Dynamic central-peak-linewidth renormalization and the piezothermoelastic response in ferroelectric KH₂PO₄

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Extensive light scattering data are presented which characterize the temperature dependence of the heat-diffusion central-peak linewidth and intensity in ferroelectric KH_2PO_4 . The equations of motion for the complete coupled polarization, strain, and thermal-diffusion modes are constructed. The resultant susceptibility leads to predictions for the intensity and linewidth that are in agreement with experiment. In particular, it is found that the linewidth renormalization coefficient is equal to ratio of the isothermal to adiabatic dielectric impermeabilities. It is shown that in the ferroelectric phase, coupling of temperature fluctuations to the spontaneous polarization introduces additional "thermal inertia" resulting in a slowing down of the thermal-diffusion process and a corresponding decrease in the dynamic central-peak linewidth.

I. INTRODUCTION

In 1970 Cowley¹ first demonstrated that the softmode response function for a piezoelectric ferroelectric crystal could yield a three-peaked spectrum. In addition to the usual soft-mode sidebands, the spectrum would exhibit a new, third, quasielastic component resulting from the coupling of the soft mode to some unspecified slow relaxation process. The intensity of this central peak is expected to increase dramatically as the transition is approached while the linewidth is expected to decrease. In 1971 Riste et al.² reported the first observation of a central peak in the neutron scattering spectrum of SrTiO₃ in the vicinity of the 105-K structural transition. This launched an extensive amount of theoretical and experimental research into the central-peak problem which has been well reviewed elsewhere.³

Light-scattering investigations of the central peak in KH₂PO₄ (KDP) have had a particularly fruitful history. Lagakos and Cummins⁴ first observed an unresolvable, highly temperature-dependent central peak in the Brillouin spectrum of the X_{ν} shear mode and the B_2 optic modes in paraelectric KDP close to the ferroelectric transition. Visual and photographic examinations of the laser scattering column by Durvasula and Gammon⁵ established the presence of speckle interference fringes characteristic of a static scattering mechanism. The specific mechanism suggested is an X_y shear-strain decoration of static lattice defects. Subsequently, Courtens⁶ showed that this static central peak (SCP) can be essentially removed from the spectrum by suitable annealing of wellgrown crystals, thereby verifying the crucial role played by annealable lattice defects. Hence, this SCP is understood to be an extrinsic phenomenon resulting from defect-induced inhomogeneous strain fields which grow in amplitude and range as the crystal softens in the vicinity of the transition. Theoretical investigations of defect-induced SCP's have been well developed in the literature.⁷

In 1977 Mermelstein and Cummins⁸ published a preliminary report of a clearly resolvable dynamic central peak (DCP) in KDP. This strongly temperature-dependent feature appears within 0.1 K of the transition and exhibits a linewidth of approximately 70 MHz. This DCP is identified with the low-frequency structure of the ferroelectric soft-mode fluctuations due to the coupling of the soft-mode coordinates equilibrium position to the slow thermaldiffusion (TD) mode. For the electrically shorted crystal, i.e., with zero electric field, this equilibrium position is the strongly temperature-dependent spontaneous polarization $P_s(T)$ and is therefore nonzero only in the ferroelectric phase. Application of an external electric field along the ferroelectric axes produces a DCP in the paraelectric phase where the soft-mode equilibrium position becomes nonzero due to the field-induced net polarization.⁹

The dynamical problem of the interacting soft and thermal-diffusion modes in the low-temperature phase has been treated previously by several authors. Pytte and Thomas¹⁰ first demonstrated that in a first-order displacive transition the thermal diffusivity is renormalized by its interaction with the soft mode as the transition is approached from below. The renormalization coefficient is equal to the ratio of the isothermal to adiabatic dielectric impermeabilities. This result is also contained in the hydrodynamic calculation by Ohnari and Takada.¹¹ Courtens and Gam-

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mon¹² have recently constructed the equations of motion for the coupled polarization, strain, and thermal-diffusion modes in KDP, thereby elucidating the complete dynamics for this ferroelectric system.

The intent of this paper is to supplement our preliminary report with more extensive data characterizing this heat-diffusion central peak appearing in the ferroelectric KDP with zero electric field. In order to facilitate a clear interpretation of the linewidth measurements presented here, special attention is directed towards formulating the piezothermoelastic response function for the ferroelectric system. It is demonstrated that coupling of the thermal-diffusion mode to the spontaneous polarization slows down the thermal diffusion process, thereby producing a renormalized DCP linewidth.

II. EXPERIMENT

The experimental configuration and general procedure have been discussed earlier and will not be discussed in detail here.⁸ The sample used in these experiments was a commercially grown crystal of exceptionally high optical quality.¹³ The crystal was oriented and cut by the manufacturer and polished in this laboratory. The temperature-controlling apparatus was upgraded to achieve a temperature stability of ± 2 mK over a period of an hour. Furthermore, the temperature could be maintained at the transition point for a period of several days, facilitating extended experiments. These thermal conditions were essential since the DCP appears in a very limited temperature range with a severely temperature sensitive intensity.

