Nonequilibrium thermodynamics and quasielastic light scattering from crystals. II. Piezoelectric crystals

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The methodology described and utilized previously by the author, involving the use of nonequilibrium thermodynamics in the analysis of the spectrum of light scattered quasielastically by crystals, is applied to *piezoelectric* crystals. An additional thermodynamic variable, the electric polarization, is taken into account and assumed to be a relaxing variable. Solution of the resulting equations in the case of KH_2PO_4 leads, as expected, to the appearance of a polarization relaxation line in the spectrum. The spectrum is calculated for several values of the two relevant parameters: the polarization relaxation frequency and the ratio of C_{66} isothermal elastic constants at constant electric field and constant polarization. For a fixed polarization-relaxation frequency, it is found that as the ratio of elastic constants decreases (the characteristic behavior as the ferroelectric phase transition in KH_2PO_4 is approached), the intensity of the relaxation line *increases* at the expense of the Brillouin lines. In contrast with standard treatments of coupled modes in piezoelectric crystals, *no* adjustable parameters are involved in determining the spectrum.

I. INTRODUCTION

In previous work by the same author[1] (hereafter referred to as I) a description was given and illustrate examples provided of the utilization of *nonequilibrium thermodynamics* (NETD) in the determination of quasielastic light scattering spectra of crystals. The methodology is summarized in Fig. 1 of I. The figure also illustrates the crucial role that the choice of thermodynamic variables plays in the implementation of the methodology. The materials considered in I were KH_2PO_4 (KDP) and the superionic conductor $RbAg_4I_5$. The choice of strain and temperature as the relevant variables and the inclusion of both thermal and mechanical dissipation (via thermal conductivity and viscosity tensors, respectively) led, in the case of KDP, to the well-known quasielastic spectrum consisting of Rayleigh and Brillouin lines. On the other hand, for $RbAg_4I_5$ the inclusion of an additional thermodynamic variable, an internal (strain-independent) temperature, led to the appearance of an extra line, a relaxation line related to the hopping motion of the silver ions in this crystal.

Now, when stress is applied to certain crystals, an electric polarization is induced which is proportional to the applied stress. This property, referred to as the (direct) *piezoelectric* effect,[2] is characteristic of crystals belonging to 20 of the 32 crystallographic classes.[3] Let us suppose that the stress in question is associated with the passage of an acoustic wave through a given piezoelectric crystal. It follows as a consequence of the piezoelectric effect that a polarization wave is also set up in the crystal. In other words, in applying the formalism of NETD to the determination of quasielastic light scattering spectra of piezoelec-

tric crystals, one should include at the outset an additional thermodynamic variable, the electric polarization $\vec{P}$.

In the present paper, we will apply the formalism developed in Sec. II to KDP. In this crystal, it is well known[4] that its anomalous dielectric properties in the paraelectric phase lead to an *elastic* anomaly near the ferroelectric phase transition ($T_c = 122.00$ K according to Brody and Cummins[5])—specifically a drop by a factor of about 90 between $T = 295$ K and $T = 122$ K in the value of $C_{66}^{S,E}$, the (66) adiabatic elastic constant measured at constant (zero) electric field.[5] Brillouin scattering is ideally suited to studying such an anomaly, since the position of the Brillouin lines, if the scattering geometry is properly chosen, is determined by $C_{66}^{S,E}$. This requires that the crystal be electrically *shorted*, as can be accomplished by plating selected faces of the crystal with gold electrodes.

Plating the crystal, although it provides striking visual evidence of the elastic anomaly in the Brillouin spectrum, also has the effect of obscuring the contribution of the polarization mode to the spectrum. What we suggest instead is that light-scattering experiments be performed on *insulated* crystals. Since physical intuition would lead one to conclude that the position of the Brillouin lines will in this case be essentially determined by $C_{66}^{S,P}$—which does *not* display any elastic anomalies[4]—the polarization contribution can thus be studied in more detail. It is shown in Sec. III how a spectrum obtained under this electrical boundary condition can be completely characterized (line positions, linewidths, relative intensities) by means of simple algebraic or numerical manipulations involving only macroscopic parameters.

The present contribution is organized as follows. In Sec. II we consider the nonequilibrium thermodynamics of piezoelectric crystals. In Sec. III the formalism developed in Sec. II is applied to KDP. In Sec. IV concluding remarks are made. In the Appendix we summarize the equilibrium thermodynamics of piezoelectric crystals, with particular emphasis on relationships pertinent to the main body of the paper.

