# Preliminary observation of a central peak in the light-scattering spectrum of $KH_2PO_4$†

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High-resolution Brillouin scattering experiments on $KH_2PO_4$ have revealed a quasielastic component whose intensity increases dramatically near the 122 °K ferroelectric phase transition. The two-coupled-mode analysis which has previously been employed in analyzing Raman spectra of $KH_2PO_4$ and its isomorphs, is reviewed and extended to simultaneously include the interacting optic, acoustic, and ferroelectric soft modes. Results of both Brillouin and Raman scattering experiments are analyzed in terms of a relaxing self-energy as proposed by Cowley for the piezoelectric ferroelectrics. We find that $\delta$, the strength of the relaxing self-energy term, is approximately 1 $cm^{-1}$ at $T_C$. The central peak was too narrow to resolve in this experiment, which implies a lower limit for the relaxation time $\tau$ of $10^{-9}$ sec.

## I. INTRODUCTION

The condensing soft-mode picture of structural phase transitions, which became widely accepted during the 1960's, has come under fundamental reconsideration during the last few years since the experimental discovery of the "central peak" in the neutron scattering spectra of a number of crystals including $SrTiO_3$, $Nb_3Sn$, $KMnF_3$, and $LaAlO_3$.[1]

The origin of the central peak—an extremely narrow quasielastic component whose strength increases rapidly as the transition is approached—is not yet completely clear, although several possible mechanisms have been proposed.[2-5] There is one particular class of crystals, the piezoelectric ferroelectrics including potassium dihydrogen phosphate (KDP) and its isomorphs, for which a specific mechanism proposed by Cowley in 1970[6] can give rise to a ferroelectric soft mode which exhibits a central peak. This mechanism has already been invoked to explain the temperature-dependent Raman spectra of several crystals of this class.[7,8]

We have performed Raman and Brillouin scattering experiments on KDP with higher resolution than was available in earlier measurements and have observed a new quasielastic component whose intensity increases dramatically near the ferroelectric phase transition at 122 °K. We tentatively identify this component, whose width was too small to resolve, as the central peak associated with the ferroelectric soft mode.

In this paper we will review and extend the coupled-oscillator formalism previously employed by other investigators in order to provide a framework for interpretation of our Raman and Brillouin scattering results. We will show that our data can be consistently interpreted in terms of a relaxing self-energy, but that the size of the observed central peak in the Brillouin spectrum is consistent with the Raman results only if the analysis is performed in a way which is consistent with the choice of phases of the mode-coupling terms.

The ferroelectric soft mode in KDP was first observed in Raman scattering by Kaminow and Damen in 1968.[9] Their data in the range 10–140 $cm^{-1}$ were fit to a damped harmonic-oscillator response function

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

which gave $\gamma = 170$ $cm^{-1}$ and $\omega_0 = 99\,[(T - T_C^x)/T]^{1/2}$ $cm^{-1}$, where $T_C^x$ is the clamped Curie temperature 117.7 °K.[10]

In 1971, Katiyar, Ryan, and Scott studied the Raman spectrum of two KDP isomorphs, $CsH_2AsO_4$ (CsDA) and $KH_2AsO_4$(KDA), and found that the overdamped ferroelectric soft mode in these crystals is strongly coupled to another optic mode of the same $B_2$ symmetry so that the parameters characterizing the ferroelectric mode must be deduced from a coupled-mode analysis.[11] The result of this analysis indicated that the soft-mode frequency extrapolates to zero at a temperature $T_0$ which is considerably lower than $T_C^x$.[7,12,13] A similar result was found for KDP by She *et al.*[14] when the spectrum in the range 140–250 $cm^{-1}$ (which had been neglected by Kaminow and Damen) was included in the analysis.[15,16] Peercy and Samara[17] report similar results for $RbH_2PO_4$, as have Leung, Lowndes, and Tornberg for $RbH_2AsO_4$, $KH_2AsO_4$, $CsH_2AsO_4$, and their deuterated isomorphs.[8] Thus, the occurrence of a temperature "gap" $\Delta T = T_C^x - T_0$ between the clamped Curie temperature and the temperature at which the frequency of the ferroelectric soft mode extrapolates to zero appears to be a general property of the KDP-type crystals, implying an apparent violation of the Lyddane-Sachs-Teller (LST) relation.[18]

