Dynamic central peak in ferroelectric KH_2PO_4†

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A dynamic central peak of width ~50 MHz has been observed in the depolarized-light-scattering spectrum of KH_2PO_4. It is seen only in the ferroelectric phase within ~0.1 °K of the transition, where its intensity exceeds that of the strongest Brillouin component, the *xy* transverse acoustic mode. We show that this strongly temperature-dependent feature arises from the coupling of the ferroelectric soft mode to the thermal diffusion mode in the ferroelectric (but not in the paraelectric) phase through the temperature dependence of the order parameter, the spontaneous polarization $P_3(T)$.

Central peaks have been investigated extensively since the discovery in 1971 by Riste and coworkers of an extremely narrow quasielastic feature in the neutron-scattering spectrum of strontium titanate whose intensity diverges as the structural phase transition at 105 °K is approached.[1] Although divergent central peaks have subsequently been found in the neutron- and light-scattering spectra of numerous other crystals, their interpretation remains controversial primarily because their linewidths have generally been elusively narrow. Several indirect linewidth determinations have been reported,[2] however, and Fleury and Lyons have obtained a direct measurement of the central peak linewidth in lead germanate.[3]

Various theoretical explanations of the central peak phenomenon have been proposed, including: (i) anharmonic coupling of the soft mode to slowly relaxing degrees of freedom[4-6]; (ii) transitory locally ordered microdomains or solitons[7-10]; (iii) inhomogeneous strain fields produced by impurities or defects[11,12]; and (iv) entropy fluctuations.[3]

In 1974, Lagakos and Cummins observed an unresolved strongly temperature dependent central peak in the light-scattering spectrum of potassium dihydrogen phosphate (KDP) in the paraelectric phase.[13] Subsequent high-resolution interferometric and photon correlation studies[14] of this feature failed to reveal any intrinsic width, and recent visual observations by Durvasula and Gammon[15] strongly suggest that it results from static defects or impurities, as discussed by Axe *et al.*[11] and Halperin and Varma.[12] The origin of this static central peak remains to be conclusively established, although Yagi *et al.* recently found that a similar central peak in potassium trihydrogen selenite gradually disappears on repeated temperature cycling and is thus presumably caused by annealable defects or domain walls.[16]

We have extended our high-resolution interferometric studies of the quasielastic light-scattering spectrum of KDP to the ferroelectric phase ($T < T_c$) and find that in addition to the elastic central peak there is a *dynamic* central peak whose width can be measured directly. (This new central peak may be related to the dynamic central peak in lead germanate.[3])

As we shall demonstrate below, our observations can be interpreted as a special case of anharmonic coupling of the soft mode to density fluctuations of the acoustic phonon gas in which the response function of the ferroelectric soft mode exhibits anomalous structure at low frequencies due to its interaction with the thermal diffusion mode via the temperature dependence of the spontaneous polarization.

EXPERIMENT

The experimental configuration employed was essentially that of Lagakos and Cummins[13] except that two interferometers were used alternately to scan the spectrum. One was a 2-cm pressure-scanned plane Fabry-Perot (FPP: free spectral range = 7.5 GHz), the other was a 25-cm piezoelectrically-scanned spherical Fabry-Perot (FPS: free spectral range = 300 MHz). Periodically, 5145-Å light scattered from a static scatterer was analyzed with the FPS to establish and monitor the instrument profile. All spectra were recorded digitally by a PDP-8E computer. The FPS spectra were analyzed by convoluting a parametrized theoretical function with the experimentally measured instrument profile and adjusting the parameters to produce a best nonlinear least-squares fit to the experimental data. Preliminary tests performed with synthetic data and with Rayleigh scattering from benzene, carbon disulfide, and acetone showed that this procedure could reliably detect linewidths down to about 5 MHz.

A series[17] of $x+z(y,x+z)-x+z$ KDP Brillouin spectra obtained with the two interferometers are shown in Fig. 1. On the right are FPP spectra showing both the central peak (dynamic plus elas-

