decays, lifting the residual exciton to a valley-orbit–split impurity state. The decay of BE's where the impurities are left in an excited state cannot account for the lines as the observed photon energies would be considerably lower. The participation of additional impurities such as isoelectronic centers is improbable since the luminescence of all lines is closely related to that of the excitons bound to boron or phosphorus.

In conclusion, the model of bound multiple-exciton complexes in silicon is in qualitative agreement with the experimental data of the new lines. Obvious alternative models are contradictory to the experiments. The model proposed does not contain microscopic details of the binding mechanism. With increasing complex number $m$ the physical concept will gradually change from that of an excitonic state to that of a condensed electron-hole plasma

The author wishes to thank R. Conradt for valuable suggestions and, together with R. W. Martin and M. H. Pilkuhn, for helpful and stimulating discussions. The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

[1]B. M. Ashkinadze *et al.*, Zh. Eksp. Teor. Fiz. 58, 507 (1970) [Sov. Phys. JETP 31, 271 (1969)].

[2]B. M. Ashkinadze *et al.*, Phys. Status Solidi (b) 46, 495 (1971).

[3]A. S. Kaminskii and Ya. E. Pokrovskii, Pis'ma Zh. Eksp. Teor. Fiz. 11, 381 (1970) [JETP Lett. 11, 255 (1970)].

[4]A. S. Kaminskii, Ya. E. Pokrovskii, and N. V. Alkeev, Zh. Eksp. Teor. Fiz. 59, 1937 (1970) [Sov. Phys. JETP 32, 1048 (1971)].

[5]K. Betzler and R. Conradt, Phys. Rev. Lett. 28, 1562 (1972).

[6]Ya. Pokrovskii, Phys. Status Solidi (a) 11, 385 (1972).

[7]P. J. Dean, J. R. Haynes, and W. F. Flood, Phys. Rev. 161, 711 (1967).

[8]E. Göbel, R. W. Martin, M. H. Pilkuhn, and R. Sauer, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Warsaw, 1972*, edited by the Polish Academy of Sciences (PWN—Polish Scientific Publishers, Warsaw, 1972), p. 691.

# Observation of an Underdamped "Soft" Mode in Potassium Dihydrogen Phosphate*

P. S. Peercy
*Sandia Laboratories, Albuquerque, New Mexico 87115*
(Received 6 June 1973)

The pressure dependence of the coupled-mode spectra in potassium dihydrogen phosphase (KDP) was measured at room temperature for hydrostatic pressures from 0 to 9.3 kbar. The soft mode, which is overdamped for all temperatures at atmospheric pressure, becomes underdamped for pressures $\geq 6$ kbar. This is the first observation of an underdamped soft mode for a crystal of the KDP class and resolves the question of whether the excitation should be considered as diffusive or oscillatory in nature.

We report the observation of an underdamped "soft" mode in potassium dihydrogen phosphate (KDP). The mode was made underdamped by the application of hydrostatic pressure ($\gtrsim 6$ kbar) at room temperature. This is the first observation of an actual peak in the spectral response of the soft mode for any member of the KDP class of ferroelectrics and reveals important information concerning the nature of this excitation. A brief discussion of the previous work relevant to this work is given before presenting the results of these measurements.

Since the original observation of Raman scattering from the soft ("proton") mode in KDP by Kaminow and Damen,[1] several authors have investigated this mode in KDP, as well as in many of its isomorphs. Wilson[2] and Wilson and Cummins[3] made detailed measurements of the temperature and electric field dependences of the Raman spectra of KDP in an attempt to find conditions for which this mode is underdamped. Their measurements showed the mode to be overdamped at all temperatures; furthermore, these measurements suggested that, at least near the transition temperature, the response of this mode might be relaxational rather than oscillatory in nature. More recently, Reese, Fritz, and Cummins[4] measured the soft-optic–acoustic mode interactions in deuterated KDP (KD*P) and concluded that the soft mode response in KD*P corresponds to a diffusive excitation rather than a propageting mode.

An important aspect of the soft mode for the KDP crystal class is the coupling of this mode with another optic mode of the same symmetry.