II. NONEQUILIBRIUM THERMODYNAMICS OF PIEZOELECTRIC CRYSTALS

In considering the *nonequilibrium* thermodynamics of piezoelectric crystals, a description in terms of space- and time-dependent counterparts of equilibrium variables (cf. the Appendix) will be utilized, as is customary in treatments of linear NETD.[6] The assumption will also be made that the polarization can be treated as a *relaxing* thermodynamic variable in the context of the Mandelshtam-Leontowich hypothesis,[7] namely, that the time variation of a given relaxing variable is simply proportional to the variation of the system's free energy with respect to the same variable (in I, the relaxing internal temperature postulated for $RbAg_4I_5$ was handled in this fashion—cf. Secs. II C and V of that paper).

Before implementing the program set forth above, a brief digression is called for in order to justify regarding the polarization in piezoelectrics as a relaxing thermodynamic variable. This is consistent with one's physical intuition inasmuch as an applied stress induces an electric polarization in such crystals, but once such stress is "turned off" and thermodynamic equilibrium has been reached, the average polarization is *zero* and the state of the crystal is again describable in terms of strain and temperature variables. One may thus characterize the situation by saying that the polarization has relaxed to its average value of zero. Parenthetically, one may remark that an analogous description is also appropriate in ferroelectrics, except that in such crystals the equilibrium value of the polarization is nonzero and it is to this value that the additional polarization induced by the stress relaxes once the stress is removed.

Since $\eta_{kl}(\vec{K}) = \frac{1}{2}i[K_l u_k(\vec{K}) + K_k u_l(\vec{K})]$, and we will later wish to set $\vec{K} = (K_x, 0, 0)$, the only relevant strain components will be η_1, η_5, and η_6. Furthermore, we will wish to consider crystals belonging to the tetragonal class $\bar{4}2m$, for which class the matrix of (Voigt) piezoelectric stress coefficients $\{e_{ij}\}$ is [4]

$$\begin{bmatrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & e_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & e_{36} \end{bmatrix}$$

From Eq. (A14) in the Appendix, disregarding for the moment the $k^\eta E$ terms, it follows that $P_3 = e_{36}\eta_6$. Since we will select a scattering geometry to probe the η_6 component, the only polarization component of interest to our discussion will be P_3—in other words, one is justified in postulating the following functional dependence for the system's local free-energy density $F(\vec{r}, t)$ (Ref. 8):

$$F(\vec{r}, t) = F(\{\eta_{ij}(\vec{r}, t)\}, T(\vec{r}, t), P_3(\vec{r}, t)) .$$

At equilibrium, $(\partial F / \partial P_3)_{T\eta} = 0$ and therefore

$$\Delta\left(\frac{\partial F}{\partial P_3}\right) = F_{P_3\eta_{ij}}\Delta\eta_{ij} + F_{P_3T}\Delta T + F_{P_3P_3}\Delta P_3 = 0 ,$$

$$(2.1)$$

where

$$F_{P_3\eta_{ij}} \equiv \left(\frac{\partial^2 F}{\partial P_3 \partial \eta_{ij}}\right)_{T\eta'} ,$$

$$F_{P_3T} \equiv \left(\frac{\partial^2 F}{\partial P_3 \partial T}\right)_\eta ,$$

$$F_{P_3P_3} \equiv \left(\frac{\partial^2 F}{\partial P_3^2}\right)_{T\eta} .$$

From (A6), it follows that $F_{P_3P_3} = \chi_3^{\eta,T}$, $F_{P_3\eta_{ij}} = -a_{3ij}$, and Eq. (2.1) further yields

$$F_{P_3T} = -\chi_3^{\eta,T}\left(\frac{\partial P_3}{\partial T}\right)_\eta .$$

$$(2.2)$$

If one writes (σ is the entropy density)

$$\tau_{ij} = \tau_{ij}(\{\eta_{ij}\}, T, P_3) ,$$

$$\sigma = \sigma(\{\eta_{ij}\}, T, P_3) ,$$

one can show that (henceforth we shall omit the superscripts associated with $\{\chi_{ij}\}$ and $\{k_{ij}\}$)

$$\left(\frac{\partial \tau_{ij}}{\partial \eta_{kl}}\right)_{T\eta'P_3} = C_{ijkl}^{T,P} + k_3 a_{3ij} a_{3kl} ,$$

$$(2.3)$$

$$\left(\frac{\partial \tau_{ij}}{\partial T}\right)_{\eta P_3} = -C_{ijkl}^{T,P}\beta_{kl} + a_{3ij}\left(\frac{\partial P_3}{\partial T}\right)_\eta ,$$