The crystal was cooled to approximately 0.2 K below T_c^+ and allowed to come to thermal equilibrium.¹⁴ The transition temperature T_c^+ was estimated by noting when the DCP first appeared upon cooling. The temperature was then slowly increased by small increments. After each temperature increment, the crystal was allowed to come to thermal equilibrium as indicated by the thermometer. This would take typically 20-30 min. Once the temperature stabilized, the scattered light was scanned by the piezoelectrically driven 25-cm spherical Fabry-Perot interferometer (FPS). The spectra were recorded by a PDP-8E minicomputer. At each temperature three separate spectra were taken. This procedure was continued as the temperature was gradually increased up through the transition. The transition temperature T_c^{-} was taken to lie between the temperatures corresponding to the last spectrum exhibiting the DCP and the first spectrum with no DCP.

The digitally recorded FPS spectra were transferred to the PDP-10 computer and subsequently analyzed by convoluting an experimentally measured instrument profile with a parametrized theoretical function representing the DCP.¹⁵ These parameters were varied in a nonlinear least-squares-fitting routine to produce the best fit to the experimental data. The instrument profile was conveniently measured by recording the spectrum of the SCP just above the transition, since it is known that this is an elastic feature (as discussed above). The computer analysis of the spectra yield two principle quantities: the integrated intensity and the linewidth.

In Fig. 1 the relative integrated intensity of the DCP as a function of T_c -T is presented on a log-log plot. These intensities were measured relative to the laser intensity entering the light scattering Dewar. Shown are the results for two separate experiments, indicated by opened and closed circles, performed on the same crystal under identical experimental conditions. The solid line and the differential cross section per unit volume, R, will be discussed below in the interpretation.

Several nonlinear least-squares-fitting runs, with different initial parameter values, were made on each of the three spectra corresponding to a single temperature. The best fits for each of the three spectra were retained. The intensity error bars correspond to the standard deviation of the intensities of these three fits. The temperature error bars primarily result from the uncertainty in the transition temperature which for these two experiments was ± 0.005



FIG. 1. Log-log plot of the dynamic central-peak relative integrated intensity as a function of the temperature difference below the transition temperature T_c . The ordinate axis is expressed in terms of the differential scattering cross section per unit volume R. The solid line is the prediction for R(DCP) expressed by Eq. (23). The data points, shown by the opened and closed circles, have all been rescaled by matching the prediction and experimental data point indicated by the arrow. The intensity and temperature error bars are discussed in the text.



FIG. 2. Dynamic central-peak linewidth data (full width at half maximum) as a function of temperature difference below the transition point. The open and closed circles represent two sets of data. The error bars are determined in the same manner as those in the intensity measurements.

and ± 0.010 K. The DCP intensity is seen to increase by approximately 20 times over the observable temperature range.

The linewidth measurements (full width at half maximum) are presented in Fig. 2. The linewidth variation with temperature is seen to be relatively flat with values lying in the range of approximately 60 to 85 MHz. These measurements were performed with a 90° scattering angle in the x + z(y, x + z) - x + z geometry. The construction of the light scattering Dewar did not permit a variation in the scattering angle so that we were unable to verify the expected q^2 dependence to the DCP linewidth.

III. EQUILIBRIUM PROPERTIES

In a piezothermoelastic material the thermodynamic state variables, which for the purposes of this presentation are taken to be the polarization \vec{P} , the elastic strain tensor \vec{e} , and the scalar temperature T, are all interdependent.¹⁶ In general, there is a total of ten state variables: three polarization-vector components, six strain-tensor components (excluding rotations), and the scalar temperature. The equilibrium state of the crystal may be found from the Helmholtz free-energy density $A(\vec{r})$ which is a function of the equilibrium state variables:

$$A(\vec{r}) = A(\vec{P}, \vec{e}, T) \quad . \tag{1}$$

The particular values of the state variables are determined by minimizing the free-energy density. The piezoelectric ferroelectric crystal in the polar phase represents a particularly simple example of a piezothermoelastic substance in the sense that the state variables are linearly coupled in the simplest approximation. In the Landau-Devonshire theory^{17, 18, 25} of the ferroelectric transition in KDP, the free-energy density is expanded in terms of the order parameter: the polarization along the crystallographic z direction, P_3 . Since the crystal is piezoelectric with P_3 coupling to the e_6 shear strain, terms representing the elastic contribution to the free-energy density are included. The Helmholtz free-energy density may then be written

$$A = \frac{1}{2} \alpha P_3^2 + \left(\frac{1}{2} C_{66}^{P_T} e_6^2 - a_{36}^T e_6 P_3\right) + \phi(P_3) + \frac{1}{2} \kappa |\nabla P_3|^2 + A_1(T) \quad .$$
(2)

