

# Brillouin Scattering Spectroscopy of Ferroelectric and Ferroelastic Phase Transitions

H. Z. Cummins

*Phil. Trans. R. Soc. Lond. A* 1979 **293**, 393-405  
doi: 10.1098/rsta.1979.0106

## Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

To subscribe to *Phil. Trans. R. Soc. Lond. A* go to: <http://rsta.royalsocietypublishing.org/subscriptions>

## Brillouin scattering spectroscopy of ferroelectric and ferroelastic phase transitions

BY H. Z. CUMMINS

*École Normale Supérieure, Paris, France, and City College – C.U.N.Y., New York, U.S.A.*

Light scattering spectroscopy has played a crucial role in the study of numerous phase transitions and critical phenomena. In the case of structural phase transitions in crystalline solids, high resolution Raman and Brillouin scattering experiments have provided detailed information on the ‘soft modes’, the highly temperature-dependent lattice vibrations whose frequencies fall towards zero at the transition temperature. The condensation of the soft modes precipitates the spontaneous symmetry breaking which inevitably accompanies these transitions.

Ferroelectrics comprise a particular class of crystals exhibiting structural phase transitions which have been investigated extensively by light scattering techniques. In addition to numerous soft mode studies, other subtle aspects of these transitions have been investigated by light scattering, including mode interactions and central peaks.

In this presentation, the fundamental aspects of structural phase transitions and their relation to light scattering will be reviewed. A number of light scattering studies of ferroelectric crystals spanning the past decade will be summarized and used to illustrate the current level of understanding of these phenomena.

### 1. INTRODUCTION

Light scattering spectroscopy has been widely applied to the study of numerous phase transitions and critical phenomena during the past 15 years, including the liquid–vapour critical point, hydrodynamic instabilities, liquid crystals and structural phase transitions in solids. Most investigations of structural transitions in solids have focused on the study of soft optic modes, which are usually observed as strongly temperature dependent features in the Raman spectrum. It is the soft mode, whose frequency approaches zero at the transition, that condenses in the low temperature phase, resulting in spontaneous symmetry breaking. Raman scattering experiments, often in conjunction with inelastic neutron scattering and X-ray studies, have provided considerable information on the dynamical aspects of structural phase transitions in a great number of crystals.

In some crystals, a structural phase transition can also involve anomalous temperature dependence of acoustic modes, which can be conveniently studied by Brillouin scattering spectroscopy with a Fabry–Perot interferometer. Such experiments can also provide considerable information on the dynamics of phase transitions, which is often complementary to Raman scattering measurements.

Of the various structural phase transitions which have been studied by Brillouin scattering, there are three classes of crystals that I will discuss. These are: (1) piezoelectric ferroelectrics, such as potassium dihydrogen phosphate (KDP), (2) non-piezoelectric ferroelectrics such as triglycine phosphate (TGS), and (3) improper ferroelectrics such as gadolinium molybdate (GMO). The primary goal of this discussion will be to show how the dynamical analysis applied

[ 183 ]

in the past to classes (1) and (2) can be extended and applied to class (3), and to suggest ways in which Brillouin scattering and ultrasonic studies of improper ferroelectrics might be combined to further elucidate these dynamical properties. In particular, we will show that although the thermodynamic analysis of the elastic constants previously employed for class 3 materials predicts identical results for ultrasonic and Brillouin experiments, a dynamical analysis suggests that there should be differences in the results related to the soft mode frequency or relaxation rate.