Cowley *et al.*[7,19] suggested an explanation for the

occurrence of the gap based on a mechanism which Cowley had proposed previously.[6] For piezoelectric ferroelectrics like KDP, the soft-ferroelectric mode can couple to pairs of acoustic phonons through third-order anharmonicity, giving rise to low-frequency structure in the self-energy of the soft mode for which the response function becomes

$$G(\omega) = [\omega_\infty^2 - \omega^2 - i\omega\gamma - \delta^2/(1 - i\omega\tau)]^{-1} \quad , \qquad (2)$$

where $\tau$ is the relaxation time of a "typical" acoustic phonon, estimated by Cowley *et al.* as $10^{-10}$–$10^{-11}$ sec.[7,19] Thus, $\omega_\infty$ would be the soft-mode frequency deduced from the Raman experiments which are presumably performed at frequencies far above $1/\tau$, while the static response of the soft mode, $G(0) = (\omega_\infty^2 - \delta^2)^{-1}$ is governed by $\omega_0^2 = \omega_\infty^2 - \delta^2$. If the temperature dependence of $\delta^2$ is of the form $\delta^2 = \alpha T$ while $\omega_\infty^2 = K(T - T_0)$, one has

$$\omega_0^2 = K(T - T_0) - \alpha T = (K - \alpha)\ (T - T_C^x) \quad , \qquad (3a)$$

where

$$T_0 = [(K - \alpha)/K]\, T_C^x \quad . \qquad (3b)$$

This mechanism then explains the occurrence of the temperature gap if $\alpha$ (or $\delta$) is presumed to be large enough to satisfy Eq. (3b). The magnitude of $\delta$ has not been directly calculated for these crystals, however, and Cowley and Coombs[19] state that the anharmonic force constants required to perform such a calculation are not available. Silberglitt estimates that $\delta$ should be on the order of an acoustic-phonon linewidth.[20]

The relaxing self-energy term in Eq. (2), which was included to account for the temperature gap suggested by the analysis of the Raman scattering experiments, has some additional important consequences which have not yet been tested. Cowley and Coombs,[19] Scott and Worlock,[18] and Ryan[16] have pointed out that there will be additional low-frequency structure in the spectrum of a crystal with a response function of the form of Eq. (2). In fact, this same form has been invoked in describing the central peak in $SrTiO_3$, $Nb_3Sn$, $KMnF_3$, and $LaAlO_3$.[1]

The $x$, $y$ acoustic mode which couples piezoelectrically to the ferroelectric soft mode has been studied in KDP by Brillouin scattering by Brody and Cummins,[21,22] in KD*P by Reese, Fritz, and Cummins,[23] and recently in KDP and CsDA by Azoulay *et al.*[24] In those experiments, the strong temperature dependence of the Brillouin components was observed, but the resolution was inadequate to permit observation of the new feature which we will discuss below.

Reese, Fritz, and Cummins[23] have discussed the coupled-ferroelectric and acoustic modes in terms of a coupled-mode analysis which parallels the coupled-ferroelectric and optic-mode analysis employed by Katiyar *et al.*[11] In Sec. III we combine those analyses to produce a single three-coupled-mode formalism for the acoustic, optic, and soft-ferroelectric modes. In this analysis we will show that inclusion of a relaxing self-energy term (which leads to the central peak) in the response function of the ferroelectric soft mode also has important consequences for the Brillouin spectrum, since the piezoelectrically coupled acoustic mode is highly sensitive to the low-frequency response of the soft-ferroelectric mode.

## II. TWO-OSCILLATOR MODEL

We first consider the coupled-ferroelectric soft-mode–optic-mode system for the clamped crystal reserving the added complication of the coupled-acoustic mode until Sec. III. We present this review primarily to clarify the consequences of the choice of phase for the coupling which has led to some confusion in the past.