In the usual Landau approach, the coefficient α is assumed to have the following temperature dependence:

$$\alpha = \alpha_0 \left(T - T_0^e \right) \quad , \tag{3}$$

where T_6^{e} is the clamped Curie temperature. The saturation function ϕ contains higher than quadratic terms in P_3 which are permitted by symmetry, $C_{66}^{P,T}$ is the background elastic constant associated with e_6 , and a_{36}^{T} is the isothermal piezoelectric coupling coefficient. The damping of spatial fluctuations of increasing wave vector is expressed in the gradient term¹⁹ and contributions to A due to lattice degrees of freedom that do not participate in the transition are contained in A_1 . In the following it is assumed that the spatial fluctuations of interest are of sufficiently long wavelength that they do not significantly contribute to A and are therefore neglected. For the stress-free crystal, the free-energy density may be rewritten in the simpler form

$$A = \frac{1}{2}\alpha_0 (T - T_0^{\sigma}) P_3^2 + \phi + A_1^{-1} , \qquad (4)$$

where T_0^{σ} is the free Curie temperature

$$T_0^{\sigma} = T_0^{e} + \frac{a_{36}^{T^2}}{\alpha_0 C^{P,T}}$$
(5)

and the strain is proportional to the polarization

$$e_6 = \frac{a_{36}^7}{C_{66}^{P_0 T}} P_3 \quad . \tag{6}$$

Since the transition is first order, the transition occurs at the higer temperature T_c .

The constitutive equations are material-dependent relations between the state variables and the conjugate variables. The variables conjugate to the polarization P_3 , strain e_6 , and temperature T are the electric field E_3 , stress σ_6 , and entropy S, respectively. These constitutive equations for KDP are determined by the free energy A and are constructed in the Appendix.

IV. FLUCTUATIONS AND THE EQUATIONS OF MOTION

The state variables will spontaneously fluctuate about their equilibrium positions.¹⁷ It is assumed that the constitutive relations for the time-dependent fluctuating components have the same form as those for the equilibrium values:

$$\delta E = \beta^{e,T} \delta P + d^{P,T} \delta e + t^{P,e} \delta T + \delta E^{ap} \quad , \tag{7a}$$

$$\delta \sigma = d^{e,T} \delta P + K^{P,T} \delta e + f^{P,e} \delta T + \delta \sigma^{ap} \quad , \tag{7b}$$

$$\delta S = t^{e,T} \delta P + f^{P,T} \delta e + \frac{\tilde{C}^{P,e}}{T} \delta T + \delta S^{ap} \quad . \tag{7c}$$

The fourth terms on the right-hand side of Eqs. (7) represent fictitious applied fluctuations in the conjugate variables which serve to "drive" the naturally occurring thermodynamic fluctuations. These relations implicitly assume that the responses are instantaneous, since no retardation effects are included, and that the fluctuations are small since the susceptibilites are assumed to be unchanged by the fluctuations.

The polarization dynamics may be formulated in a model calculation that has met with considerable success in characterizing the Raman spectrum.²⁰ Fluctuations in the polarization $\delta P(\vec{\tau}, t)$ are represented by the displacement of an effective charge Q of mass M through a distance $\delta z(\vec{\tau}, t)$ along the z axis. If Nis the number density of such charges, then the polarization resulting from such a displacement is: $\delta P = NQ \, \delta z$. The displacement of the charge Q will be accompanied by a fluctuation in the local electric field $\delta E(\vec{\tau}, t)$ which thereby exerts a restoring force. Hence, the equation of motion for the charge is

$$M\delta \ddot{z}(\vec{r},t) + Q\delta E(\vec{r},t) = 0$$
(8)

The constitutive equations show that the fluctuations in the electric field can be decomposed into contributions from the polarization, strain, and temperature. Use of Eq. (7a) and the definition of the polarization yield the following equation of motion for the polarization:

$$\tilde{Q}^{-1}\delta \ddot{P} + \beta^{e,T}\delta P + d^{P,T}\delta e + t^{P,e}\delta T = -\delta E^{ap} \quad , \quad (9a)$$

where $\tilde{Q} = NQ^2/M$. In the absence of piezoelectric and electrothermal coupling, this model is equivalent to a simple harmonic oscillator in which the charge oscillates with a harmonic resonant frequency squared proportional to the clamped isothermal dielectric impermeability $\omega_p^2 = \tilde{Q} \beta^{e,T}$.

The equations of motion for the strain and temperature proceed from more fundamental considerations. The dynamics of the strains are governed by the elastic wave equation.²¹ For the specific case of the e_6 shear strain propagating in the \hat{x} direction with wave vector \vec{q} , the wave equation is

$$\rho \frac{\partial^2 \delta u_y(\vec{r},t)}{\partial t^2} + \frac{\partial \delta \sigma(\vec{r},t)}{\partial x} = 0 \quad , \tag{10}$$

where ρ is the density of the material and $u_y(\vec{\tau},t)$ is the local displacement field in the \hat{y} direction. The strain and displacement are related by $e_6 = iqu_y$. Here use has been made of the plane-wave approximation and the definition of the e_6 shear strain. This, along with Eq. (7b) yield the equation of motion for the X_y shear strain

$$+ iqd^{e,T}\frac{\partial\delta P}{\partial x} + \rho \frac{\partial\delta e}{\partial t^2} + iqK^{P,T}\frac{\partial\delta e}{\partial x} + iqf^{P,e}\frac{\partial\delta T}{\partial x} = -iq\frac{\partial\delta\sigma^{ap}}{\partial x} \quad . \tag{9b}$$