## 2. THERMODYNAMICS

As a first step we review the standard method of analysing the equilibrium properties, particularly the static elastic constants, of the three classes of crystals. We begin with a Landau–Devonshire free energy expansion  $A(\eta, x)$  where  $\eta$  is the order parameter and  $x$  is a strain. For ferroelectric crystals of type (1) or (2),  $\eta$  is the electric polarization  $P$ . For class (3), it is the amplitude of the soft mode which is at the edge, rather than the centre, of the Brillouin zone. In general  $\eta$  may have more than one component, and all the strains should be included, leading to a rather complicated free energy expression. We will work with a simplified  $A(\eta, x)$  including only one strain and a single-component  $\eta$ . More complete free energy expressions can be found in the book by Jona & Shirane (1962) for classes 1 and 2, and in Dvorak (1971) for class 3. The connection between Dvorak's expression and a single-component form has been discussed, for example, by Dorner *et al.* (1972). We take for our model free energy:

$$A(\eta, x) - A_0 = \frac{1}{2}\alpha\eta^2 + \frac{1}{4}\beta\eta^4 + \frac{1}{6}\gamma\eta^6 + \dots + \frac{1}{2}Cx^2 + \dots - ax\eta - \frac{1}{2}Kx\eta^2. \quad (1)$$

The first three terms in equation (1) are the usual Landau expression for the free energy associated with the order parameter  $\eta$  at zero strain. With the additional assumption that

$$\alpha = \alpha_0(T - T_0), \quad (2)$$

these three terms (which give the free energy of the clamped crystal) predict a first order transition if  $\beta < 0$  and a second order transition if  $\beta > 0$ . For second order transitions, the transition occurs at  $T_0$ ; below  $T_0$  the equilibrium value of the order parameter increases as  $(T_0 - T)^{\frac{1}{2}}$ , while the susceptibility  $(\partial^2 A / \partial \eta^2)^{-1}$  diverges as  $|T_0 - T|^{-1}$  from both sides.

The fourth term in equation (1) is the leading (harmonic) term in the elastic energy. The elastic constant  $C$  is taken at  $\eta = 0$ . Finally, the last two terms in equation (1) represent the lowest orders of coupling between the order parameter  $\eta$  and the strain  $x$ . For crystals in which  $\eta$  and  $x$  have the same wavevector and same symmetry (i.e., transform according to the same irreducible representation of the crystal point group), the first term is allowed. This is the case for our class (1), the piezoelectric ferroelectrics, where  $a$  is the linear piezoelectric constant. For crystals where linear coupling is forbidden by symmetry, the lowest order coupling possible is via the last term in equation (1). For the non-piezoelectric ferroelectrics, class (2), this coupling represents electrostriction. For the improper ferroelectrics of class (3) it represents anharmonic coupling of a zone centre acoustic mode to two zone edge soft modes. For all three classes, the coupling produces a spontaneous elastic deformation in the low temperature phase which led Aizu (1969) to introduce the term 'ferroelastic'. Following him, we will henceforth refer to the high temperature high symmetry phase as  $P$  (paraelectric or paraelastic) and the low temperature phase as  $F$  (ferroelectric or ferroelastic). We will also restrict the discussion to cases where  $\beta > 0$  so that the transition is of second order.

## (a) Case 1

In the presence of linear coupling we neglect the last term in equation (1). Minimizing  $A$  by setting  $(\partial A/\partial \eta) = (\partial A/\partial x) = 0$ ,

$$F_\eta = (\partial A/\partial \eta) = \alpha\eta + \beta\eta^3 + \gamma\eta^5 - ax = 0, \quad (3a)$$

$$X = (\partial A/\partial x) = Cx - \alpha\eta = 0, \quad (3b)$$

where  $X$  is the stress and  $F_\eta$  is the force conjugate to  $\eta$ . Solving equations (3), one obtains