$$(2.4)$$

$$\left(\frac{\partial \sigma}{\partial \eta_{ij}}\right)_{T\eta'P_3} = C_{ijkl}^{T,P}\beta_{kl} - a_{3ij}\left(\frac{\partial P_3}{\partial T}\right)_\eta ,$$

$$(2.5)$$

$$\left(\frac{\partial \sigma}{\partial T}\right)_{\eta P_3} = \frac{\rho C_\eta}{T} - \chi_3\left[\left(\frac{\partial P_3}{\partial T}\right)_\eta\right]^2 ,$$

$$(2.6)$$

where use was made of standard thermodynamic results[9] as well as of the following relations [cf. Eqs. (A14), (A9), (2.2)]:

$$\left(\frac{\partial P_3}{\partial \eta_{ij}}\right)_{T\eta'} \equiv e_{3ij} = k_3 a_{3ij} ,$$

$$\left(\frac{\partial \tau_{ij}}{\partial P_3}\right)_{T\eta} \equiv -a_{3ij},$$

$$\left(\frac{\partial \sigma}{\partial P_3}\right)_{T\eta} = -\left(\frac{\partial^2 F}{\partial P_3 \partial T}\right) = -F_{P_3 T} = \chi_3\left(\frac{\partial P_3}{\partial T}\right)_\eta.$$

Equations (2.3)–(2.6) thus yield (including the viscous contribution to the stress tensor[10])

$$\Delta\tau_{ij} = (C_{ijkl}^{T,P} + k_3 a_{3ij} a_{3kl})\Delta\eta_k$$

$$- \left[C_{ijkl}^{T,P}\beta_{kl} - a_{3ij}\left(\frac{\partial P_3}{\partial T}\right)_\eta\right]\Delta T$$

$$- a_{3ij}\Delta P_3 + v_{ijkl}\frac{\partial}{\partial t}\Delta\eta_{kl}, \qquad (2.7)$$

$$\Delta\sigma = \left[C_{ijkl}^{T,P}\beta_{kl} - a_{3ij}\left(\frac{\partial P_3}{\partial T}\right)_\eta\right]\Delta\eta_{ij}$$

$$+ \left\{\frac{\rho C_\eta}{T} - \chi_3\left[\left(\frac{\partial P_3}{\partial T}\right)_\eta\right]^2\right\}\Delta T + \left[\chi_3\left(\frac{\partial P_3}{\partial T}\right)_\eta\right]\Delta P_3. \qquad (2.8)$$

One now assumes that the polarization relaxes according to the Mandelshtam-Leontowich rela-

tion[7]

$$\frac{\partial}{\partial t}\Delta P_3 = -L\left(\frac{\partial F}{\partial P_3}\right)_{T\eta}.$$

Expanding $(\partial F/\partial P_3)_{T\eta}$, one obtains

$$\frac{\partial}{\partial t}\Delta P_3 = -(\chi_3 L)\Delta P_3 + \chi_3 L\left[e_{3ij}\Delta\eta_{ij} + \left(\frac{\partial P_3}{\partial T}\right)_\eta \Delta T\right]. \qquad (2.9)$$

The structure of Eq. (2.9) suggests the definition

$$(\chi_3 L)^{-1} \equiv \tau,$$

where τ is the *relaxation time* (at constant strain and temperature).

Therefore the dynamical equation for ΔP_3 is

$$\frac{\partial}{\partial t}\Delta P_3 = -\frac{1}{\tau}\Delta P_3 + \frac{1}{\tau}\left[k_3 a_{3ij}\Delta\eta_{ij} + \left(\frac{\partial P_3}{\partial T}\right)_\eta \Delta T\right]. \qquad (2.10)$$

Use of Eq. (2.10) allows one to eliminate the ΔP_3 dependence of Eqs. (2.7) and (2.8); one finds

$$\Delta\tau_{ij} + \tau\frac{\partial}{\partial t}\Delta\tau_{ij} = C_{ijkl}^{T,P}\Delta\eta_{kl} + (C_{ijkl}^{T,P} + k_3 a_{3ij} a_{3kl})\tau\frac{\partial}{\partial t}\Delta\eta_{kl}$$