The rate of change in entropy $S(\vec{r},t)$ is related to the heat flux $\vec{j}(\vec{r},t)$ by the heat diffusion equation in local form²²:

$$T\delta \dot{S}(\vec{r},t) = -\vec{\nabla} \cdot \vec{j}(\vec{r},t) \quad . \tag{11}$$

Fluctuations in the temperature produce a flow of heat governed by Fourier's law of heat conduction:

$$\vec{j}(\vec{r},t) = -\vec{\lambda} \cdot \vec{\nabla} \delta T(\vec{r},t)$$

where $\vec{\lambda}$ is the thermal conductivity tensor. This relation is simplified by assuming that the conductivity tensor is both isotropic and constant, in which case we have²³

$$\vec{\mathbf{j}}(\vec{\mathbf{r}},t) = -\lambda_0 \vec{\nabla} \delta T(\vec{\mathbf{r}},t)$$

Constitutive Eq. (7c) shows that changes in entropy are induced by polarization and strain fluctuations, via the heat of polarization and heat of deformation effects, respectively, as well as by temperature fluctuations. Hence the complete heat-conduction equa-

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tion is

$$Tt^{e,T}\delta\dot{P} + Tf^{P,T}\delta\dot{e} + \tilde{C}^{P,e}\left[\delta\dot{T} + \frac{\lambda_0}{\tilde{C}^{P,e}}\nabla^2\delta T\right] = -\delta W^{ap} ,$$

(9c)

where $\delta W^{ap} = T \delta \dot{S}^{ap}$ is the fictitious applied heat source expressed in units of power.

Equations (9) may be put into more suitable form by taking the space-time Fourier transform of the state variables, represented collectively by η

$$\eta(\vec{\mathbf{q}}, \boldsymbol{\omega}) = \int_{-\infty}^{+\infty} dt \ e^{-i\boldsymbol{\omega}t} \times \int_{V} d^{3}r \ e^{i\vec{\mathbf{q}}\cdot\vec{\mathbf{r}}} \eta(\vec{\mathbf{r}}, t)$$

The three equations of motion (9) may now be written in compact matrix notation as

$$\vec{\mathbf{Y}}^{ap}(\vec{\mathbf{q}},\omega) = [\vec{\mathbf{G}}(\vec{\mathbf{q}},\omega)]^{-1} \vec{\mathbf{X}}(\vec{\mathbf{q}},\omega)$$
(12)

where $[\vec{G}]^{-1}$ is the inverse piezothermoelastic susceptibility of the ferroelectric system and is given by

$$[\vec{G}(\vec{q},\omega)]^{-1} = \begin{pmatrix} [G_P^0(\vec{q},\omega)]^{-1} & -d^{P,T} & -t^{P,e} \\ -d^{e,T} & [G_e^0(\vec{q},\omega)]^{-1} & -f^{P,e} \\ i\,\omega\,Tt^{e,T} & i\,\omega\,Tf^{P,T} & [G_T^0(\vec{q},\omega)]^{-1} \end{pmatrix} .$$
(13)

The state vector \vec{X} and the driving vector \vec{Y}^{ap} are

$$\vec{X}(\vec{q},\omega) = \begin{pmatrix} \delta P(\vec{q},\omega) \\ \delta e(\vec{q},\omega) \\ \delta T(\vec{q},\omega) \end{pmatrix}, \quad \vec{Y}^{ap}(\vec{q},\omega) = \begin{pmatrix} \delta E^{ap}(\vec{q},\omega) \\ \delta \sigma^{ap}(\vec{q},\omega) \\ \delta W^{ap}(\vec{q},\omega) \end{pmatrix}.$$
(14)

The uncoupled polarization, elastic, and thermal susceptibilities are, by definition: polarization

$$G_{P}^{0}(\vec{\mathbf{q}},\omega) \equiv \frac{\delta P(\vec{\mathbf{q}},\omega)}{\delta E^{ap}(\vec{\mathbf{q}},\omega)}\Big|_{e,T}$$
$$= \frac{\tilde{Q}}{\omega^{2} - \omega_{p}^{2}}, \quad \omega_{p}^{2} = \tilde{Q}\beta^{e,T} , \quad (15a)$$

elastic

$$\begin{aligned} G_{e}^{0}(\vec{q},\omega) &= \frac{\delta e(\vec{q},\omega)}{\delta \sigma^{ap}(\vec{q},\omega)} \Big|_{P,T} \\ &= -\frac{q^{2}/\rho}{\omega^{2} - \omega_{a}^{2}}, \quad \omega_{a}^{2} = \left(\frac{C_{\delta\delta}^{P,T}}{\rho}\right) q^{2} \quad , \quad (15b) \end{aligned}$$

thermal

$$G_T^0(\vec{q},\omega) = \frac{\delta T(\vec{q},\omega)}{\delta W^{ap}(\vec{q},\omega)} \Big|_{P,e}$$
$$= -\frac{\tau/\tilde{C}^{P,e}}{1-i\omega\tau}, \quad \tau^{-1} = D^{P,e}q^2, \quad D^{P,e} = \frac{\lambda_0}{\tilde{C}^{P,e}} \quad .$$
(15c)