$$x_0 = (a/C)\eta_0, \quad (4)$$

$$\eta_0[\alpha_0(T - T'_0) + \beta\eta_0^2 + \gamma\eta_0^4] = 0, \quad (5)$$

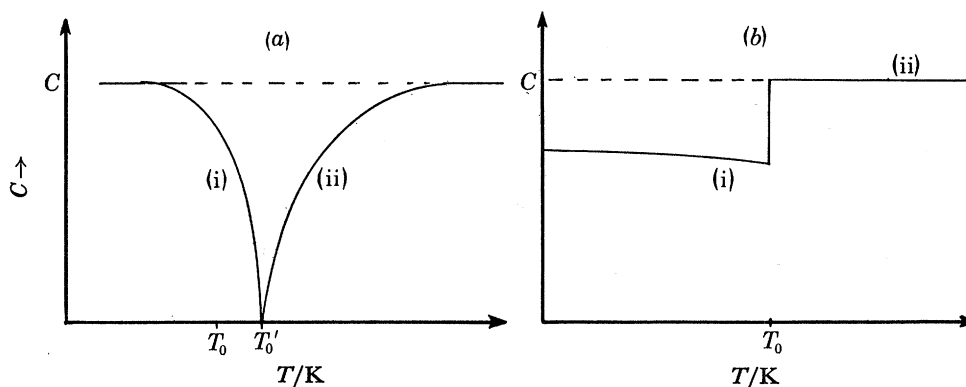


FIGURE 1. Temperature dependence of the static elastic constant  $C(0)$ . (a) Case (1), linear coupling. (i)  $C(0) = C - a^2/(2\alpha_0(T'_0 - T) + a^2/C)$ ; (ii)  $C(0) = C - a^2/(\alpha_0(T - T'_0))$ . (b) Cases (2) and (3), quadratic coupling. (i)  $C(0) = C - K^2/(2\beta + 4\gamma\eta_0^2)$ ; (ii)  $C(0) = C$ .

where  $x_0$  and  $\eta_0$  are the equilibrium values of the strain and order parameter and  $T'_0 = T_0 + a^2/C\alpha_0$ . Equation (5) shows that for  $T > T'_0$ ,  $\eta_0 \equiv 0$  while for  $T < T'_0$ ,  $\eta_0^2 \approx \alpha_0(T'_0 - T)/\beta$ . Equation (4) shows that  $x_0$  increases linearly with  $\eta_0$ . The major effect of the linear coupling term is to shift the transition temperature from  $T_0$  (clamped Curie temperature) to  $T'_0$  (free Curie temperature), where  $T'_0 - T_0$  is typically a few Centigrade degrees.

To find the elastic constant we start with the two minimization equations (3), and set  $\eta = \eta_0 + \delta\eta$ ,  $x = x_0 + \delta x$ . Multiplying out the results and keeping only linear terms in the small deviations  $\delta\eta$  and  $\delta x$  yields:

$$\delta\eta[\alpha + 3\beta\eta_0^2 + 5\gamma\eta_0^4] - a\delta x = 0. \quad (6)$$

In the thermodynamic limit, the stress is assumed to change slowly enough so that  $\eta$  always stays in equilibrium with  $x$  via equation (6). Then the stress produced by small strains is given by

$$X = (\partial A/\partial x) = C\delta x - a\delta\eta = [C - a^2/(\alpha + 3\beta\eta_0^2 + 5\gamma\eta_0^4)]\delta x. \quad (7)$$

The expression in square brackets in equation (7) is the static elastic constant  $C(0)$ . Its temperature dependence is illustrated schematically in figure 1 (a).

## (b) Cases 2 and 3

Repeating the above analysis with the coupling represented by the last term in equation (1), we find

$$x_0 = (K/2C)\eta_0^2, \quad (8)$$

$$\eta_0[\alpha_0(T - T_0) + (\beta - K^2/2C)\eta_0^2 + \gamma\eta_0^4] = 0. \quad (9)$$

Assuming that  $K$  is small enough that  $(\beta - K^2/2C) > 0$ , the transition still occurs at  $T_0$ , below which  $\eta_0^2 \approx \alpha_0(T_0 - T)/(\beta - (K^2/2C))$  while  $x_0$  increases quadratically with  $\eta_0$ , and hence linearly with  $(T_0 - T)$ . The fact that a quadratic (electrostrictive) coupling term in the Landau–Devonshire free energy would produce a spontaneous strain proportional to  $\eta_0^2$  was first noted for the case of TGS by O'Brien & Litovitz (1964). Note that the coupling does not modify the transition temperature  $T_0$  in this case, but leads instead to a modification of  $\beta$ .

