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Proton-Phonon Coupling in CsH_2 AsO_4 and KH_2 AsO_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 $T_c = 143$ °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 Kobayashi[2] using a pseudospin formalism to represent the two proton tunneling positions.[3] On the basis of the Raman study of Kaminow and Damen[4] on the paraelectric phase of KDP and of Levstek and Lavrencic[5] 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 Cochran[6] 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 KDP[4] (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 ($T_c = 143$ °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

$$\chi''(\omega) = \operatorname{Im} \sum_{ij} P_i P_j G_{ij}(\omega) \; . \tag{1}$$

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,

$$S(\omega) = R\chi''(\omega)[\bar{n}(\omega) + 1] \; , \tag{2}$$

where

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

and R is a constant.

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

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

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 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-

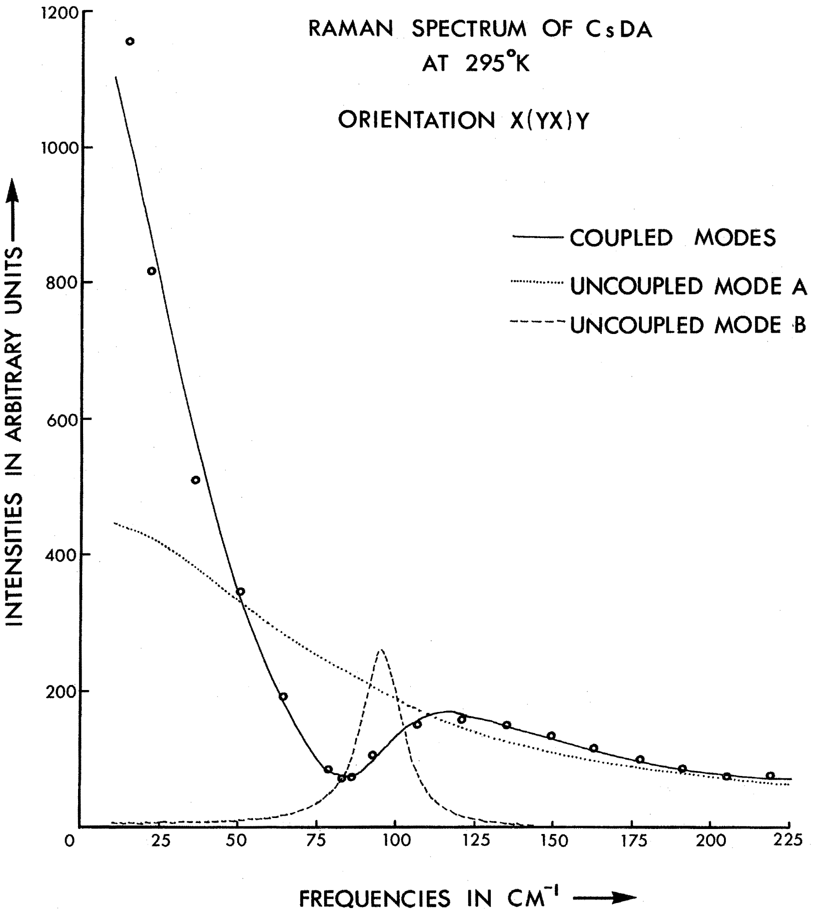

FIG. 1. Raman spectrum of CsH_2AsO_4 at 153 °K with $x(yx)y$ orientation. Spectral slit width is 10 cm^{-1}. Other experimental details as described in the text. The calculated spectrum corresponds to the parameters listed under Model 1 in Table I.

ically by Maradudin and Fein[8] 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 $AlPO_4$,[10] where a Green's-function treatment by Zawadowski and Ruvalds[11] 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 ω_a, $\omega_b\gg\Gamma_a$, Γ_b. The latter approximations are not valid

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

Parameter	Model 1 (Barker-Hopfield)	Model 2 (Kobayashi)
P_a	4887	0
Γ_a	2375[a]	29.0
ω_a	403[a]	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

[a] Other choices of Γ_a and ω_a consistent with $\tau_a=\Gamma_a/\omega_a^2=5\times10^{-3}$ 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 (~ 217 °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
$\tau_a(10^{-13}$ sec)	4.8	5.0	5.4	6.6

in CsH_2AsO_4.

As discussed by Barker and Hopfield[12] 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 Hopfield[12] 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 *under*damped (this corresponds to the tunneling mode which is *over*damped 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 observed[4] 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 Scott[10] and by Zawadowski and Ruvalds[11] 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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Quantum Crystal Effects in Solid Hydrogen at Zero Temperature

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Using our theory of correlation effects in quantum crystals, which was originally developed to calculate the properties of solid helium, we obtain the ground-state energy and pressure of solid hydrogen for molar volumes in the range 24–10 cm^3. The results are applied to a determination of the effect of zero-point motion on the intermolecular interaction and on the λ-transition temperature. The crystal field is also discussed.

I. INTRODUCTION

Correlation effects in crystals of small atomic or molecular mass have been extensively studied[1–8] in recent years. The large zero-point motions of the atoms in a "quantum crystal," such as helium, lead to instability of the calculated phonon spectrum[2] if not treated properly. This difficulty was overcome by Nosanow, who took the short-range correlations into account,[3] and a self-consistent scheme for computing the phonon spectrum has been given.[4] It appears that a good understanding of quantum crystals has been achieved.

Despite the fact that solid hydrogen H_2 has a smaller molecular mass than solid He, short-range correlations are not expected to be more important in the former material; the reason is the deeper attractive well in the intermolecular potential which causes a H_2 molecule to be more effectively localized than a He atom.[9] Thus, one does not expect any particularly novel behavior of solid hydrogen. The present study is motivated in part by the interest in solid H_2 at extremely high pressures, $\sim 10^6$ atm, where it is thought that molecular hydrogen should undergo a transition to a metallic phase[10,11] and may even become superconducting.[12] The astrophysical implications, needless to say, are very interesting.[11] A reasonable conclusion concerning these speculations requires, however, accurate equations of state which have also been calculated by Krumhansl and Wu[13] and Trubitsyn.[14]

Also, solid hydrogen has been subjected to intensive experimental investigation recently. Certain types of experiments, for example, Raman scattering[15] and magnetic resonance,[16] are conducted with great precision. It was pointed out by Harris[17] and by Noolandi and Van Kranendonk[18] that in order to achieve meaningful comparison of theory with these experiments, the effect of the zero-point motion on the various intermolecular interactions must be included. Because of the generally satisfactory agreement with experiment we have obtained in calculating the static properties of crystalline helium,[8] we believe it is worthwhile to use the same formalism to calculate various properties of solid molecular hydrogen.

As pointed out in Ref. 8, our numerical results depend quite strongly on the intermolecular potentials used in the numerical calculations. For both He and H_2, there are a number of different but equally acceptable potentials available for use. These are generally determined at least in part phenomenologically by fitting experimental data in the gaseous phase and cannot be taken too seriously in calculations at high pressure in the solid phase.[13] We believe that our formalism should work even better in H_2 than in He and that comparison of our calculated ground-state energy and pressure with