The background thermal diffusion relaxation time is τ and the background thermal diffusivity is $D^{P.e.}$. The free-energy expansion discussed above predicts that the heat of deformation coefficient $f^{P,T}$ and the thermal pressure coefficient $f^{P,e}$ are both zero while the electrothermal coefficient $t^{P,e}$ and the heat of polarization coefficient $t^{e,T}$ are equal in magnitude and opposite in sign with $t^{P,e} = \alpha_0 P$. Therefore, temperature fluctuations directly couple only to the polarization fluctuations in the ferroelectric phase where P is nonzero. The piezoelectric coefficient $d^{P,T}$ is equal to $-a^T$ and $d^{e,T}$ is equal to $+a^T$.

V. SPECTRUM OF SCATTERED LIGHT

The light scattering spectrum is given by the classical fluctuation-dissipation theorem together with the far-field dipole approximation as^{24}

$$I_{s}(\vec{\mathbf{q}},\omega,r) = nK \left(\frac{k_{B}T}{\pi \omega} \right) \sum_{i,j} P_{i}P_{j} \operatorname{Im} G_{ij}(\vec{\mathbf{q}},\omega) \quad . \quad (16)$$

 I_s is the intensity of light scattered with wave vector \vec{q} and frequency ω , and detected at a distance r from the scattering center. n is a numerical factor resulting from the specific scattering geometry which for these experiments is $n = \frac{1}{2}$. The constant K is determined by experiment and is $K = \pi^2 I_0 V^2 / \lambda^4 r^4$, where I_0 is the incident laser intensity, λ is the laser wavelength in the medium, and V is the scattering volume. The optical coupling coefficients P_i connect the fluctuations in the optical dielectric constant to the fluctuations in the state variables. The dynamics of the coupled mode system are contained in the tensor components $G_{ij}(\vec{q}, \omega)$ which are the susceptibilities of the *i*th state variable to driving by the *j*th conjugate variable. The complete 3×3 tensor $\vec{G}(\vec{q}, \omega)$ is obtained

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by taking the matrix inverse of Eq. (13). Previously we have shown that the dominant scattering mechanism results from electro-optic coupling, in which case (16) reduces to

$$I_{s}(\vec{q}, \omega, r) = \frac{1}{2} K \left(\frac{k_{B}T}{\pi \omega} \right) P_{P}^{2} \operatorname{Im} G_{PP}(\vec{q}, \omega) \quad , \quad (17)$$

where $\rho_{63}^{e,T} = P_P/n_0^4$ is the electro-optic coupling coefficient, n_0 is the ordinary refractive index, and $G_{PP}(\vec{q}, \omega)$ is the polarization response to electric field driving:

$$G_{PP}(\vec{q},\omega) = \frac{\delta P(\vec{q},\omega)}{\delta E^{ap}(\vec{q},\omega)} \bigg|_{s,\sigma} ,$$

$$G_{PP}(\vec{q},\omega) = \left(\frac{\omega^2 - \omega_P^2}{\tilde{Q}} - \frac{a^2 q^2 / \rho}{\omega^2 - \omega_P^2} + \frac{i\omega\tau\Delta^2}{1 - i\omega\tau}\right)^{-1} . (18)$$

Here we recognize the "adiabatic correction term," $\Delta^2 = \alpha_0^2 T P^2 / \tilde{C}^{P,e}$, which reflects the stiffening of the adiabatic responses.²⁵ This susceptibility represents

the response, without approximation, over the entire frequency range, as predicted by the equations of motion (9).

At this point it is worthwhile to pause a moment and examine the polarization response function (18). The intensity spectrum of the scattered light may be approximated by investigating the three principle frequency ranges; the thermal diffusion range ($\omega \tau \simeq 1$), the acoustic phonon range $(\omega^2 \simeq \omega_a^2)$, and the optical phonon range $(\omega^2 \simeq \omega_p^2)$. The spectrum predicted by Eqs. (17) and (18) will exhibit five peaks; a quasielastic Rayleigh component whose linewidth is determined by the renormalized thermal diffusion mode relaxation time $\tau' = (\beta^{\sigma,S}/\beta^{\sigma,T})\tau$, two Brillouin sidebands whose renormalized harmonic resonant frequency squared is $\omega_a^{\prime 2} = (\beta^{\sigma,S} / \beta^{e,S}) \omega_a^2$, and two Raman sidebands whose renormalized harmonic resonant frequency squared is $\omega_p^{\prime 2} = (\beta^{e,S} / \beta^{e,T}) \omega_p^2$. By introducing phenomenological damping coefficients Γ_a and Γ_p for the acoustic and polarization modes, respectively, the complete light scattering spectrum may be approximated by