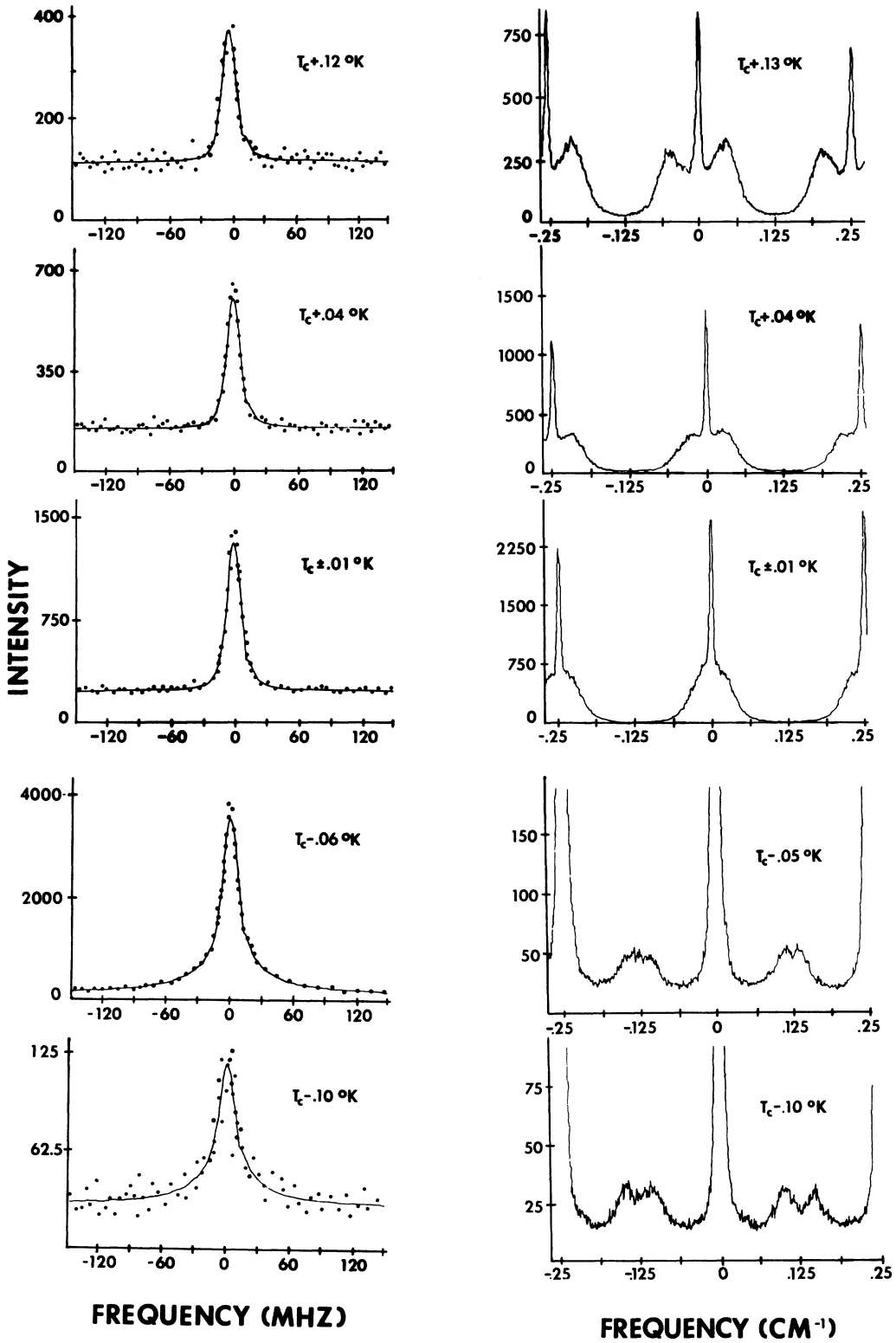

FIG. 1. Brillouin spectra of KDP near the ferroelectric transition. High resolution (FPS) spectra appear on left, exhibiting the temperature dependence of the central peak. Lower resolution Brillouin spectra (FPP) appear on the right, at corresponding temperatures. Note the very rapid movement of the Brillouin peaks just below T_c.

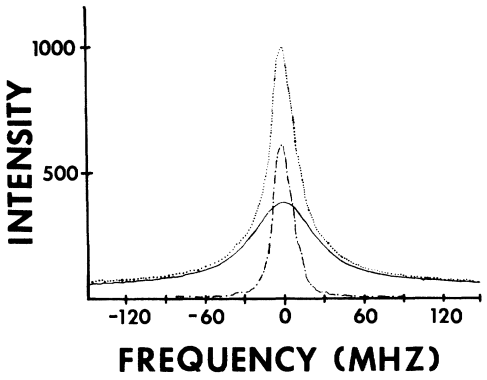

FIG. 2. Computer fit to observed central peak spectrum at $T_c - T = 0.05 \pm 0.02$ °K. •••• represents the nonlinear least-squares fit to the experimental data obtained by the convolution of the measured instrument profile with the trial function (1). •-•- represents that portion of the spectrum due to elastic scattering. —— is the dynamic central peak, that portion of the spectrum due to inelastic scattering.

tic) and the Brillouin components. Corresponding spectra obtained with the FPS are shown on the left.