This interaction was first investigated in $KH_2AsO_4$ and $CsH_2AsO_4$ by Katiyar, Ryan, and Scott.[5] A model for the coupled-mode spectra for KDP, based on the treatment for the isomorphous arsenates, was subsequently given by Scott and Wilson,[6] and measurements of the temperature dependence of these spectra in KDP were reported by She *et al.*[7] Recently, Peercy and Samara[8] measured the temperature and pressure dependences of the static dielectric constant and Raman spectra in $RbH_2PO_4$. These data were analyzed within both the framework of Kobayashi's model[9] for a collective proton mode coupled to a transverse-optic phonon, and the coupled-mode model of Scott and Wilson.[6] While these two treatments were shown to be formally equivalent, it was found that even the combined temperature and pressure dependences of the dielectric constant and Raman spectra were insufficient to determine uniquely the important microscopic parameters of the Kobayashi model; indeed, the measurements indicated the existence of internal inconsistencies resulting from approximations made in the model calculations.

Concerns over the validity of current models for KDP have been expressed by other authors.[4,5,10] A major concern is the applicability of a damped harmonic oscillator response function for the soft mode. Cowley *et al.*[11] have suggested that such a response is inadequate for piezoelectric ferroelectrics because it neglects contributions to the self-energy of the mode which arises from fluctuations in the phonon density. Also, de Gennes[10] and Blinc *et al.*[10] have questioned the applicability of models which employ well-defined proton collective modes above the transition temperature; they suggest that these modes may be diffusive rather than oscillatory in nature. This point was recently re-emphasized by Reese, Fritz, and Cummins.[4]

Since the soft mode in KDP (as well as in all of its isomorphs which have been examined to date) is overdamped at all temperatures, it is difficult to determine unambiguously if the response should be examined within the framework of a damped harmonic oscillator or a Debye relaxationlike response function. Our earlier measurements[8] on $RbH_2PO_4$ demonstrated that the primary effect of pressure (0–4 kbar) on the soft-optic mode was to increase the relaxation rate,[5] $\tau_a^{1} = \omega_a^2/\Gamma_a$, through a decrease in $\Gamma_a$. ($\omega_a$ is the mode frequency and $\Gamma_a$ is the mode damping.) We have therefore made detailed measurements of the pressure dependence of the coupled spectra of KDP to higher pressures (~9 kbar) to determine if the mode can be made underdamped. As we shall see below, the soft mode becomes underdamped for pressures $\gtrsim 6$ kbar at room temperature and therefore cannot be described as a diffusive excitation. This is thus the first observation of an underdamped soft mode for any crystal of the KDP class and has important implications concerning the fundamental nature of this excitation.

The experimental arrangement is identical to that described previously[8] except that a different pressure cell was used for pressures $\gtrsim 4$ kbar. Data taken for the $B_2$ symmetry modes at room temperature are shown in Fig. 1 for pressures of 1 bar and 4.1 and 9.3 kbar. These data demonstrate that, while the mode is heavily overdamped at atmospheric pressure, hydrostatic