$$- C_{ijkl}^{T,P}\beta_{kl}\Delta T - \left[C_{ijkl}^{T,P}\beta_{kl} - a_{3ij}\left(\frac{\partial T_3}{\partial T}\right)_\eta\right]\tau\frac{\partial}{\partial t}\Delta T + v_{ijkl}\left(\frac{\partial}{\partial t}\Delta\eta_{kl} + \tau\frac{\partial^2}{\partial t^2}\Delta\eta_{kl}\right), \qquad (2.11)$$

$$\Delta\sigma + \tau\frac{\partial}{\partial t}\Delta\sigma = C_{ijkl}^{T,P}\beta_{kl}\Delta\eta_{ij} + \left[C_{ijkl}^{T,P}\beta_{kl} - a_{3ij}\left(\frac{\partial P_3}{\partial T}\right)_\eta\right]\tau\frac{\partial}{\partial t}\Delta\eta_{ij} + \left(\frac{\rho C_\eta}{T}\right)\Delta T + \left\{\frac{\rho C_\eta}{T} - \chi_3\left[\left(\frac{\partial P_3}{\partial T}\right)_\eta\right]^2\right\}\tau\frac{\partial}{\partial t}\Delta T. \qquad (2.12)$$

Once $\Delta\tau_{ij}(\vec{r},t)$ and $\Delta\sigma(\vec{r},t)$ have been specified, the equations to be solved are [cf. Eqs. (2.2) and (2.5) in I]

$$T\frac{\partial}{\partial t}\Delta\sigma(\vec{r},t) = \lambda_{ij}\frac{\partial^2}{\partial r_i \partial r_j}\Delta T(\vec{r},t), \qquad (2.13)$$

$$\rho\frac{\partial^2}{\partial t^2}\Delta u_i(\vec{r},t) = \frac{\partial}{\partial r_j}\Delta\tau_{ij}(\vec{r},t). \qquad (2.14)$$

We shall solve Eqs. (2.13) and (2.14) for a particular choice of wave vector, namely (as in I), $\vec{K} = (\vec{K}_x, 0, 0)$. The Fourier-Laplace transforms (FLT's) of Eqs. (2.13) and (2.14) for this wave vector are

$$T(s\Delta\sigma(K_x, s) - \Delta\sigma(K_x)) = -K_x^2\lambda_1 \Delta T(K_x, s), \qquad (2.15)$$

$$\rho(s^2\Delta u_i(K_x, s) - s\Delta u_i(K_x)) = iK_x\Delta\tau_{ix}(K_x, s) \qquad (2.16)$$

[it has been assumed, as is customary,[11] that, at $t=0$, $(\partial/\partial t)\Delta\vec{u}(\vec{r},t) = 0$]. The coupled equations for the FLT's are then obtained utilizing the facts that

$$\Delta\sigma(K_x) = (\rho C_\eta/T)\Delta T(K_x) + C_{ijkl}^{T,P}\Delta\eta_{ij}(K_x), \qquad (2.17)$$

$$\Delta\tau_{ij}(K_x) = C_{ijkl}^{T,P}[\Delta\eta_{kl}(K_x) - \beta_{kl}\Delta T(K_x)], \qquad (2.18)$$

and the expression for $\Delta\sigma(K_x, s)$ and $\Delta\tau_{ij}(K_x, s)$ obtainable from (2.11) and (2.12).

III. APPLICATION OF THE FORMALISM TO KDP

For the choice $\vec{K} = (K_x, 0, 0)$, the piezoelectric effect in crystals such as KDP that belong to the class $\bar{4}2m$ is manifested through the relation $P_3 = e_{36}\eta_6$. Since pyroelectricity is ruled out in this class, $(\partial P_3/\partial T)_\eta = 0$. Utilizing Eqs. (2.11)–(2.18) one thus obtains the following equations of motion:

$$(s^2 + as + b)\Delta u_x(K_x, s) + ic\Delta T(K_x, s) = (s+a)\Delta u_x(K_x),$$

$$\left(s^2 + a's + b' + \frac{\tau s}{1+\tau s}e'\right)\Delta u_y(K_x, s)$$

$$= \left(s + a' + \frac{\tau}{1+\tau s}e'\right)\Delta u_y(K_x),$$

$$(s^2 + a''s + b'')\Delta u_z(K_x, s) = (s+a'')\Delta u_z(K_x),$$

$$(s+d)\Delta T(K_x, s) + i(c's)\Delta u_x(K_x, s)$$

$$= \Delta T(K_x) + i(c')\Delta u_x(K_x), \qquad (3.1)$$

where (cf. I)

$$a = (v_{11}/\rho)K_x^2, \quad a' = (v_{66}/\rho)K_x^2, \quad a'' = (v_{44}/\rho)K_x^2,$$