In each FPS spectrum the experimental points are shown as dots, while the solid curve is a best nonlinear least-squares fit to the data of the convolution of the experimental instrument profile with the trial function

$$I(\omega) = A\delta(\omega) + B\Gamma_c/(\omega^2 + \Gamma_c^2) + \text{C} \qquad (1)$$

where C represents the background, the first term represents the elastic temperature-dependent scattering, and the second term, a Lorentzian of half width Γ_c, represents the dynamic central peak. The new dynamic central peak can be seen in the FPS spectrum at $T = T_c - 0.06$ °K where it appears as a broad "skirt" beneath the elastic component. In Fig. 2 we show the result of the computer fit of this spectrum to Eq. (1). The central-peak linewidth [full width at half maximum (FWHM)] resulting from the computer fit at $T = T_c - 0.06$ °K was 47 ± 6 MHz, while its intensity was estimated to be 13 times larger than that of a transverse Brillouin component. At $T = T_c - 0.1$ °K, the central peak was very weak, as can be seen in Fig. 1, and at $T = T_c - 0.18$ °K it was not visible. The experimental results are summarized in Table I along with the theoretical predictions of the following sections.

COUPLED MODE ANALYSIS

Cowley and his coworkers have considered anharmonic coupling between the soft mode and fluctuations in the acoustic phonon density as the source of central peaks in piezoelectric ferroelectrics such as KDP.[4,18] These density fluctuations include the collective hydrodynamic modes of the acoustic phonon gas which have the same wave vector as the soft mode. In particular, there is a thermal diffusion mode which can couple to the soft mode in the ferroelectric phase where the equilibrium value of the order parameter, $P_3(T)$, is extremely temperature dependent.[19] This thermal diffusion mode can be represented by a relaxational response function as discussed, for example, by Wehner and Klein,[20] leading to a two-coupled-mode picture with an effective bilinear coupling Δ between the soft mode (A) and the thermal diffusion mode (B). The spectrum is given by[21]

$$I(\omega) \propto \sum_{i,j=A,B} P_i P_j G_{ij}(\omega) , \qquad (2)$$

where P_A and P_B are the optical coupling constants and the G_{ij} are solutions of the matrix equation

$$\begin{bmatrix} (G_A^0)^{-1} & \Delta^2 \\ \Delta^2 & (G_B^0)^{-1} \end{bmatrix} \times \begin{pmatrix} G_{AA} & G_{AB} \\ G_{BA} & G_{BB} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} , \qquad (3)$$

where G_A^0 and G_B^0, the response functions of the uncoupled ferroelectric soft mode and entropy mode, are given by

$$G_A^0 = (\omega_\infty^2 - \omega^2 - i\omega\Gamma_A)^{-1} , \qquad (4a)$$

$$G_B^0 = c/(1 - i\omega\tau) . \qquad (4b)$$

If we assume that $P_B = 0$ so that only the ferroelectric mode couples to the light, then

$$I(\omega) \propto P_A^2 \, \mathrm{Im} \left| G_A^0/(1 - G_A^0 G_B^0 \Delta^4) \right| , \qquad (5)$$

TABLE I. Summary of experimental results.

$T_c - T$ (°K)		0.05 ± 0.01	0.06 ± 0.01	0.1	0.18
$\Delta\nu_{FWHM}$ (MHz)	observed	48 ± 6	47 ± 6	39 ± 6	(not observed)
	predicted	61	62	66	85
$\left(\frac{\text{I (Central peak)}}{\text{I (Trans. Brill.)}}\right)$	observed	?	13	?	
	predicted	~35	~32	~26	~18

which, together with the Eq. (4), gives

$$I(\omega) \propto P_A^2 \mathrm{Im}\{1/[\omega_\infty^2 - \omega^2 - i\omega\Gamma_A - c\Delta^4/(1 - i\omega\tau)]\}, \quad (6)$$

which is one of a number of equivalent expressions frequently used to represent the combined soft mode plus central peak spectrum.[5,11,18]

For the case of a heavily overdamped soft mode ($\Gamma_A \gg \omega_\infty$) the spectrum of Eq. (6) separates approximately into two Lorentzians[5]: the soft mode of width $\Gamma_V = \omega_\infty^2/\Gamma_A$ and intensity $\propto 1/\omega_\infty^2$ and the central peak of width $\Gamma_c = (\omega_0/\omega_\infty)^2/\tau$ and intensity $\propto c\Delta^4/\omega_0^2\omega_\infty^2$. The total intensity $\propto 1/\omega_0^2$, where $\omega_0^2 = \omega_\infty^2 - c\Delta^4$ determines the static susceptibility.