$$I_{s}(\vec{q},\omega,r) = \frac{1}{2} K \left(\frac{k_{B}T}{\pi} \right) P_{p}^{2} \left[\left(\frac{\Delta^{2}}{\beta^{\sigma,T} \beta^{\sigma,S}} \right) \left(\frac{\tau'}{1 + (\omega\tau')^{2}} \right)_{\text{Rayleigh}}^{\text{DCP}} + \left(\frac{a^{2}/C^{P,T}}{\beta^{e,S} \beta^{\sigma,S}} \right) \left(\frac{\omega_{a}^{\prime 2} \Gamma_{a}}{(\omega^{2} - \omega_{a}^{\prime 2})^{2} + (\omega\Gamma_{a})^{2}} \right)_{\text{Brillouin}} + \left(\frac{\tilde{Q} \Gamma_{p}}{(\omega^{2} - \omega_{p}^{\prime 2})^{2} + (\omega\Gamma_{p})^{2}} \right)_{\text{Raman}} \right].$$

$$(19)$$

The quasielastic component (first term on the righthand side) is recognized as the DCP resulting from the interaction of the ferroelectric soft mode and the thermal diffusion mode. Here we have the crucial result that the DCP linewidth is equal to the renormalized thermal diffusion mode linewidth

$$\Gamma^{\rm DCP} = \mu \Gamma^{\rm TD} \quad (20a)$$

where

$$\Gamma^{\rm TD} = 1/\pi\tau \quad . \tag{20b}$$

The linewidth renormalization coefficient μ is equal to the ratio of the isothermal to adiabatic-free dielectric impermeabilities

$$\mu = \frac{\beta^{\sigma, T}}{\beta^{\sigma, S}} \quad . \tag{21a}$$

The renormalization of the acoustic harmonic resonant frequency squared, ω_a^2 , means that the velocity of sound is determined by the adiabatic elastic constant at constant electric field (as opposed to constant polarization). Physically, this reflects the fact that the rapid polarization fluctuations are able to maintain thermodynamic equilibrium with the relatively slow strain fluctuations. The renormalization of the harmonic polarization resonant frequency squared, ω_p^2 , indicates that these rapid fluctuations occur adiabatically.

The DCP integrated intensity, expressed via the Rayleigh ratio R, may be found by direct integration over frequency of the quasielastic component in Eq. (19):

$$R^{\rm DCP} = \frac{I_s^{\rm DCP}(\text{int})}{I_0 V} r^4$$
$$= \frac{\pi^2}{2\lambda^4} n_0^8 \left(\rho_{63}^{e,T}\right)^2 V k_B T \left(\frac{\Delta^2}{\beta^{\sigma,T} \beta^{\sigma,S}}\right) , \qquad (22a)$$

where

$$\beta^{\sigma,S} = \beta^{\sigma,T} + \Delta^2 \quad (22b)$$

By use of several thermodynamic identities, 26 it may be shown that Eq. (22a) is equal to our previous result

$$R^{\rm DCP} = \frac{\pi^2}{2\lambda^4} n_0^8 \left(\rho_{63}^{e,T}\right)^2 \left(\frac{\delta P}{\delta T}\right)_{\sigma,E}^2 \frac{k_B T^2}{\rho \tilde{C}^{\prime\sigma,E}} , \qquad (23)$$

where $\tilde{C}^{\prime\sigma,E}$ is the specific heat per unit mass at constant stress and field. The ratio of the DCP intensity to the total intensity resulting from the polarization fluctuations is²⁷

$$r = \frac{R^{\text{DCP}}}{R^{\text{tot}}} = \frac{\beta^{\sigma, S} - \beta^{\sigma, T}}{\beta^{\sigma, S}} \quad .$$
(24)

This leads to the simple connection between the intensity ratio r and the linewidth renormalization coefficient μ :

$$r = 1 - \mu \tag{25}$$

thereby relating two experimentally accessible quantities.

VI. COMPARISON WITH EXPERIMENT

The DCP linewidth measurements as a function of temperature are tabulated in Table I in the first two columns. In the third column are the linewidth results for the DCP linewidth renormalization coefficient μ determined by the ratio of the DCP and TD

mode linewidths. In the absence of a direct linewidth measurement, the bare TD mode linewidth is estimated from the thermal conductivity and back-ground specific heat to be $\Gamma^{\text{TD}} = 320 \text{ MHz.}^{28}$ By a thermodynamic identity, μ may also be expressed by the ratio of the specific heat at constant polarization and strain and the specific heat at constant field and stress:

$$\mu = \tilde{C}^{P,e} / \tilde{C}^{E,\sigma} \quad . \tag{21b}$$

Specific-heat results for μ were taken from the measurements by Reese and May²⁹ and are listed in column four. I have assumed that the transition temperature in the specific-heat experiments corresponds to the peak in the data. It is seen that the agreement between the specific-heat measurements and the DCP linewidth measurements is quite good.