$$b = (C_{11}^{T,P}/\rho)K_x^2, \quad b' = (C_{66}^{T,P}/\rho)K_x^2, \quad b'' = (C_{44}^{T,P}/\rho)K_x^2,$$

$$c = K_x[C_{11}^{T,P} + C_{12}^{T,P})\beta_1 + C_{13}^{T,P}\beta_3]/\rho, \quad c' = (T/C_\eta)c,$$

$$d = (\lambda_1/\rho C_\eta)K_x^2, \quad e' = K_x^2 k_3^\eta a_{36}/\rho.$$

Setting $R = s/i\omega_0$, where $\omega_0 = K_x(C_{66}^{T,P}/\rho)^{1/2}$, $\Delta u_y(K_x, s)$ may be written as

$$\Delta u_y(K_x, R) = [N(R)/i\omega_0 D(R)]\Delta u_y(K_x),$$

with

$$N(R) = R^2 - i(\alpha + 2n)R - 2(n\alpha + r),$$

$$D(R) = R^3 - i(\alpha + 2n)R^2 - [1 + 2(n\alpha + r)]R + i\alpha, \qquad (3.2)$$

and $\alpha = (\omega_0\tau)^{-1}$, $n = a/2\omega_0$, $r = \frac{1}{2}(k_3^\eta a_{36}^2/C_{66}^{T,P})$. From (A18), it follows that

$$2r = 1 - (C_{66}^{T,E}/C_{66}^{T,P}).$$

At 269 K, the adiabatic elastic stiffnesses are [5] $C_{66}^{S,E} = 6.15 \times 10^{10}$ dyn/cm^2, $C_{66}^{S,P} = 6.31 \times 10^{10}$ dyn/cm^2.[12] These experimental values imply that $2r = 0.025$. In view of the smallness of $2r$ at 269 K one is justified in effecting the following approximate factorization of $D(R)$:

$$D(R) \approx (R - i\alpha)[R - in - (1+r)][R - in + (1+r)] \qquad (3.3)$$

[this leads to an R-independent term equal to $i\alpha(1 + 2r)$, rather than $i\alpha$ as in the original equation]. Partial fraction decomposition results in

$$\Delta u_y(K_x, s) = \left[\frac{A(\alpha)}{s + \nu_R} + \frac{1}{2}\left(\frac{B(\alpha)}{s + \frac{1}{2}a + i(1+r)\omega_0} + \frac{B^*(\alpha)}{s + \frac{1}{2}a - i(1+r)\omega_0}\right)\right]\Delta u_y(K_x), \qquad (3.4)$$

where $\nu_R = \tau^{-1}$ and

$$A(\alpha) = 2r/F(\alpha),$$

$$B(\alpha) = [(1 + r + in)\alpha^2$$
$$+ 2i(r + in)\alpha + (1 + r + in)]/F(\alpha),$$

$$F(\alpha) = (1 + r)\alpha^2 - 2n\alpha + 1 + 3r.$$

The power spectral density will be proportional to the function obtained by setting $s = -i\Omega$ in Eq. (3.4) and taking its real part. One finds that the spectrum consists of three lines, specified as follows:

Relaxation:

$$L_1(\Omega) = A(\alpha)\nu_R/(\Omega^2 + \nu_R^2),$$

Brillouin:

$$L_2(\Omega) = \{\frac{1}{2}a\,\mathrm{Re}B(\alpha) - [\Omega + (1+r)\omega_0]\mathrm{Im}B(\alpha)\}$$
$$\times \{[\Omega + (1+r)\omega_0]^2 + (\frac{1}{2}a)^2\}^{-1},$$

Brillouin:

$$L_3(\Omega) = L_2(-\Omega).$$

The integrated intensities will be proportional to $2r/F(\alpha)$ (relaxation line) and

$$[(1 + r)\alpha^2 - 2n\alpha + 1 + r]/F(\alpha)$$

(Brillouin lines).