For a second-order transition, the central peak linewidth

$$\Delta\nu_{\mathrm{FWHM}}\ (\text{central peak}) = (1/\pi\tau)(\omega_0/\omega_\infty)^2 \quad (7)$$

should approach zero at T_c, even if τ is temperature independent, since ω_0^2 goes to zero while ω_∞^2 is still finite.

In KDP, however, the transition is first order at atmospheric pressure, so that ω_0^2 does *not* reach zero. The maximum narrowing (smallest value of $\omega_0^2/\omega_\infty^2$) should occur at $T = T_c^-$ where we can estimate[22] $\omega_0^2(T_c) \approx 200\ \mathrm{cm}^{-2}$. An estimate of $c\Delta^4$ close to T_c can be deduced from the relative strengths of the central peak and the soft mode. Since the dynamic and elastic central peaks are of similar strength, we can make use of a previous intensity analysis involving the elastic peak just above T_c, which gave[13] $c\Delta^4 \sim 1\ \mathrm{cm}^{-2}$. We therefore have, as a rough approximation, $(\omega_0^2/\omega_\infty^2)_{T=T_c^-} \approx 0.99$ in the ferroelectric phase. Therefore, the central peak linewidth will be indistinguishable from $(\pi\tau)^{-1}$ at all temperatures.

The relaxation time τ of the thermal diffusion mode at $T = T_c - 0.06°$ can be found from available thermal conductivity λ_c and specific heat C_p data[23,24]:

$$\tau = \rho C_p/\lambda_C q^2 = 5.14 \times 10^{-9}\ \mathrm{sec}, \quad (8)$$

with

$$\lambda_C = 1.62 \times 10^5 \mathrm{erg/sec\,°K\,cm},$$

$$C_p = 2.39 \times 10^7 \mathrm{erg/°K\,gm},$$

$$\rho = 2.338 \mathrm{gm/cm^3},$$

and

$$q^2 = 6.71 \times 10^{10}\ \mathrm{cm}^{-2},$$

which predicts a central peak linewidth for $\theta = 90°$ of 62 MHz, in reasonable agreement with our experimental value of 47 ± 6 MHz. The q^2 dependence predicted by Eq. (8) could not be explored in our apparatus which is restricted to $\theta = 90°$.

INTENSITIES

Analysis of the intensities can be most easily accomplished via thermodynamic fluctuation theory which leads to predictions which can be evaluated using the extensive thermodynamic data available for KDP.

The relevant dynamical variables for this problem are the polarization P_3, the xy shear strain x_6, and the entropy S. Solutions to the dynamical equations for these variables yield a ferroelectric mode, a transverse xy acoustic mode, and a thermal diffusion mode. If the equations of motion contained no coupling terms, then the ferroelectric mode would be pure P_3, the transverse acoustic mode pure x_6, and the thermal diffusion mode pure S.

In the paraelectric phase of KDP, neither P_3 nor x_6 couples to the entropy. Therefore, the thermal diffusion mode can be analyzed independently, although the piezoelectric coupling constant a_{36}, which couples P_3 and x_6, hybridizes the acoustic and ferroelectric modes.[25] In the ferroelectric phase however, KDP develops spontaneous shear and polarization which both depend strongly on temperature. Thus fluctuations in the entropy will couple to P_3 and x_6, in addition to the piezoelectric coupling between P_3 and x_6.

The intensity of light scattered by thermodynamic fluctuations in condensed matter is conveniently represented by the Rayleigh ratio (differential cross section per unit volume)

$$R = \frac{1}{V}\frac{d\sigma}{d\Omega} = \frac{\pi^2}{\lambda_0^4} v\langle(\hat{e}_s \cdot \vec{\epsilon}_q \cdot \hat{e}_0)^2\rangle\ \mathrm{cm^{-1}\ sr^{-1}}, \quad (9)$$

where λ_0 is the wavelength of the incident light in the medium, v is the scattering volume, $\hat{e}_0$ and $\hat{e}_s$ are unit polarization vectors of the incident and scattered light, and $\epsilon_q^{\alpha\beta}$ is the qth Fourier component of the fluctuation in the $\alpha\beta$ component of the dielectric tensor.