Following Katiyar *et al.*,[11,7] we write the coupled-mode equation as

$$\begin{bmatrix} G_1^{-1} & \triangle^2 - i\omega\Gamma \\ \triangle^2 - i\omega\Gamma & G_2^{-1} \end{bmatrix} \begin{bmatrix} G_{11} & G_{12} \\ G_{12} & G_{22} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} , \qquad (4)$$

where $G_1$ and $G_2$ are the Green's functions of the uncoupled ferroelectric and optic modes which are given by Eqs. (10a) and (10b) below. The Stokes/anti-Stokes spectrum is given by

$$I(\omega) = R \begin{bmatrix} n(\omega) + 1 \\ n(\omega) \end{bmatrix} \mathrm{Im} \sum_{ij} P_i\ P_j\ G_{ij}(\omega) \quad , \qquad (5)$$

where $P_i$ are optical coupling constants, $n(\omega)$ is the Bose-Einstein factor, and $R$ is a normalization constant. From Eq. (4),

$$\chi(\omega) = \sum_{ij} P_i\ P_j\ G_{ij}(\omega)$$

$$= \frac{P_1^2 G_1 + P_2^2 G_2 - 2P_1P_2(\triangle^2 - i\omega\Gamma) G_1 G_2}{1 - (\triangle^2 - i\omega\Gamma)^2\ G_1\ G_2} \quad . \qquad (6)$$

Barker and Hopfield pointed out that the equations of motion of damped oscillators coupled by a spring ($\Gamma = 0$) can be transformed to describe oscillators coupled by a dashpot ($\triangle = 0$) so that the choice of real or imaginary coupling is arbitrary.[25] (That is, one can always find a unitary transformation which diagonalizes either the force-constant tensor or the damping tensor for any set of coupled oscillators.) Katiyar *et al.* chose real coupling ($\Gamma = 0$) since they found that only this choice produced simple temperature dependences for the parameters,[11] and this choice has been widely followed in subsequent publications.[14,17] With this choice, however, the temperature at which the soft-mode frequency extrapolates to zero is *necessarily* lower than $T_C^x$, even in the absence of a relaxing self-energy. From Eq. (6), the clamped Curie tem-

perature must occur when $\chi(0) \to \infty$, i.e.,

$$[1 - \Delta^4 G_1(0) G_2(0)]_{T=T_C^x} = 0 \ , \tag{7}$$

and this will occur at a temperature above the temperature $T_0$ at which $G_1(0) \to \infty$. Thus, the appearance of a finite temperature gap resulting from an analysis with real coupling does not necessarily indicate the presence of low-frequency structure in the soft-mode self-energy. The divergence of the static susceptibility at $T_C^x$ is a property of the coupled modes and not of the ferroelectric mode alone, as She *et al.*[14] and Ryan[16] have previously pointed out.

If, however, the coupling is taken to be imaginary ($\Delta = 0$), then from Eq. (6) the static susceptibility is given by

$$\chi(0) = P_1^2 \, G_1(0) + P_2^2 \, G_2(0) \ , \tag{8}$$

and in this representation $\chi(0)$ and $G_1(0)$ must diverge at the same temperature, $T_C^x$. Physically, this result shows that the *static* susceptibility of oscillators coupled by dashpots is just the sum of the individual susceptibilities and is unaffected by the coupling.

Although the choice of phase for the coupling constant is arbitrary, the choice must be consistent with the method of analysis if meaningful estimates of $\delta$ or $\alpha$ are to be extracted from the Raman data. Thus, the most straightforward approach is to analyze the data in the imaginary coupling representation since the temperature $T_0$ at which $\omega_1$ extrapolates to zero then gives $\alpha$ directly through Eq. (3b).[16,26] If the analysis is performed in the real-coupling representation, one should either apply the Barker-Hopfield transformation to the resulting parameters, or else compare $T_C^x$ to the temperature for which Eq. (7) is satisfied. But Eq. (3b) *cannot* be used directly if $T_0$ is deduced from an analysis with real coupling. The published results of Katiyar, Ryan and Scott give the temperature dependence of the soft-mode parameters and $T_0$ only for the real-coupling case ($\Gamma = 0$). However, Ryan has also analyzed the Raman data in the imaginary coupling representation ($\Delta = 0$) for which he found[16]

$$\text{CsDA, } T_0/T_C = 0.4; \quad \text{KDP, } T_0/T_C = 0.9;$$

$$\text{KDA, } T_0/T_C = 1.0 \ ,$$

implying that the temperature gaps in CsDA and KDP are associated with a relaxing self-energy, while the gap in KDA (reported in Refs. 7, 12, and 13) is an artifact of the analysis and transforms away in the $\Delta = 0$ representation. Rough estimates of $\delta$ at the transition temperature can also be extracted from Ryan's unpublished results,[16] which gives $\delta \sim 12$ cm$^{-1}$ for KDP and $\delta \sim 237$ cm$^{-1}$ for CsDA.