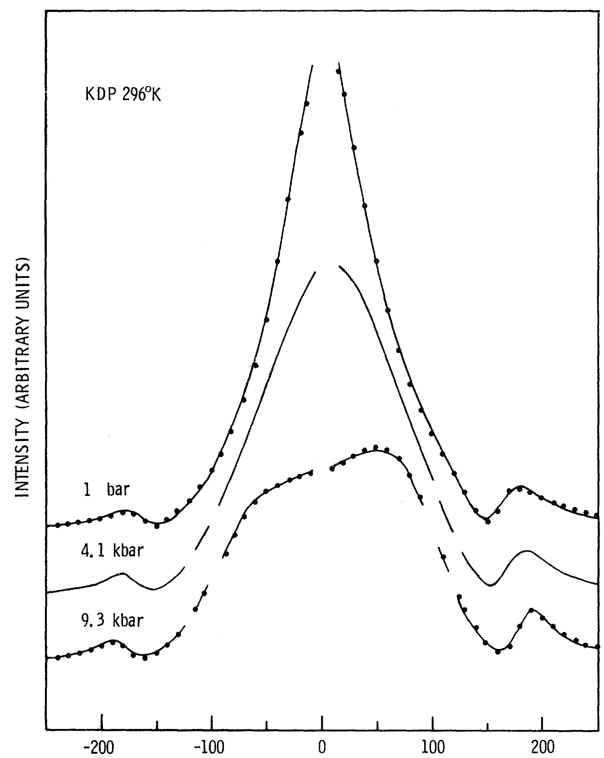


FIG. 1. Spectra for $B_2$ $[x(yx)y]$ phonons from $-250$ to 250 cm$^{-1}$ showing the coupled-mode spectra at pressures of 1 bar and 4.1 and 9.3 kbar. The solid curves are the experimental data and the points (1-bar and 9.3-kbar traces) show the calculated curves for the parameters obtained from the least squares fit. For data taken at high pressures, strain-induced birefringence in the sapphire windows caused some depolarization of the light; the portions of the traces which are deleted are where modes of different symmetries leaked into the $x(yx)y$ polarization.

pressure reduces the damping so that the mode is underdamped in the trace taken at 9.3 kbar. The fact that the response function actually peaks at $\omega \neq 0$ indicates that these spectra cannot be described by a purely relaxational excitation. Furthermore, attempts to fit the observed response with the frequency-dependent damping model discussed by Cowley and co-workers[11-13] without including the phonon coupling were unsuccessful.

The data were therefore fitted by a response function identical to that used for $RbH_2PO_4$.[8] This form for the coupled response was first used by Katiyar, Ryan, and Scott[5] to describe the temperature dependence of the coupled-mode spectra in $KH_2AsO_4$ and $CsH_2AsO_4$. Briefly, the spectral response $S(\omega)$ is given by

$$S(\omega) \propto -\operatorname{Im}\chi(\omega)\begin{Bmatrix}\bar{n}(\omega)+1\\ \\ \bar{n}(\omega)\end{Bmatrix}, \tag{1}$$

where $\bar{n}(\omega) = (e^{-\hbar\omega/kT} - 1)^{-1}$ and the complex susceptibility is

$$\chi(\omega) = \textstyle\sum_{ij} P_i P_j G_{ij}(\omega). \tag{2}$$

In Eq. (2), $P_i$ is the polarization of mode $i$ and the $G_{ij}(\omega)$ are the solutions of the coupled equations

$$\begin{pmatrix}\omega_a^2 - \omega^2 + i\omega\Gamma_a & \Delta^2\\ \Delta^2 & \omega_b^2 - \omega^2 + i\omega\Gamma_b\end{pmatrix}\begin{pmatrix}G_{11} & G_{12}\\ G_{12} & G_{22}\end{pmatrix} = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}, \tag{3}$$

where $\omega_i$ and $\Gamma_i$ are the frequency and damping of mode $i$, and $\Delta$ is the interaction (taken as real[5]) between the modes. Analysis of the data from $-250$ to 250 $cm^{-1}$ yields the parameters listed in Table I, and the resulting fit is illustrated by the points on the 1-bar and 9.3-kbar traces of Fig. 1.

The values which we obtain for the parameters at 1 bar are in good agreement with the room-

TABLE I. Parameters for the coupled-mode spectra of KDP obtained for various pressures at room temperature. The errors represent one standard deviation.

| Pressure (bar) | $\omega_a$ ($cm^{-1}$) | $\Gamma_a$ ($cm^{-1}$) | $\omega_b$ ($cm^{-1}$) | $\Delta$ ($cm^{-1}$) |
|---|---|---|---|---|
| 1 | $134 \pm 2$ | $270 \pm 7$ | $154 \pm 0.6$ | $114 \pm 0.8$ |
| $4.1 \pm 10^3$ | $135 \pm 2$ | $205 \pm 4$ | $159 \pm 0.6$ | $113.5 \pm 0.8$ |
| $9.3 \pm 10^3$ | $136 \pm 1$ | $160 \pm 2$ | $166 \pm 0.6$ | $113 \pm 0.8$ |