The fact that $2r = 1 - (C_{66}^{T,E}/C_{66}^{T,P})$ for KDP at high temperature is experimentally known to be of the order of 10^{-2} has enabled us to characterize the spectrum completely by carrying out simple algebraic manipulations. However, as T approaches $T_c = 122.00$ K,[5] it is common knowledge[4] that

$C_{66}^{S,E}$ (and hence $C_{66}^{T,E}$) goes to zero, which implies that the parameter $2r$ approaches 1. In fact, using the measured values of these elastic stiffnesses at $T = 122.00$ K, namely, $C_{66}^{T,P} = 6.96 \times 10^{10}$ dyn/cm^2,[12] and the values of $C_{66}^{S,E}$ measured by Brody and Cummins[5] for different applied electric fields, one finds that $2r$ at 122 K ranges from 0.99 ($E = 0$) to 0.42 ($E = 3937$ V/cm). In other words, the approximation $1 + r \approx 1$ which allowed us to factor Eq. (3.2) into Eq. (3.3) and hence led to the simple analytic determination of the spectrum is no longer valid.

The polarization relaxation time τ is also known to exhibit a strong temperature dependence as the ferroelectric transition is approached: In fact, ultrasonic investigations[12,13] reveal that the temperature dependence of the polarization relaxation time at constant stress, τ_{stress}, may be expressed as

$$\tau_{\mathrm{stress}} = 24 \times 10^{-12}(T - T_c)^{-1} \text{ sec K},$$

where $T_c = 121.82$ K.

In our formalism, the relaxation time is assumed to be measured at constant *strain*. Inspection of Eq. (2.9) reveals that the ratio $\tau_{\mathrm{stress}}/\tau_{\mathrm{strain}}$ is given by the ratio of the reciprocal dielectric susceptibilities at constant stress (χ^τ) and constant strain (χ^η). Since these are known[4] to display Curie-Weiss behavior, $\chi^\tau = C(T - T_c)^{-1}$ and $\chi^\eta = C(T - T_0)^{-1}$ where $C = 259$ K and $T_0 = 117.45$ K (Ref. 13) is the ferroelectric transition temperature for the clamped crystal, it follows that

$$\tau_{\mathrm{strain}} = 24 \times 10^{-12}(T - T_0)^{-1} \text{ sec K}. \qquad (3.5)$$

Since Eq. (3.2) is of the third degree, exact

analytic expressions for its roots are available,[14] and hence the spectrum can in principle be determined for any values of the parameters r, n, and α. However, such potentially obtainable expressions would hardly be enlightening in view of their algebraic complexity. Since there is no reason to suspect that the viscosity coefficient will display anomalous behavior near T_c, we have held $n = \frac{1}{2}K_x^2 v_{66}/\rho\omega_0$ fixed at the reasonable value[15] of $n = 0.01$ and have solved Eq. (3.2) numerically for several values of r and α, corresponding to several values of the temperature.

Table I summarizes the results obtained for two values of the ratio ν_R/ν_0, namely 10.0 and 1.0, for $2r = 1 - C_{66}^{T,E}/C_{66}^{T,P} = 0.0$, 0.5, and 1.0. Qualitatively, one sees that as the ratio $C_{66}^{T,E}/C_{66}^{T,P}$ decreases, the Brillouin lines move away from the origin and their widths increase, whereas the relaxation linewidth decreases.

In Fig. 1 (drawn to scale) we display the calculated spectrum for the *fixed* ratio $\nu_R/\nu_0 = 1$ and for $2r = 0.5$, 1.0 in order to dramatize the effect of the elastic anomaly. For $2r = 0.0$, corresponding to a high-temperature situation for which $C_{66}^{T,E} \approx C_{66}^{T,P}$, the polarization line has negligible intensity and the Brillouin lines, centered at $\Omega/\omega_0 = 1$, would be roughly seven to ten times higher than the Brillouin lines depicted. From the figure, one sees that the formalism predicts an increase in the polarization line intensity at the expense of the intensity of the Brillouin lines.

Figure 1 is to be regarded as illustrating the typical behavior one should expect to find in the vicinity of ferroelectric phase transitions. In the specific case of KDP, the value of the ratio ν_R/ν_0 at $T = 122.0$ K, for instance, is actually of the order of 30 rather than 1, as was assumed in drawing Fig. 1—a value that can be readily calculated by using Eq. (3.5) and the expression $\omega_0 = K_x(C_{66}^{T,P}/\rho)^{1/2}$, where $C_{66}^{T,P} = 6.96 \times 10^{10}$ dyn/cm²,[12] $\rho = 2.338$ g/cm³,[16] for a wavelength of about 6000 Å. Nevertheless, the value of 1 chosen for the ratio is not at all unreasonable: For instance, the polarization relaxation time for deuterated KDP (KD*P) is an order of magnitude *longer*[17] than that for KDP, which leads [all other relevant parameters being of the same order of magnitude (as they are known to be)] to frequency ratios roughly ten times *smal-*
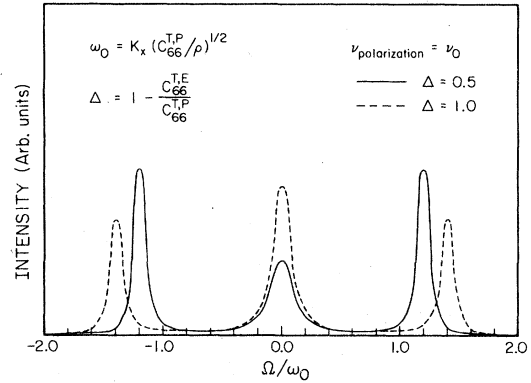