## III. THREE-OSCILLATOR MODEL

In order to include the coupling of the ferroelectric soft mode to both the $x$, $y$ transverse acoustic mode and the $B_2$ optic mode we extend the derivation from the phonon Dyson equation[27] which led to Eq. (4) to include the acoustic mode, and obtain

$$\begin{bmatrix} G_1^{-1} & \Delta_{12}^2 - i\omega\Gamma_{12} & \Delta_{13}^2 - i\omega\Gamma_{13} \\ \Delta_{12}^2 - i\omega\Gamma_{12} & G_2^{-1} & 0 \\ \Delta_{13}^2 - i\omega\Gamma_{13} & 0 & G_3^{-1} \end{bmatrix} \times \begin{bmatrix} G_{11} & G_{12} & G_{13} \\ G_{12} & G_{22} & G_{23} \\ G_{13} & G_{23} & G_{33} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} , \tag{9}$$

where the response functions of the ferroelectric soft mode (1), the optic mode (2), and the acoustic mode (3) are taken to be

$$G_1 = [\omega_1^2 - \omega^2 - i\omega\gamma_1 - \alpha T/(1 - i\omega\tau)]^{-1} \ , \tag{10a}$$

$$G_2 = [\omega_2^2 - \omega^2 - i\omega\gamma_2]^{-1} \ , \tag{10b}$$

$$G_3 = [\omega_3^2 - \omega^2 - i\omega\gamma_3]^{-1} \ . \tag{10c}$$

Direct coupling between the optic and acoustic modes is expected to be unimportant and has not been included. The scattering intensity $I(\omega)$ is given by Eq. (5).

If we choose the coupling between the optic mode and the ferroelectric soft mode as imaginary ($\Delta_{12} = 0$), and the piezoelectric coupling of the acoustic and ferroelectric modes as real ($\Gamma_{13} = 0$), then the static susceptibility is given by

$$\chi(0) = \left( \frac{P_1^2 G_1 + P_3^2 G_3 + P_2^2 G_2 (1 - \Delta_{13}^4 G_1 G_3) - 2 P_1 P_3 \Delta_{13}^2 G_1 G_3}{1 - \Delta_{13}^4 G_1 G_3} \right)_{\omega = 0} . \tag{11}$$

If the crystal is clamped, then $G_3 = 0$ and $\chi(0)$ is again given by Eq. (8) demonstrating that $G_1(0)$ should diverge at the clamped Curie temperature $T_C^x$. For the free crystal, the transition will occur at the free Curie temperature $T_C$ determined by

$$[1 - \Delta_{13}^4 G_1(0) \, G_3(0)]_{T=T_C} = 0 \ . \tag{12}$$

For KDP, the free Curie temperature $T_C = 122$ °K is 4.3 °K above the clamped Curie temperature, $T_C^x = 117.7$ °K,[21] and this fact can be used to fix the

magnitude of $\Delta_{13}$ as we will see below.

## IV. RAMAN EXPERIMENTS

Raman scattering experiments similar to those reported in Refs. 11, 14, and 17 were performed using face-cut 12-mm-cubes of KDP purchased from Isomet.[28]

The crystal under study was mounted within a small cell fitted with 2-methyl butane and attached to the cold finger of a cryotip Dewar with temperature stability of ~0.5 °K. A Spectra-Physics model No. 165 argon laser, intensity stabilized to ~0.1% provided 300 mW of 4880-Å light for the $x(y,x)y$ scattering measurements. Raman-scattered light was analyzed with a Spex No. 1401 tandem spectrometer scanned at 25 $cm^{-1}$/min, with resolution of 4.5 $cm^{-1}$. The phototube output was routed to a multiscaler swept to address one channel per wave number of scan.

The digital data were corrected by a computer routine for the background level, for counting nonlinearities in the pulse handling electronics, and for nonuniform spectrometer response. The Bose factors were then divided out of both the Stokes and anti-Stokes sides of the spectrum[9] and the temperature was adjusted to give optimum agreement between Stokes and anti-Stokes data sets. (This procedure yielded a "true" temperature typically about 3 °K above the direct thermocouple measurement indicating significant local heating by the laser.)