The DCP linewidth renormalization lends itself to a rather simple physical interpretation. In the paraelectric phase, the TD mode is not coupled to the order parameter so that its relaxation time τ is proportional to the background specific heat $(\tilde{C}^{P,e})$ associated with lattice modes not participating in the transition.

$T_c - T$ (mK)	Г ^{DCP} (MHz)		μ
		Γ^{DCP}/Γ^{TD}	$ ilde{C}^{P,e}/ ilde{C}^{E,o}$
3			0.13
9 + 10	58 + 6	0.18 ± 0.02	
10 + 7	67 ± 10	0.21 ± 0.03	
10 ± 10 11 ± 10	58 ± 3	0.18 ± 0.01	•••
13			0.15
13 + 6	67 + 6	0.21 ± 0.02	
23			0.16
24 + 10	64 + 3	0.20 ± 0.01	
26 + 7	70 + 3	0.22 ± 0.01	
28 ± 10	67 + 3	0.21 ± 0.01	• • • •
33			0.17
38 + 7	74 + 3	0.23 ± 0.01	
43		• • •	0.17
46 + 6	83 + 10	0.26 ± 0.03	
53		••••	0.18
53 + 6	87 + 5	0.27 ± 0.02	
63		••••	0.19
69 + 10	70 + 6	0.22 ± 0.02	
73		·····	0.19
83			0.20
84	74 ± 10	0.23 ± 0.03	
93			0.21
103		• • • •	0.21
113 ± 7	83 ± 6	0.26 ± 0.02	
123		••••	0.22

TABLE I. DCP linewidth measurements as a function of temperature and renormalization coefficient μ .

However, in the ferroelectric phase, the slow temperature fluctuations must be accompanied by changes in the highly temperature-sensitive order parameter P whose dynamics are relatively fast. Therefore an excess specific heat, associated with the ordering in the crystal, is introduced which increases the total specific heat to $\tilde{C}^{\sigma, \tilde{E}}$. This correspondingly increases the systems "thermal inertia" and slows down the temperature fluctuations so that the appropriate relaxation time is τ' . The ratio of the bare and renormalized relaxation times $(\tau; \tau')$ is simply equal to that of the two specific heats $(\tilde{C}^{P,e}; \tilde{C}^{\sigma, \tilde{E}})$, or equivalently to the DCP linewidth renormalization coefficient μ .

The intensity predicted by Eq. (23) is expected to grow as the transition is approached from below. This is primarily due to the increasing strength of the pyroelectric coupling $(p^{\sigma,E} = \delta P / \delta T |_{\sigma,E})$ between the polarization and temperature as the transition is approached. The DCP intensity is zero in the paraelectric phase where this coupling vanishes. The solid line in Fig. 1 is the prediction of Eq. (23) for the scattering cross section per unit volume R.³⁰ Unfortunately, in the scattering geometry used in these experiments, the background in the spectrum includes the e_6 Brillouin components so that it is not possible to extract values for the intensity ratio r. A scattering geometry probing only polarization fluctuations would facilitate such a measurement and provide a self-consistency check between the intensity and linewidth measurements.³¹

VI. CONCLUSION

Detailed DCP linewidth and relative intensity measurements within 0.1 K of the structural transition in ferroelectric KDP have been presented. Construction of the piezothermoelastic equations of motion have lead to predictions for the DCP linewidth and intensity which agree satisfactorily with experiment. It is seen that the specific-heat anomaly, just below the transition temperature, slows down the thermal diffusion mode relaxation time resulting in a renormalization of the DCP linewidth. The increase in DCP intensity, as the transition is approached from below, is attributed to the anomaly in the pyroelectric coefficient $p^{\sigma,E}$ and reflects the increasing DCP content of the order parameter fluctuations. The values of the linewidth renormalization coefficient μ have been determined from the DCP linewidth measurements and estimates for the TD mode linewidth based on thermal conductivity and specific-heat measurements. Predictions for the TD mode light scattering intensity just above the transition (see Fig. 3 in Ref. 8) show

that this spectral feature is expected to have a strength comparable to that of the longitudinal acoustic phonon sidebands which appear in the Brillouin spectra. Therefore it may be possible to directly measure the TD mode linewidth and determine μ solely by the light scattering experiment. Such a measurement would provide a useful test of the free-energy predictions for μ in the very sensitive DCP temperature region.

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APPENDIX: CONSTITUTIVE EQUATIONS FOR THE FERROELECTRIC MATERIAL KDP

The Helmholtz free energy is by definition

$$A = U - TS \quad , \tag{A1}$$

where the internal energy U for KDP is given by

$$U = TS - \sigma_6 e_6 + E_3 P_3 \quad . \tag{A2}$$

The differentials of the internal energy and, consequently, the Helmholtz free energy are

$$dU = T dS - \sigma_6 de_6 + E_3 dP_3 \quad , \tag{A3}$$

$$dA = -\sigma_6 \, de_6 + E_3 \, dP_3 - S \, dT \quad . \tag{A4}$$

These imply that the equilibrium values of the conjugate variables may be found by taking the appropriate derivatives of the Helmholtz free energy