FIG. 1. Spectrum calculated from Eq. (3.1) for the particular choice $\nu_{\text{polarization}} = \nu_0$ and two values of the ratio $C_{66}^{T,E}/C_{66}^{T,P}$. Note the *increase* in the intensity of the polarization line, at the expense of Brillouin lines, as the ratio *decreases*.

ler. It seems reasonable to conjecture that materials exist for which Fig. 1 provides an accurate representation of a real spectrum.

IV. CONCLUDING REMARKS

The formalism presented in the present contribution should be contrasted with the standard treatment of coupled modes in piezoelectric crystals.[18] Coupled-mode dynamics is discussed in the context of a phenomenological theory involving a power-series expansion of the Lagrangian energy density of the crystal. Mode lifetimes are taken into account by means of a Rayleigh dissipation function characterized by different damping constants for the different modes under study. Spectra are calculated from response functions, and description of the spectral features often requires approximate decoupling of the equations of motion. The phenomenological nature of the approach implies, in many situations, that the parameters of the theory are often only very indirectly related to quantities measured using different experimental techniques.

The approach proposed in I and in the present work, on the other hand, by virtue of its *thermodynamic* (albeit nonequilibrium) character, is firmly rooted in macroscopic quantities that can be measured (and most of the time unambiguously

TABLE I. Roots of Eq. (3.2) for the fixed ratio $n = 0.01$ and for, respectively, two and three values of the ratios α and $2r$. Note that $\alpha = \nu_{\text{polarization}}/2\pi\nu_0$.

$2r$	$\nu_{\text{polarization}}/\nu_0 = 10.0$		$\nu_{\text{polarization}}/\nu_0 = 1.0$	
0.00	($\pm$1.000, 0.010)	(0.0, 1.592)	($\pm$1.000, 0.010)	(0.0, 0.159)
0.50	($\pm$1.078, 0.131)	(0.0, 1.350)	($\pm$1.222, 0.036)	(0.0, 0.106)
1.00	($\pm$1.181, 0.262)	(0.0, 1.088)	($\pm$1.412, 0.050)	(0.0, 0.080)

identified) in widely dissimilar experiments. We believe that this point should be emphatically re-iterated. For instance, calculation of the spectra in Fig. 1 involved *no* unknown parameters: n is related to a viscosity coefficient, and r basically measures the ratio $C_{66}^{T,E}/C_{66}^{T,P}$ and α the ratio ν_R/ν_0. Furthermore, the attendant numerical manipulation was of a most mundane sort. It is our view that the present approach holds out the promise of making a significant contribution to the problem of analyzing quasielastic light scattering spectra.

APPENDIX

In the simplest situation, electric polarization can be taken into account in the context of the thermodynamics of dielectric crystals by including an additional contribution in the expression for dF, the change in the Helmholtz free energy of the deformed crystal associated with quasistatic transitions from one state of thermodynamic equilibrium to another. If polarization is not included

$$dF(T, \{\eta_{ij}\}) = -SdT + \tau_{ij} d\eta_{ij},$$

where $\{\tau_{ij}\}$ and $\{\eta_{ij}\}$ are, respectively, the stress and strain tensors and where, as convention dictates, repeated indices (here and elsewhere in this paper) are summed over. Including polarization, dF becomes[19]

$$dF_1(T, \{\eta_{ij}\}, \{E_i\}) = -SdT + \tau_{ij} d\eta_{ij} - \vec{P} \cdot d\vec{E}, \quad (A1)$$

where $\vec{P}$ is the polarization of the crystal and $\vec{E}$ is a uniform applied field. Successive changes of variables produce

$$dF_2(T, \{\eta_{ij}\}, \{P_i\}) = d(F_1 + P_i E_i)$$
$$= -SdT + \tau_{ij} d\eta_{ij} + E_i dP_i, \quad (A2)$$

$$dF_3(T, \{\tau_{ij}\}, \{E_i\}) = d(F_1 - \tau_{ij}\eta_{ij})$$
$$= -SdT - \eta_{ij} d\tau_{ij} - P_i dE_i, \quad (A3)$$

$$dF_4(T, \{\tau_{ij}\}, \{P_i\}) = d(F_1 - \tau_{ij}\eta_{ij} + P_i E_i)$$
$$= -SdT - \eta_{ij} d\tau_{ij} + E_i dP_i. \quad (A4)$$