Typical data (at 206 °K) after division by the Bose factors are shown in Fig. 1 along with the results of fitting the points from the Stokes spectrum to $\mathrm{Im}\chi(\omega)$ using Eq. (6).[29] The parameter values for this spectrum and six others are given in Table I. A linear fit of $\omega_1^2$ vs $T$ for these seven spectra in the temperature range 132.5 to 206 °K gave $\omega_1^2 = 42.75(T - 117.1\ °K)$ with an rms error of 2.8%.[30] The linear plot is shown in the inset of Fig. 1. (We also plotted $\omega_1^2 T/\gamma_1$ vs $T$ as was done in Ref. 7, but the fit was then considerably worse with rms error of 8.7%.) All other parameters were found to be relatively independent of temperature as shown in Table I: $\Gamma_1$ and $\omega_2$ decrease slowly with increasing $T$ while $\Gamma_2$, $\Gamma_{12}$, and $P_2/P_1$ increase slowly. ($\Delta_{12}$ was taken as zero.)

The principal result of this measurement is that the gap $T_C^x - T_0$ is zero (within experimental error)

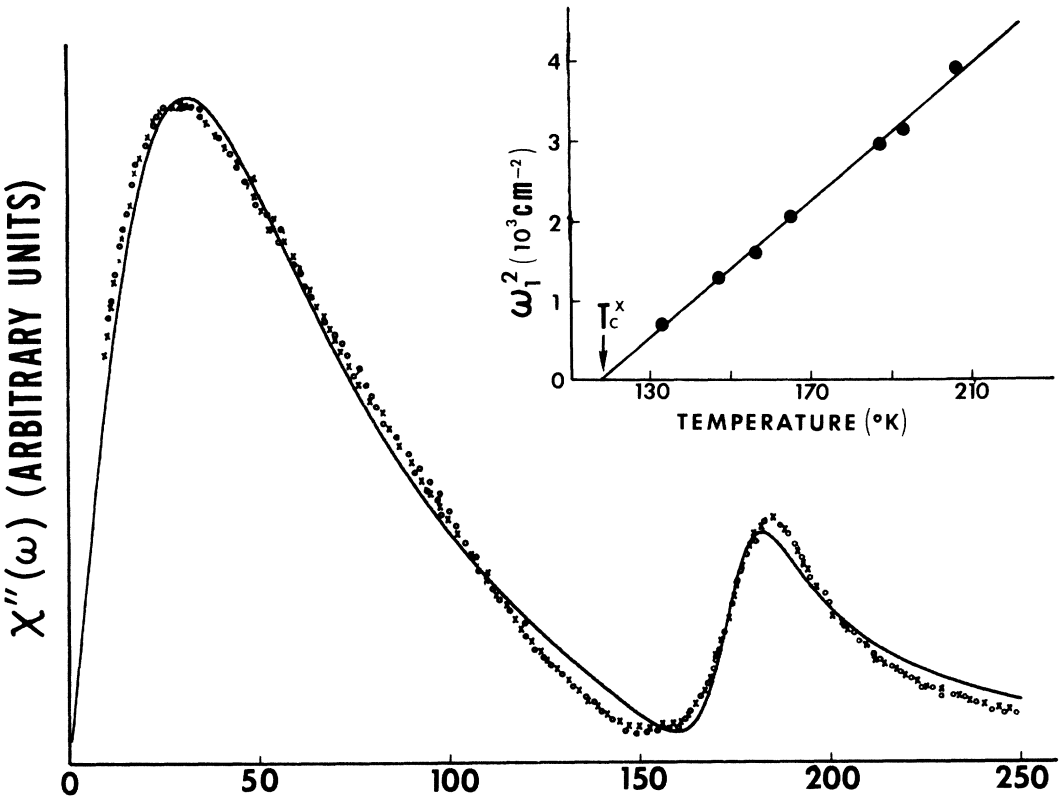


FIG. 1. Imaginary part of the susceptibility $\chi(\omega)$ of KDP deduced from the $x(y,x)y$ Raman spectrum at $T = 206$ °K. Circles: Stokes data, crosses: anti-Stokes data (only half of the data points are shown.) The solid line is the result of fitting the Stokes data in the range 10–240 $cm^{-1}$ to Eq. (4). The rms fitting error was 6.7%. The resulting parameters are given in Table I. Inset: $\omega_1^2$ vs $T$. The intercept is at $T_0 = 117.1$ °K. The arrow is at $T_C^x = 117.7$ °K.