The small deviation expansion for this case gives

$$\delta\eta[\alpha + 3\beta\eta_0^2 + 5\gamma\eta_0^4 - (K^2/2C)\eta_0^2] = K\eta_0\delta x, \quad (10)$$

and finally,

$$\begin{aligned} X = \frac{\partial A}{\partial x} &= C\delta x - K\eta_0\delta\eta = \left[ C - \frac{K^2\eta_0^2}{\alpha + (3\beta - K^2/2C)\eta_0^2 + 5\gamma\eta_0^4} \right] \delta x \\ &= C\delta x (T > T_0) = \left[ C - \frac{K^2}{2\beta + 4\gamma\eta_0^2} \right] \delta x (T < T_0). \end{aligned} \quad (11)$$

The static elastic constant  $C(0)$  given by equation (11) is illustrated in figure 1(b). Note that in this case there is no effect for  $T > T_0$ , while for  $T < T_0$  there is a nearly temperature independent downward shift in  $C(0)$  relative to  $C$ .

Although the thermodynamic elastic constants of equations (7) and (11) are in qualitative agreement with various ultrasonic and Brillouin scattering experiments, there are a number of problems which arise when a detailed comparison with experiment is attempted:

(1) ultrasonics and Brillouin scattering are dynamic measurements. If the characteristic frequency (or relaxation rate) of the soft mode is not very much higher than the acoustic frequencies involved in the experiment, the thermodynamic predictions should not be expected to apply;

(2) the above thermodynamic analysis predicts isothermal elastic constants, whereas Brillouin scattering experiments measure adiabatic elastic constants. The necessary 'adiabatic correction' can be made to the analysis if appropriate thermodynamic parameters are available. For example, for KDP, that adiabatic correction can increase the predicted elastic constant in the ferroelectric phase within  $1^\circ$  of the transition by 50% or more (Brody & Cummins 1974);

(3) the thermodynamic analysis completely neglects fluctuations, but the discontinuous step in  $C(0)$  for the quadratic coupling case, shown in figure 1(b), rests on the validity of equations (9) and (10) in the F phase right into  $T = T_0$ . At some point, however, the fluctuations in  $\eta_0$  will become comparable to  $\eta_0$  and the linearization procedure will break down leading to some rounding of the step.

The consequences of higher order anharmonic coupling between the acoustic and soft modes in renormalizing the elastic constants near  $T_0$  were considered for quartz by Axe & Shirane (1970) and discussed in relation to GMO by Höchli (1972).

### 3. DYNAMIC ANALYSIS

In order to proceed beyond the thermodynamic predictions of § 2, the acoustic mode and soft modes must be treated as dynamical degrees of freedom. In § 3(c) we will discuss a general method for analysing light scattering from systems of coupled dynamical modes. First, however, we will examine two approximate methods which provide useful physical insights into the effects of mode interaction.

(a) *Coupled harmonic oscillators*

Consider first the well known problem of two linearly coupled undamped harmonic oscillators. The Lagrangian is

$$L = T - V = \frac{1}{2}M_1\dot{X}_1^2 + \frac{1}{2}M_2\dot{X}_2^2 - \frac{1}{2}K_1X_1^2 - \frac{1}{2}K_2X_2^2 - K_{12}X_1X_2. \quad (12)$$

The equations of motion derived from equation (12), together with the substitution  $X(t) = X \exp(i\omega t)$  give:

$$X_1(\omega_1^2 - \omega^2) + X_2K_{12}/M_1 = 0, \quad X_1(K_{12}/M_2) + X_2(\omega_2^2 - \omega^2) = 0, \quad (13)$$

$$(\omega_1^2 - \omega^2)(\omega_2^2 - \omega^2) - k^2 = 0, \quad (14)$$

where  $k^2 = K_{12}^2/M_1M_2$ . The two roots of the secular equation (14) give the eigenfrequencies of the coupled oscillators,  $\omega_+$  and  $\omega_-$ :

$$\omega_{\pm}^2 = \frac{1}{2}[\omega_1^2 + \omega_2^2 \pm \{(\omega_1^2 - \omega_2^2)^2 + 4k^2\}^{1/2}]. \quad (15)$$