$$E_3 = \frac{\partial A}{\partial P_3} \Big|_{e,T} , \qquad (A5a)$$

$$\sigma_6 = -\frac{\partial A}{\partial e_6}\Big|_{P,T} , \qquad (A5b)$$

$$S = -\frac{\partial A}{\partial T}\Big|_{P,\epsilon} \quad (A5c)$$

Imagine that the ferroelectric system is in a natural state of thermodynamic equilibrium characterized by the triplet of state variables (P^0, e^0, T^0) in response to the surrounding conditions. This natural state corresponds to an absolute minimum in the free energy whose value is: $A_0 = A(P^0, e^0, T^0)$. We can also consider a neighboring state of thermodynamic equilibrium described by (P, e, T). The free energy for this neighboring state may be expressed in terms of a Taylor-series expansion about the natural state

$$A(P,e,T) = A_{0} + \frac{1}{2} \left(\frac{\partial^{2}A}{\partial P^{2}} \bigg|_{0}^{0} (P_{3} - P_{3}^{0})^{2} + \frac{\partial^{2}A}{\partial e^{2}} \bigg|_{0}^{0} (e_{6} - e_{6}^{0})^{2} + \frac{\partial^{2}A}{\partial e^{2}} \bigg|_{0}^{0} (T - T^{0})^{2} + 2 \frac{\partial^{2}A}{\partial P \partial e} \bigg|_{0}^{0} \times (P_{3} - P_{3}^{0}) (e_{6} - e_{6}^{0}) + 2 \frac{\partial^{2}A}{\partial P \partial T} \bigg|_{0}^{0} (P_{3} - P_{3}^{0}) (T - T^{0}) + 2 \frac{\partial^{2}A}{\partial e \partial T} \bigg|_{0}^{0} (e_{6} - e_{6}^{0}) (T - T^{0}) \bigg|_{0}^{0} + \cdots,$$
(A6)

where the ellipsis represents higher-order terms. The first derivatives of A evaluated at the natural state are zero since A is a minimum at that point. Higher than second-order terms in the expansion are assumed to make negligible contributions to A. The three Eqs. (A5) and the expansion (A6) together yield the three constitutive relations connecting the state and conjugate thermodynamic variables. The connecting coefficients are expressed in terms of the appropriate second-order derivatives of the free energy. For reasons that will become clear below, P^0 and e^0 are taken to be zero and, ΔT represents the temperature change. These three relations are written in matrix form below

$$\begin{pmatrix} E \\ \sigma \\ \Delta S \end{pmatrix} = \begin{pmatrix} \frac{\partial^2 A}{\partial P^2} \Big|_0 & \frac{\partial^2 A}{\partial P \partial e} \Big|_0 & \frac{\partial^2 A}{\partial P \partial T} \Big|_0 \\ -\frac{\partial^2 A}{\partial P \partial e} \Big|_0 & -\frac{\partial^2 A}{\partial e^2} \Big|_0 & -\frac{\partial^2 A}{\partial e \partial T} \Big|_0 \\ -\frac{\partial^2 A}{\partial P \partial T} \Big|_0 & -\frac{\partial^2 A}{\partial e \partial T} \Big|_0 & -\frac{\partial^2 A}{\partial T^2} \Big|_0 \end{pmatrix} \begin{pmatrix} P \\ e \\ \Delta T \end{pmatrix} .$$

Following Nye, the above 3×3 coefficient matrix, denoted by \vec{M}^{-1} , is expressed in the notation given below along with the associated physical process

$$\vec{\mathbf{M}}^{-1} = \begin{pmatrix} \beta_{33}^{e_{3}T} & d_{36}^{P_{3}T} & t_{5}^{P_{4}e} \\ d_{63}^{P_{4}T} & K_{66}^{P_{4}T} & f_{5}^{P_{4}e} \\ t_{3}^{e_{3}T} & f_{6}^{P_{4}T} & \frac{1}{T}\tilde{C}^{P_{4}e} \end{pmatrix} , \quad \vec{\mathbf{M}}^{-1} = \begin{pmatrix} \text{dielectric} & \text{converse piezo-} & \text{electrothermal} \\ \text{impermeability} & \text{elect. coeff.} & \text{coeff.} \\ \text{direct piezo-} & \text{elastic stiffness} & \text{thermal pressure} \\ \text{elect. coeff.} & \text{constant} & \text{coeff.} \\ \text{heat of} & \text{heat of} & \text{heat capacity} \\ \text{polarization} & \text{deformation} \end{pmatrix} .$$
(A8)

The Landau-Devonshire free-energy expansion about the transition point represents a particular choice for the free energy A and leads to the following coefficient matrix:

$$\vec{\mathbf{M}}^{-1} = \begin{pmatrix} \alpha_0 (T - T_0^e) + \frac{\partial^2 \phi}{\partial P^2} \Big|_0 & -a^T & \alpha_0 P \\ + a^T & -C^{P,T} & 0 \\ -\alpha_0 P & 0 & \frac{1}{T} \tilde{C}^{P,e} \end{pmatrix} .$$
(A9)

(A7)

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