TABLE I. Parameters from two-coupled-oscillator fits of KDP Raman spectra.

| $T$(°K) | $\omega_1$(cm$^{-1}$) | $\Gamma_1$(cm$^{-1}$) | $\omega_2$(cm$^{-1}$) | $\Gamma_2$(cm$^{-1}$) | $P_2/P_1$ | $\Gamma_{12}$(cm$^{-1}$) | Fractional r.m.s. error in % |
|---|---|---|---|---|---|---|---|
| 132.5 | 26.6 | 146.7 | 187.1 | 30.9 | 0.60 | 59.77 | 5.5 |
| 147 | 36.0 | 153.1 | 186.5 | 34.3 | 0.60 | 64.61 | 6.4 |
| 156 | 39.9 | 144.5 | 185.8 | 33.2 | 0.61 | 63.00 | 5.6 |
| 165 | 45.4 | 149.5 | 185.7 | 34.7 | 0.61 | 64.63 | 6.7 |
| 187 | 54.4 | 140.6 | 184.2 | 37.4 | 0.62 | 65.07 | 6.5 |
| 193 | 56.2 | 144.4 | 184.0 | 38.3 | 0.62 | 67.17 | 6.7 |
| 206 | 62.5 | 140.6 | 183.8 | 41.1 | 0.65 | 68.51 | 6.7 |

and is not likely to be greater than 2 °K, so that $\alpha$ is probably less than 0.7 cm$^{-2}$/°K or equivalently, at $T_C$, $0 \leq \delta < 9$ cm$^{-1}$.

## V. BRILLOUIN EXPERIMENTS

Brillouin scattering experiments were performed using one of the same KDP crystals used in the Raman experiments, but oriented to permit scattering with $\vec{q}$ along [100].[31] Sample preparation, electrical shorting arrangements, and the Dewar, which was stable to 0.01 °K, were all essentially as described by Brody.[10,22]

A single-mode Spectra Physics model No. 165 argon laser provided 150 mW of 5145-Å light which was focused into the crystal with a long focal-length lens (50.8 cm) to avoid local heating. A pressure-scanned Fabry-Perot with a 2-cm spacer and a finesse of 45 was scanned over three orders in approximately 13 min, and the photocounts routed to a 1024-channel multiscaler.

A set of four digital spectra are shown in Fig. 2 for $T$ = 129.20, 122.52, 122.23, and 122.13 °K (all measured relative to the transition temperature taken to be $T_C$ = 122 °K). For temperatures from 300 °K down to ~135 °K the Brillouin components are relatively independent of temperature—the Brillouin shift is nearly equal to the free spectral range of 0.25 cm$^{-1}$—and there is a small elastic Rayleigh line due to inevitable parasitic scattering.

Below 135 °K, the Brillouin components broaden and increase in intensity. They approach the Rayleigh line, crossing the Brillouin component from the adjacent order at ~123.7 °K, and gradually develop an asymmetric line shape. The intensity of the Rayleigh line also increases gradually with decreasing temperature; below 123 °K, however, there is a rapid increase in intensity. At 122.13 °K the Rayleigh intensity has increased by a factor of 30 from its value at room temperature.

## VI. ANALYSIS

In fitting the Brillouin spectra of Fig. 2 to the predictions of Eqs. (5) and (9), we first reduced the number of free parameters as follows: $\Gamma_1$, $\omega_2$, $\Gamma_2$, $\Gamma_{12}$, and $P_2/P_1$ were taken directly from the Raman experiments.[31] The Raman result for $\omega_1$ was combined with Eq. (3b) to allow variation in $\alpha$, giving $\omega_1^2 = K[T - (1 - \alpha/K)T_C^x]$, with $K$ = 42.75 and $T_C^x$ = 117.7 °K.

The coupling constant $\triangle_{13}$ can be related to the piezoelectric coefficient $a_{36}$, and for our geometry should be ~2 cm$^{-1}$.[23] We evaluated $\omega_3$ and $\triangle_{13}$ from the temperature dependence of the Brillouin peaks above 125 °K and the requirement that Eq. (12) be satisfied for $T_C = T_C^x + 4.3$ °K. This procedure gave $\omega_3$ = 0.239 cm$^{-1}$ and $\triangle_{13} \simeq 1.8$ cm$^{-1}$ (the exact value of $\triangle_{13}$ varies with $\alpha$). $\gamma_3$, which could not be measured, was taken as $5 \times 10^{-5}$ cm$^{-1}$. This left, apart from the normalization constant, only $\alpha$, $\tau$, and $P_3/P_1$ as free parameters. These were then varied to simultaneously produce a good fit to all the spectra (eight) in the range 122.13–129.2 °K, of which four are shown in Fig. 2.