The solutions to equation (15) are shown in figure 2. For the case where  $\omega_1$  and  $\omega_2$  represent the soft mode and the acoustic mode respectively:

$$\omega_1^2 = \omega_0^2(T - T_0), \quad \omega_2^2 = \text{constant}. \quad (16)$$

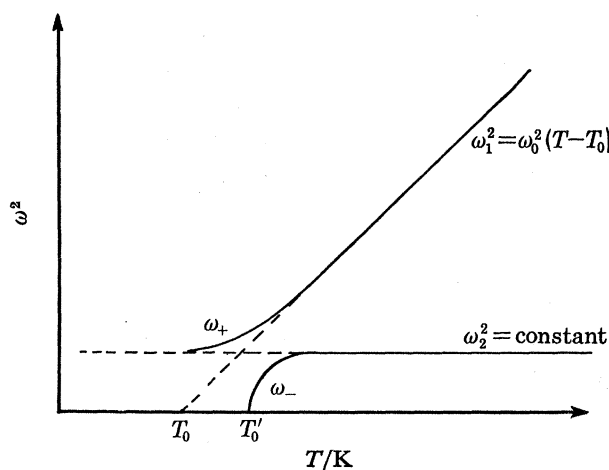


FIGURE 2. Temperature dependence of the eigenfrequencies  $\omega_{\pm}$  of two linearly coupled simple harmonic oscillators (equation 15).

If  $\omega_1 \gg \omega_2$  and  $(\omega_1^2 - \omega_2^2) \gg k$ , equation (15) becomes

$$\left. \begin{aligned} \omega_{\pm}^2 &\approx \frac{1}{2}\{\omega_1^2 + \omega_2^2 \pm [\omega_1^2 - \omega_2^2 + 2k^2/(\omega_1^2 - \omega_2^2)]\}, \\ \omega_+^2 &\approx \omega_1^2 + 2k^2/(\omega_1^2 - \omega_2^2) \approx \omega_1^2, \end{aligned} \right\} \quad (17)$$

$$\omega_-^2 \approx \omega_2^2 - 2k^2/\omega_1^2. \quad (18)$$

For crystals of class 1, the proper ferroelectrics, the piezoelectric coupling between the soft mode and the acoustic mode is essentially independent of temperature, so that the approximate result of equation (18) for  $\omega_-^2$  is seen to be of the same form as the thermodynamic prediction, equation (7) for the elastic constant.

For the improper ferroelastics (classes 2 and 3) there is no linear coupling in the P phase. However, in the F phase, there is an effective linear coupling of  $K\eta_0$  which, in the case of class 2



materials like TGS, results in morphic linear piezoelectricity. The induced linear coupling is produced by the spontaneous symmetry breaking and is thus proportional to the equilibrium value of the order parameter.

For class 3 materials the presence of induced linear coupling in the F phase seems paradoxical at first glance, since in the P phase the soft mode lies at the boundary of the Brillouin zone so that linear coupling to a zone centre acoustic phonon is forbidden by momentum conservation. However, the condensation of the soft mode produces a multiplication of the size of the unit cell which causes the soft mode to move to the centre of the Brillouin zone in the F phase. Therefore, both class 2 and 3 materials in the F phase can be considered as examples of linearly coupled oscillators which differ from class 1 only in that the coupling constant is strongly temperature dependent.

The approximate coupled oscillator result (18) for this case then becomes (for the F phase)

$$\omega_-^2 \approx \omega_2^2 - 2K^2\eta_0^2/\omega_1^2. \quad (19)$$

Since both  $\omega_1^2$  and  $\eta_0^2$  are very nearly proportional to  $(T_0 - T)$ , equation (19) predicts a constant downward shift of  $\omega_-^2$  in the F phase in agreement with the thermodynamic prediction equation (11). However, this approximation is not valid unless  $\omega_1 \gg \omega_2$ .