If the frequency ranges of the dynamical modes are well separated, $\epsilon_q^{\alpha\beta}$ can be separated into distinct contributions from each mode and the total intensity for that mode can be predicted from Eq. (9).

The intensity of light scattered by the thermal diffusion (TD) mode will be proportional to

$$\langle\epsilon_{\alpha\beta}^2\ (\mathrm{TD})\rangle = \left(\frac{\partial\epsilon_{\alpha\beta}}{\partial S}\right)_p^2 \langle S_q^2\rangle, \quad (10)$$

where $\langle S_q^2\rangle$ is the mean square entropy fluctuation. Equation (10) reduces, via standard thermodynamic relations, to[26]

$$\langle\epsilon_{\alpha\beta}^2\ (\mathrm{TD})\rangle = \frac{1}{v}\left(\frac{\partial\epsilon_{\alpha\beta}}{\partial T}\right)_p^2 \frac{kT^2}{\rho C_p}. \quad (11)$$

Since entropy fluctuations occur very slowly com-

pared to the characteristic times of P_3 and x_6, we assume that the spontaneous polarization P_3 and shear strain x_6 remain in thermodynamic equilibrium with S. Then

$$\left(\frac{\partial \epsilon}{\partial T}(\mathrm{TD})\right)^2 = \left[\left(\frac{\partial \epsilon}{\partial T}\right)_{x,P} + \left(\frac{\partial \epsilon}{\partial x}\right)_{T,P}\left(\frac{\partial x}{\partial T}\right) + \left(\frac{\partial \epsilon}{\partial P}\right)_{T,x}\left(\frac{\partial P}{\partial T}\right)\right]^2 \tag{12}$$

(where all derivatives are at constant zero stress). The first term on the right-hand side of Eq. (12) includes both the direct and indirect (thermal expansion) components of $\epsilon_{\alpha\beta}$ (TD).[3,20] The two new terms represent additional indirect optical coupling via the temperature dependence of the spontaneous strain x_6 and polarization P_3.

The "normal" term $(\partial\epsilon/\partial T)_{x,P}$ which accounts for the nonsingular central peak in $KTaO_3$ observed by Lyons and Fleury[3] is only expected to occur in diagonal polarization. Its value for KDP in the paraelectric phase can be estimated from the refractive index measurements of Yamazaki and Ogawa,[27,28] $(\partial\epsilon/\partial T)_{x,P} \sim 1\times10^{-4}$. (We note that this term may exhibit anomalous behavior near T_c where there is an apparent anomaly in the thermal expansion coefficient.[28])

The 2nd and 3rd terms in Eq. (12) vanish in the paraelectric phase since $x_6(T)$ and $P_3(T)$ are both zero for $T>T_c$. For $T<T_c$, the spontaneous polarization $P_3(T)$, as measured by Benepe and Reese,[19] is given by[29]

$$P_3(T) = 1.06\times10^4(T_c - T + 0.026)^{1/6}\ \mathrm{esu/cm^2}, \tag{13}$$

$$\frac{\partial P_3}{\partial T} = -1.77\times10^3(T_c - T + 0.026)^{-5/6}\ \mathrm{esu/cm^2\,^\circ K}. \tag{14}$$

The spontaneous shear strain $x_6(T)$ which is proportional to $P_3(T)$[30] can be obtained from the experimentally observed shear (~1000 sec at $T=T_c - 1\,^\circ$K)[31] and Eq. (13). The 2nd and 3rd terms in Eq. (12) for ϵ_{xy} (TD) at $T<T_c$ are given in terms of the usual electro-optic and elasto-optic coefficients by[28]

$$\left[\epsilon_0^2 p_{66}^P \frac{\partial x_6}{\partial T} + \epsilon_0^2 \rho_{63}^x \frac{\partial P_3}{\partial T}\right], \tag{15}$$

where p_{66}^P is the Pockel's (elasto-optic) coefficient and ρ_{63}^x is the electro-optic coefficient.