temperature values obtained by She *et al.*[7] As the pressure is increased the damping decreases at an initial rate of $(d\ln\Gamma_a/dP)_T \cong -7.5\%$/kbar, similar to the case for $RbH_2PO_4$.[8] For the case of an uncoupled mode that has a damped harmonic oscillator response, the mode becomes underdamped for $\Gamma \leqslant \sqrt{2}\omega$. This implies that for $\omega_a \cong 135$ $cm^{-1}$ an uncoupled mode would be underdamped for $\Gamma_a \leqslant 191$ $cm^{-1}$, which corresponds to a pressure of ~7 kbar. However, for the present coupled spectra, in which the mode energies are comparable to $kT$, the calculated response exhibits a very weak $\omega \neq 0$ maximum on the Stokes side for $\omega_a = 135$ $cm^{-1}$ and $\Gamma = 200$ $cm^{-1}$. This peak occurs at $\omega \simeq 12$ $cm^{-1}$ but is not readily observable because its weak, broad structure is masked by light scattered parasitically from crystal imperfections. As can be deduced from the data shown in Fig. 1, an $\omega \neq 0$ maximum is easily resolvable at higher pressures. For the 9.3-kbar trace this peak occurs at $\omega \approx 50$ $cm^{-1}$, and the soft-mode parameters obtained at this pressure are $\omega_a = 136$ $cm^{-1}$ and $\Gamma_a = 160$ $cm^{-1}$. Calculations for various values of damping which include the population factor $\bar{n}(\omega)$ indicate that the anti-Stokes response will not show a true maximum until $\Gamma_a \lesssim 140$ $cm^{-1}$ for $\omega_a = 135$ $cm^{-1}$. This result is in agreement with the observations; although the Stokes spectra exhibit a resolvable maximum for $\Gamma_a \lesssim 190$ $cm^{-1}$, the anti-Stokes spectra do not peak even for $\Gamma_a = 160$ $cm^{-1}$.

The measured response $S(\omega)$ is the result of two modes with frequencies $\omega_a$ and $\omega_b$ coupled through an interaction $\Delta$. If damping were neglected, the coupled system would exhibit spectral peaks at frequencies $\omega_\pm$, where[6,8]

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

In the present heavily damped case, $\omega_\pm$ are approximately the frequencies one would obtain by fitting the two regions of the spectra independently. The effect of pressure is to increase $\omega_-$ from ~89 $cm^{-1}$ at 1 bar to ~96 $cm^{-1}$ at 9.3 kbar. Similarly, $\omega_+$ increases from ~185 to ~192 $cm^{-1}$ for the same pressure change. The largest pressure dependence is exhibited by $\tau_a^{-1} = \omega_a^2/\Gamma_a$ and this dependence is exhibited by $\tau_a^{-1} = \omega_a^2/\Gamma_a$, and this large increase in $\tau_a^{-1}$ [$(d\ln\tau_a^{-1}/dP)_T = 7.9\%$/kbar], which results primarily from the decrease in $\Gamma_a$ with pressure, is similar to the case for $RbH_2PO_4$.[8] The smaller pressure dependences for $\omega_\pm$ noted above just reflect the combined result of the small pressure dependences of $\omega_a$, $\omega_b$, and $\Delta$.

It is evident from both the qualitative change in

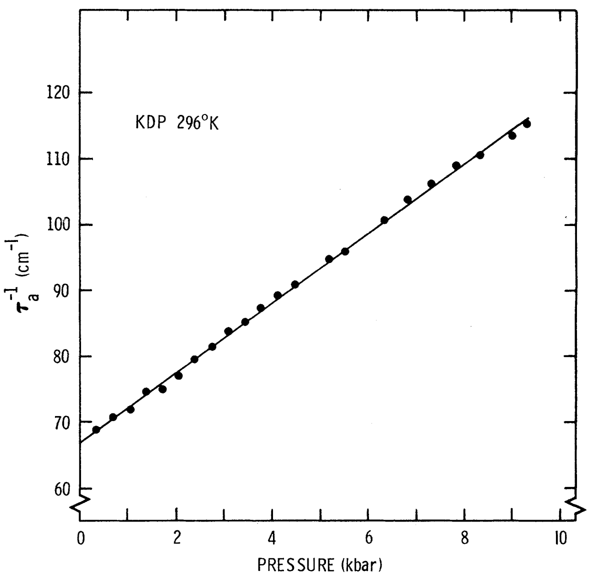


FIG. 2. Pressure dependence of the relaxation rate $\tau_a^{-1} = \omega_a^{2}/\Gamma_a$ from 0 to 9.3 kbar.