For an improper ferroelastic exhibiting a second order transition,  $\omega_1$  should become very small as the transition is approached from below, and eventually there will be an additional downward trend in  $\omega_-^2$  due to the 'level repulsion' or 'anticrossing' effect. Since this additional downward curvature is expected to occur in the temperature range where  $\omega_1$  becomes comparable to  $\omega_2$ , it will depend crucially on the frequency of the sound wave involved, and should therefore cause a difference between the elastic constants determined from Brillouin scattering or ultrasonic measurements.

(b) *Method of O'Brien & Litovitz (1964)*

If the soft mode is heavily overdamped, it can be considered as a purely relaxational mode governed by a kinetic equation of the form

$$\frac{d}{dt}(\eta - \eta_0) = -\Gamma \frac{\partial A}{\partial \eta}. \quad (20)$$

Landau & Khalatnikov (1954) first noted that when equation (20) is combined with the Landau free energy, the relaxation rate is

$$\tau^{-1} = \frac{\Gamma}{\eta} \frac{\partial A}{\partial \eta} \propto \Gamma |T - T_0|,$$

so that (assuming that  $\Gamma$  is independent of  $T$ ) the width of the soft mode should decrease linearly with  $T - T_0$  as the transition is approached: a manifestation of 'critical slowing down.'

O'Brien & Litovitz (1964) showed how the complex frequency dependent sound velocity of TGS can be deduced with the help of the kinetic equation (20).

Returning to the free energy (1) for classes 2 and 3, we have the two thermodynamic forces  $X$  and  $F_\eta$ :

$$X = \delta A / \delta x = Cx - \frac{1}{2}K\eta^2, \quad (21)$$

$$F_\eta = \delta A / \delta \eta = \alpha\eta + \beta\eta^3 + \gamma\eta^5 - Kx\eta. \quad (22)$$

At equilibrium,  $X = F_\eta = 0$ . For small departures from equilibrium,

$$\delta X = C\delta x - K\eta_0\delta\eta, \quad (23)$$

$$\delta F_\eta = \delta\eta(2\beta\eta_0^2 + 4\gamma\eta_0^4) - K\eta_0\delta x. \quad (24)$$

We define the complex elastic constant  $\tilde{C}$ :

$$\tilde{C} = \delta X/\delta x = C - K\eta_0(\delta\eta/\delta x). \quad (25)$$

If the relaxation time for order parameter fluctuations is so short that  $\eta$  always remains in equilibrium with  $x$ , then  $F_\eta = 0$  even when  $X \neq 0$ , and from equation (24) we get  $\delta\eta/\delta x = K\eta_0/(2\beta\eta_0^2 + 4\gamma\eta_0^4)$ , whence

$$\tilde{C} = C - \frac{K^2\eta_0^2}{(2\beta\eta_0^2 + 4\gamma\eta_0^4)} = C - \frac{K^2}{2\beta + 4\gamma\eta_0^2}, \quad (26)$$

which is simply the thermodynamic result of equation (11).

If the frequency  $\omega$  of the sound wave is not very small compared to  $\tau^{-1}$ , then  $\eta$  will not stay in equilibrium with  $x$  and  $F_\eta$  will not be zero.

Let 
$$\delta x(t) = \delta x \exp i(\omega t - q \cdot r),$$

$$\delta\eta(t) = \delta\eta \exp i(\omega t - q \cdot r);$$

the kinetic equation (20) together with equation (24) for  $F_\eta$  then gives

$$\left. \begin{aligned} i\omega\delta\eta &= -\Gamma\{\delta\eta(2\beta\eta_0^2 + 4\gamma\eta_0^4) - K\eta_0\delta x\}, \\ \delta\eta/\delta x &= \frac{K\eta_0}{2\beta\eta_0^2 + 4\gamma\eta_0^4 + (i\omega/\Gamma)}, \\ \tilde{C}(\omega) &= C - \frac{K^2}{2\beta + 4\gamma\eta_0^2 + (i\omega/\Gamma\eta_0^2)}, \end{aligned} \right\} \quad (27)$$

which, in the limit  $\omega \rightarrow 0$ , again recovers the thermodynamic result.