Substituting available numerical values[32] for the thermodynamic parameters in Eq. (15) then gives the cross sections for diagonal ($\alpha\alpha$) and depolarized (VH) scattering from the thermal diffusion mode:

$$R_{\alpha\alpha}(\mathrm{TD}) \cong \left(\frac{\pi^2}{\lambda_0^4}\frac{kT^2}{\rho C_p}\right)[1\times10^{-4}]^2, \tag{16a}$$

$$R_{VH}(\mathrm{TD})_{T>T_c} = 0, \tag{16b}$$

$$R_{VH}(\mathrm{TD})_{T<T_c} = \frac{1}{2}\frac{\pi^2}{\lambda_0^4}\frac{kT^2}{\rho C_p}[1.4\times10^{-4}(T_c - T + 0.026)^{-5/6} + 1.88\times10^{-3}(T_c - T + 0.026)^{-5/6}]^2. \tag{16c}$$

Note that it is the polarization term rather than the strain term which dominates in (16c). At $T=T_c^-$, the quantity in square brackets in Eq. (16c) is $\sim4.2\times10^{-2}$, so that the VH cross section should be $\sim10^5$ times greater than the "normal" thermal diffusion diagonal cross section of Eq. (16a).

The VH intensity of the central peak is thus seen to be primarily due to the admixture of polarization fluctuations in the thermal diffusion mode in agreement with the assumptions made in our coupled modes discussion, while the observed dramatic temperature dependence of the intensity comes from the coupling $\partial P_3/\partial T$ via the term $[(T_c - T + 0.026)^{-5/6}]^2$ in Eq. (16c) which decreases ~14 times between T_c and $T_c - 0.1\,^\circ$K.

The theoretical cross sections of Eq. (16) are plotted in Fig. 3 along with cross sections for the

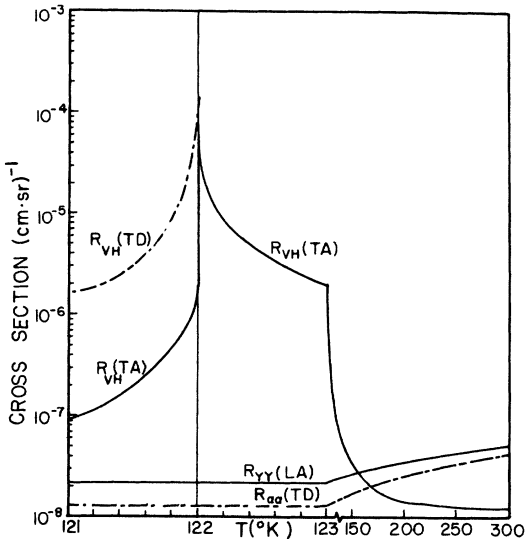

FIG. 3. Calculated cross sections (Rayleigh ratios) for thermal diffusion (TD), longitudinal acoustic (LA) and transverse acoustic (TA) modes in KDP. The "normal" thermal diffusion component $R_{\alpha\alpha}$(TD) was estimated from data well above the transition and does not show possible anomalies near T_c. $R_{\alpha\alpha}$(TD) and R_{VH}(TD) are from Eqs. (16) in the text.

transverse and longitudinal Brillouin components.[33,34] The figure shows that the dynamic central peak cross section should exceed that of the strong transverse Brillouin component in the ferroelectric phase and is highly temperature dependent, in agreement with the experimental observations. At $T = T_c - 0.06°$, the central peak intensity is predicted to be ~30 times greater than that of the transverse Brillouin component, which compares reasonably with our rough experimental estimate of 13 for tnis ratio.

In conclusion, we have shown that the dynamic central peak that we have observed in ferroelectric KDP can be viewed as the low-frequency structure of the ferroelectric soft mode induced by its coupling to the slowly relaxing thermal diffusion mode via the strongly temperature-dependent spontaneous polarization. The analysis has succeeded in explaining both the width and intensity of this new feature. We note that this mechanism is not restricted to ferroelectrics but should apply to *all* structural phase transitions since the order parameter always couples to entropy fluctuations in the ordered phase through its temperature dependence. Indeed, related effects have previously been observed near magnetic transitions.[5]

The results of the present experiments can be explained entirely by the simple thermodynamic analysis since the critical narrowing of the central peak predicted by the relaxing self-energy formulation has not been observed, and is inaccessible at atmospheric pressure due to the first-order nature of the KDP transition. However, recent experiments by Schmidt *et al.*[35] indicate that the ferroelectric transition in KDP may become second order under hydrostatic stress. Additional light-scattering experiments under stress are currently being planned in order to test the predicted critical narrowing of the dynamic central peak.

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