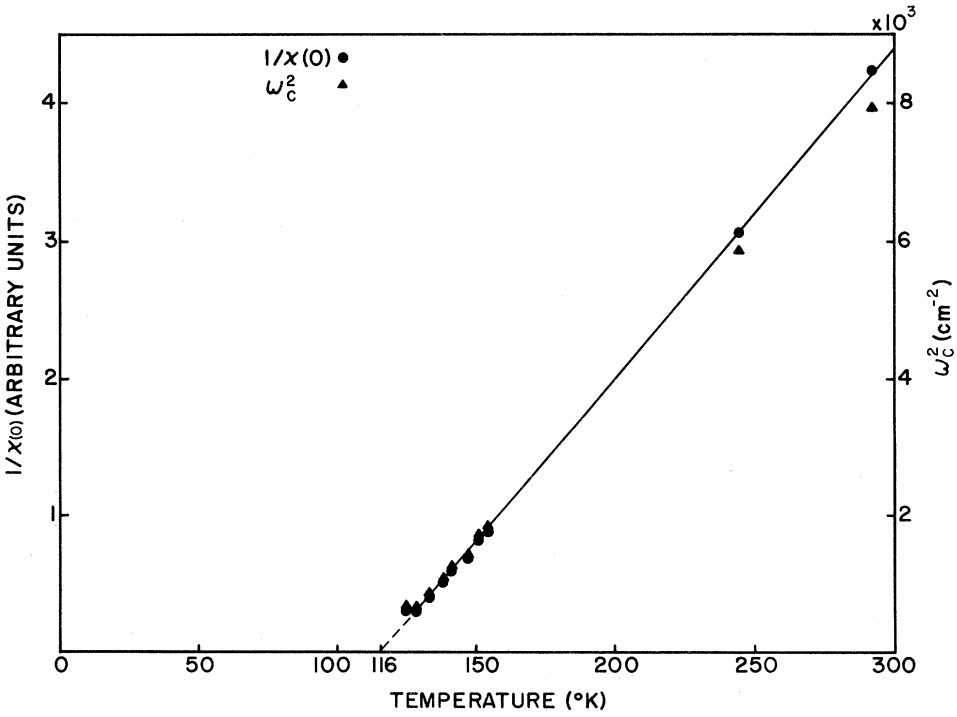

FIG. 2. Temperature dependence of the inverse static susceptibility $1/\chi(0)$ and the coupled-mode frequency ω_c^2 above the Curie point in KH_2PO_4.

region. They also suggested the linear temperature dependence of ω_a^2 and T/τ for temperatures above the Curie point in KDP. Our data presented here have confirmed their prediction.

In summary, we have presented the temperature dependence of $1/\chi(0)$, ω_a^2, and $1/\tau$ for temperatures above the Curie point. These were deduced from a detailed analysis and interpretation of Raman scattering data of the B_2 mode of crystal KDP in terms of a model of two coupled oscillators. The data were analyzed exactly (i.e., including all the Δ^4 terms) in accordance with our present understanding of the problem. The square of the uncoupled-soft-mode frequency ω_a^2 was found to depend on the temperature linearly. The temperature-weighted inverse equivalent relaxation time of the uncoupled soft mode for KDP, T/τ, also have a simple linear temperature dependence. The corresponding linewidth Γ_a increases approximately linearly with temperature contrary to previous findings.[2,3] The extrapolated transition temperature (30 °K) of the uncoupled soft mode is much lower than that extrapolated from inverse susceptibility $1/\chi(0)$ at 116 °K. In general, there is agreement with the results in CsDA and KDA.[8,13]

The proton-phonon coupling Δ was found to be temperature independent and equals 114 ± 2 cm^{-1}. This fact and the linear dependence of ω_a^2 in temperature make the validity of using the collective pseudospin model to describe the long-range order of the tunneling protons[15] questionable. A lattice dynamical treatment of the proton system may be more appropriate. The discrepancy between the extrapolated transition temperatures (30 and 116 °K) which is larger than the prediction of Kobayashi[1] but in line with the estimation of Cochran,[16] also reflects the importance of the proton-phonon interaction. By comparing the temperature dependences of the inverse susceptibility $1/\chi(0)$ and the coupled-mode-frequency square ω_c^2, we have demonstrated for the first time that this discrepancy in extrapolated transition temperatures is a natural consequence of the strong (linear) proton-phonon coupling whose level-repulsion forces the coupled mode to become soft at a much higher temperature (116 °K), long before the transition temperature of the uncoupled soft mode is reached.

The authors wish to thank J. M. Worlock and J. C. Raich for helpful discussions and H. Z. Cummins and J. F. Scott for critical comments on the manuscript. A specialized equipment grant by NSF is also acknowledged.

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