We rewrite equation (27) as

$$\tilde{C}(\omega) = C - \frac{K^2/(2\beta + 4\gamma\eta_0^2)}{1 + i\omega\tau}, \quad (28)$$

where  $\tau = [\Gamma\eta_0^2(2\beta + 4\gamma\eta_0^2)]^{-1}$  is the relaxation time of the soft mode.

From equation (28), the sound velocity is

$$V^2(\omega) = V_\infty^2 - \frac{(V_\infty^2 - V_0^2)}{1 + \omega^2\tau^2}, \quad (29)$$

where  $V_\infty^2 = C/\rho$  and  $V_\infty^2 - V_0^2 = (C_\infty - C_0)/\rho = K^2/\rho(2\beta + 4\gamma\eta_0^2)$ . Equation (29) predicts that for fixed  $\omega$ , as  $T$  approaches  $T_0$  from below, the sound velocity will increase from  $V_0$  to  $V_\infty$  with an inflexion point at  $\omega\tau = 1$ . Note that this is the same increase in  $V$  predicted by the thermodynamic equation, but it occurs below (rather than at)  $T_0$ , and  $V(t)$  is now a smooth function of  $T$  rather than a step function.

The attenuation predicted by equation (28) is

$$\alpha = \frac{V_\infty^2 - V_0^2}{2V_\infty^3} \frac{\omega\tau}{1 + \omega^2\tau^2}. \quad (30)$$

If the relaxation time  $\tau$  of the soft mode is sufficiently long, then its temperature dependence can be studied by noting, for each ultrasonic frequency  $\omega$ , the temperature at which  $V$  increases



from  $V_0$  to  $V_\infty$  or at which attenuation is a maximum. Brillouin scattering experiments in TGS were able to detect the velocity change predicted by equation (29) and thus explore  $\tau(T)$ . These experiments will be described in § 4 (b).

(c) *General coupled mode formalism*

The approximate analyses of 3 (a) and 3 (b) for undamped or highly overdamped soft modes can only provide the frequencies of the coupled mode system. A more general approach which predicts the entire light scattering spectrum  $I(\omega)$  will be described briefly in this section. The details of the method as applied to KD\*P (potassium di-deuterium phosphate) can be found in Reese *et al.* (1973).

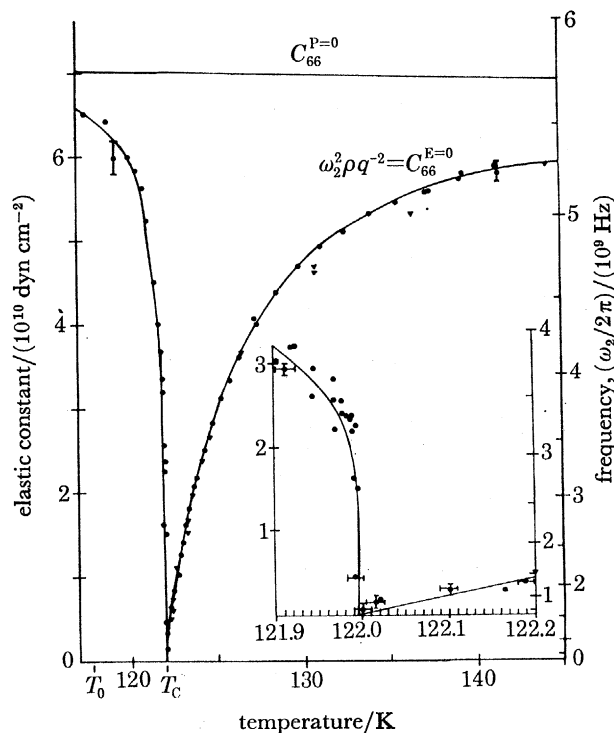


FIGURE 3. Temperature dependence of the elastic constant  $C_{66}^{E=0}$  of KDP deduced from Brillouin scattering and ultrasonic measurements (from Brody & Cummins (1968)).