In the fitting procedure, a constant background was added which was computed from the same theoretical spectrum but which covered the spectral range of ~140 cm$^{-1}$ transmitted by a filter in front of the phototube. The complete spectrum was convoluted with a Gaussian resolution function with full width 0.0055 cm$^{-1}$, which closely matched the instrument profile.

In preliminary computer experiments we observed several general trends. First, the form of the Brillouin spectra, apart from the central peak, could be well fit using a self-energy for the ferroelectric mode without a relaxing term. Second, $\tau$ in the range $10^{-10}$–$10^{-11}$ sec, as suggested in Ref. 7, produces a central peak much broader than what we observed. Third, $\delta \gtrsim 10$ cm$^{-1}$ not only produces an unrealistically large central peak, but also leads to a saturation of the softening in the Brillouin components which get "frozen out" as $T \to T_C$. A good fit to all our Brillouin data was obtained with the following parameters: $\tau = 4 \times 10^{-9}$ sec, $P_3/P_1 = -0.007$, and $\alpha$ = 0.009 cm$^{-2}$/°K. Thus, $\delta \simeq 1$ cm$^{-1}$ and $\triangle T \sim 0.025$ °K.

The small temperature gap is consistent with the results of the Raman experiments discussed earlier. The value of $\tau$ is apparently considerably longer than previously assumed,[7] and may indicate

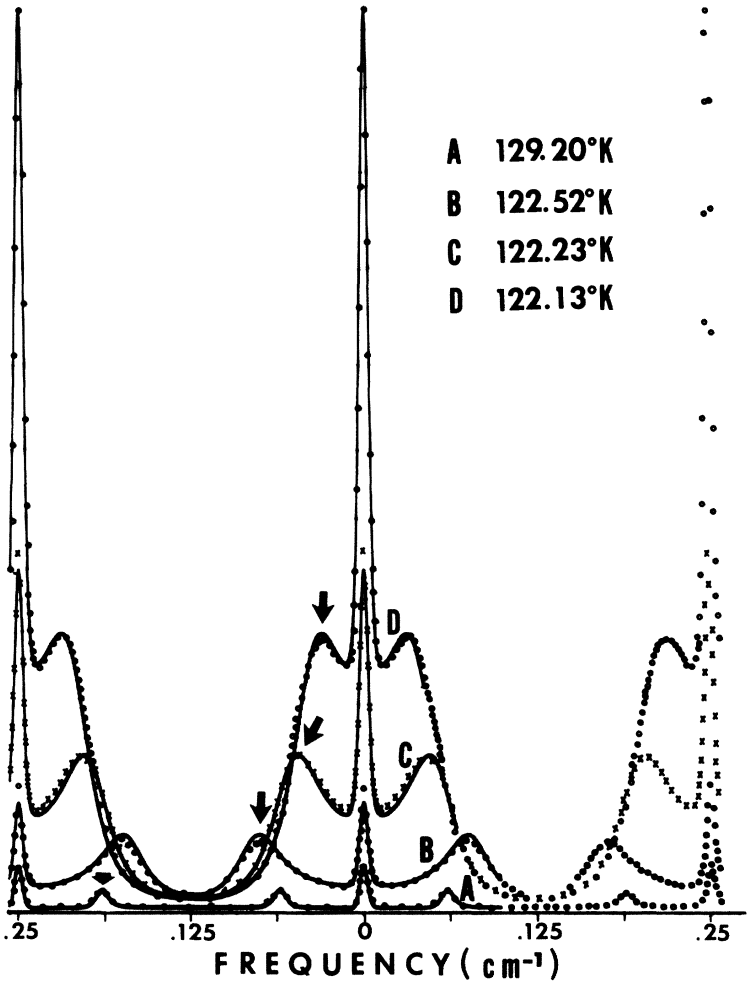


FIG. 2. Brillouin spectra of KDP at $T = 129.29$, 122.52, 122.23, and 122.13°K with $x+z(x-z, y)x-z$ scattering geometry. The arrows indicate the positions of the anti-Stokes Brillouin peaks of the order centered at zero. Each spectrum consists of 620 data points of which approximately $\frac{1}{4}$ are plotted. The solid lines are given by Eqs. (5) and (9) with the parameters given in the text.