the spectra and the quantitative results of the analysis that the important pressure effect is on the damping of the proton mode. Models for proton tunneling[14] predict that the tunneling energy is a strong function of the separation of the minima of the proton double-well potential. However, the soft mode in the spectra presumably reflects a collective excitation of the protons rather than the tunneling of a single proton in the unit cell.[15] The present data indicate that the frequency of the collective excitation is not as dependent as the damping on the O⋅⋅H⋅⋅O bond length. Unfortunately, no theoretical treatment of the proton excitation and the coupled proton-lattice modes has included the effects of damping on the soft mode, so that only qualitative statements can be made concerning its origin. Furthermore, the results of our pressure studies emphasize that realistic models for KDP-type crystals must include damping.

In the Kobayashi treatment of the collective proton excitation coupled to the transverse optic mode, the interaction is taken to be bilinear in the proton and phonon coordinates and thus does not include the effect of higher order anharmonicities which produce damping. However, the small pressure dependence of $\Delta$($\Delta$ decreases by $<2\%$ throughout the entire pressure range studied) suggests that the change in damping probably does not occur because of a change in the proton-phonon anharmonicities. If this is the case, the pressure dependence of $\Gamma_a$ is primarily due to the pressure dependence of the proton-proton interactions, and the decrease in damping causes the collective excitation to become a more well-defined propagating excitation—i.e., the correlation length of the excitation increases as the proton-proton separation decreases. In any event, the important result is that the "soft" mode response can be made underdamped and must therefore be considered as a propagating rather than a diffusive excitation, within the framework of this model. This result thus resolves an important long-standing uncertainty about the nature of the protonic excitation in KDP-type ferroelectrics.

We wish to acknowledge the expert technical assistance of J. D. Kluck in performing these measurements. Helpful discussions with I. J. Fritz and G. A. Samara are also gratefully acknowledged.

*Work supported by the U. S. Atomic Energy Commission.

[1] I. P. Kaminow and T. C. Damen, Phys. Rev. Lett. 20, 1105 (1968); I. P. Kaminow, in *Light Scattering Spectra of Solids,* edited by G. B. Wright (Springer, Berlin, 1969), p. 675.

[2] C. M. Wilson, Ph. D. thesis, The Johns Hopkins University, 1970 (unpublished).

[3] C. M. Wilson and H. Z. Cummins, in *Light Scattering in Solids,* edited by M. Balkanski (Flammarion, Paris, 1971), p. 420.

[4] R. L. Reese, I. J. Fritz, and H. Z. Cummins, Phys. Rev. B 7, 4165 (1973).

[5] R. S. Katiyar, J. F. Ryan, and J. F. Scott, Phys. Rev. B 4, 2685 (1971).

[6] J. F. Scott and C. M. Wilson, Solid State Commun. 10, 597 (1972).

[7] C. Y. She, T. W. Broberg, L. S. Wall, and D. F. Edwards, Phys. Rev. B 6, 1847 (1972).

[8] P. S. Peercy and G. A. Samara, Phys. Rev. B (to be published).

[9] K. K. Kobayashi, J. Phys. Soc. Jap. 24, 497 (1968).

[10] P. G. de Gennes, Solid State Commun. 1, 132 (1963); R. Blinc, V. Dimic, J. Petkovsek, and E. Pirkmajer, Phys. Lett. 26A, 8 (1967).

[11] R. A. Cowley, G. J. Coombs, R. S. Katiyar, J. F. Ryan, and J. F. Scott, J. Phys. C: Proc. Phys. Soc., London 4, 4203 (1971).

[12] G. J. Coombs and R. A. Cowley, J. Phys. C: Proc. Phys. Soc., London 6, 121 (1973).

[13] R. A. Cowley and G. J. Coombs, J. Phys. C: Proc. Phys. Soc., London 6, 143 (1973).

[14] See, e.g., E. Merzbacher, *Quantum Mechanics* (Wiley, New York, 1961), pp. 64–76.

[15] See, e.g., R. Brout, K. A. Müller, and H. Thomas, Solid State Commun. 4, 1105 (1967).