To simplify matters at this point, we will ignore the influence of temperature (such influence will later be taken into account explicitly) and concentrate our attention on the interplay between elastic deformation and electric polarization, the hallmark of piezoelectric behavior. For notational convenience, we shall also omit subscripts for now.

Depending on the choice of thermodynamic variables, four different (quadratic-bilinear) expressions for the free energy describing the coupled deformation-polarization system may be written[20]:

$$F_1' = \tfrac{1}{2} C^{T,E}\eta^2 - \tfrac{1}{2}k^\eta E^2 - e\eta E, \quad (A5)$$

$$F_2' = \tfrac{1}{2} C^{T,P}\eta^2 + \tfrac{1}{2}\chi^\eta P^2 - a\eta P, \quad (A6)$$

$$F_3' = -\tfrac{1}{2} S^{T,E}\tau^2 - \tfrac{1}{2}k^\tau E^2 - d\tau E, \quad (A7)$$

$$F_4' = -\tfrac{1}{2} S^{T,P}\tau^2 + \tfrac{1}{2}\chi^\tau P^2 - b\tau P, \quad (A8)$$

where the primes indicate that the terms involving the temperature have been left out; $C^{T,P}$ ($C^{T,E}$) is an isothermal elastic stiffness coefficient at constant polarization (electric field), $S^{T,P}$ ($S^{T,E}$) is an isothermal elastic compliance coefficient at constant polarization (electric field), k^η (k^τ) is a dielectric susceptibility at constant strain (stress), χ^η (χ^τ) is a reciprocal dielectric susceptibility at constant strain (stress), and the coupling coefficients are,[2] respectively, Mueller and Voigt piezoelectric *stress* coefficients (a and e) and Mueller and Voigt piezoelectric *strain* coefficients (b and d).

Combining (A1)–(A4) and (A5)–(A8), it is a simple matter to derive the following thermodynamic relations (these will be of future utility):

$$\tau = C^{T,P}\eta - aP, \quad (A9)$$

$$\eta = S^{T,P}\tau + bP, \quad (A10)$$

$$\tau = C^{T,E}\eta - eE, \quad (A11)$$

$$\eta = S^{T,E}\tau + dE, \quad (A12)$$

$$E = \chi^\eta P - a\eta, \quad (A13)$$

$$P = k^\eta E + e\eta, \quad (A14)$$

$$E = \chi^\tau P - b\tau, \quad (A15)$$

$$P = k^\tau E + d\tau. \quad (A16)$$

Relations (A9), (A11), (A13) and (A14) may be used to derive two results of future utility. From (A13) and (A14), recalling that $k\chi = 1$, it follows that

$$e = k^\eta a. \quad (A17)$$

On the other hand, subtracting (A9) and (A11) and employing (A13) and (A17) one finds

$$C^{T,P} - C^{T,E} = k^\eta a^2. \quad (A18)$$

[1]A. F. Silva-Moreira, Phys. Rev. B 19, 979 (1979).

[2]W. G. Cady, *Piezoelectricity* (Dover, New York, 1964).

[3]Electric polarization can be induced not only by stress, but also by changes in temperature—this is the phenomenon of *pyroelectricity*. Whereas piezoelectricity can occur in any of 20 crystallographic classes, pyroelectricity is restricted to the following 10 classes: 1, *m*, 2, *mm*2, 3, 3*m*, 4, 4*mm*, 6, and 6*mm*.

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[5]E. M. Brody and H. Z. Cummins, Phys. Rev. B 9, 179 (1974).

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[7]L. I. Mandelshtam and M. A. Leontowich, Zh. Eksp. Teor. Fiz. 7, 438 (1948).

[8]This corresponds to the free-energy expression labeled F_2 in the Appendix—cf. Eq. (A6).

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[18]For a review, cf. R. L. Rees, I. J. Fritz, and H. Z. Cummins, Phys. Rev. B 7, 4165 (1973).

[19]L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1960).

[20]These correspond to Eqs. (1), (2), (240) and (241) of Cady (Ref. 2).