that the acoustic phonons which participate in the phonon-density fluctuations leading to the central peak are long-wavelength phonons whose lifetimes far exceed that of a "typical" acoustic phonon. A better estimate of $\tau$ can hopefully be obtained from higher-resolution measurements employing light-beating techniques, although Lyons, Mockler, and O'Sullivan have previously searched for a quasi-elastic component in the small-angle spectrum of KDP unsuccessfully.[32]

Since we were unable to detect any width for the central component, there is a possibility that it is nondynamical in origin. Axe has discussed a mechanism in which point defects or impurities produce an inhomogeneous strain field which increases as the lattice "softens" as the phase transition is approached.[33] Since this mechanism would cause a divergent central-peak intensity, it cannot be ruled out until a finite width has been measured. However, we have recorded Brillouin spectra of two KDP crystals obtained from Isomet nearly two years apart. Although the optical quality of the newer crystal was far superior to the older one in terms of visible inclusions indicating significant change in the growing technique, the intensities of the central peaks were nearly identical in the two crystals and so was the temperature dependence. Furthermore, we observed the scattering column visually near the transition and saw a spatially uniform increase in intensity with none of the speckle pattern characterizing static inhomogeneous effects. Though hardly conclusive, these observations strongly suggest that the central peak is dynamical in origin.

In conclusion, we have shown that our Brillouin and Raman scattering spectra of KDP can be interpreted in terms of a three-coupled-oscillator formalism in which the Green's function of the ferroelectric soft mode includes a relaxing self-energy term of the form $\delta^2/(1-i\omega\tau)$, with $\delta \sim 1$ cm$^{-1}$ at $T_C$. The experiments also indicate a lower limit for $\tau$ of $10^{-9}$ sec. Although we have discussed this relaxing self-energy term in the context of the mechanism proposed by Cowley, the extreme narrowness of the central peak leaves the question of its origin open. The similarity of our observations

for KDP to the results of neutron scattering experiments on $SrTiO_3$, $Nb_3Sn$, $KMnF_3$, and $LaAlO_3$ may indicate that the central peaks in all these materials result from some common mechanism which has yet to be elucidated. Additional experiments on $KH_2PO_4$ and $CsH_2AsO_4$ are in progress and will be reported in a subsequent paper.

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[29]Systematic fitting errors in the range 100–200 $cm^{-1}$ apparently reflect the shortcomings of the model. Similar deviations were observed by She *et al.* [C. Y. She (private communication)], by Ryan (Ref. 16, Fig. 6.6), and by V. Mazzacurati *et al.* [V. Mazzacurati, S. Mobilio, M. Sampoli, and G. Signorelli unpublished]. We also attempted to fit the Raman data with the form for $G_1(\omega)$ proposed by R. Blinc and B. Zeks [Adv. Phys. 21, 693 (1972), Eq. 131]. Although the fit was improved by $\sim 30\%$, the resulting values of $\omega_1$ showed no simple $T$ dependence, and $T_2$ was negative.

[30]Although spectra were analyzed at temperatures up to 300°K, we found that parameters deduced from those experiments with $T > 240$°K deviated significantly from the simple temperature dependence closer to the transition, presumably because of other temperature-dependent effects not directly associated with the transition. We therefore excluded those points from the analysis.

[31]Only for $\vec{q}$ along [100] is there an acoustic mode whose velocity is determined solely by $c_{66}$, the one elastic constant which piezoelectrically couples to the polarization $P_3$ of the soft ferroelectric mode. Unfortunately, the Raman spectrum of the $B_2$ ferroelectric modes cannot be observed for $\vec{q}$ along [100] owing to the structure of the Raman tensors. Consequently, the Raman and Brillouin experiments reported in this paper were performed with nonequivalent phonon-propagation directions so that the use of parameters deduced from the Raman experiments in analyzing the Brillouin experiments involves an untested assumption that these parameters are equivalent for all propagation directions perpendicular to the $z$ axis.

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