(1) Starting with the Helmholtz free energy, equation (1), one constructs the Lagrangian density for the coupled mode system and from it finds the coupled equations of motion.

(2) From these one finds the four susceptibilities  $\chi_{xx}$ ,  $\chi_{\eta\eta}$ ,  $\chi_{x\eta}$  and  $\chi_{\eta x}$  (there will be  $N^2$  such susceptibilities if  $N$  coupled modes are included).

(3) With the help of the Wiener–Khinchine and fluctuation–dissipation theorems the spectrum can be shown to be:

$$I(\omega) \propto \{kT/n(\omega)\} \Sigma B_i B_j \chi_{ij}''(\omega), \quad (31)$$

where the  $B_i$  are optical coupling constants (e.g. Pockel's elasto-optic coefficients) and  $n(\omega)$  is the Bose factor.

Equation (31) permits a detailed comparison between Brillouin scattering experiments and

various models of the soft mode dynamics. When the frequencies of the two modes are comparable and there is considerable damping, the spectrum is rather complicated and cannot be simply analysed in terms of a Brillouin shift and linewidth.

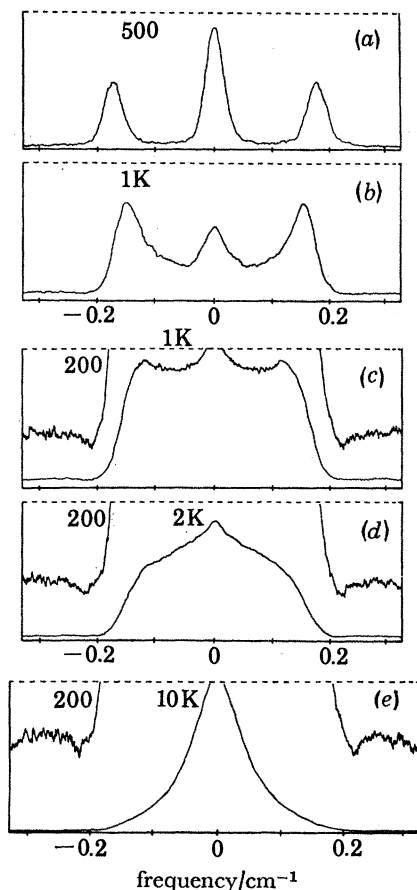


FIGURE 4. Brillouin spectra of KD\*P at five different temperatures.  $\Delta T = T - T'_0$  where  $T'_0 = 220.68$  K. (a)  $\Delta T = 74.28$  K, (b)  $\Delta T = 14.24$  K, (c)  $\Delta T = 6.08$  K, (d)  $\Delta T = 4.35$  K, (e)  $\Delta T = 0.98$  K. (From Reese *et al.* (1973).)

#### 4. SURVEY OF EXPERIMENTS

##### (a) Class 1 materials

As an example of a class 1 material we consider potassium dihydrogen phosphate (KDP) and its deuterated isomorph KD\*P. The temperature dependence of the  $xy$  shear mode in KDP, which is linearly coupled to the polarization  $P_3$  via the piezoelectric constant  $a_{36}$  is shown in figure 3 from Brody (1968). The transition is actually slightly first order, although recent experiments by Schmidt *et al.* (1976) and Bastie *et al.* (1978) indicate that it becomes second order under hydrostatic stress of *ca.* 2 kbar.†

In the P phase, the frequency of the (overdamped) soft mode is much higher than that of the acoustic modes seen in Brillouin scattering so that the elastic constant deduced from the Brillouin data follows the thermodynamic prediction of equation (7) (Brody & Cummins 1968, 1974).

† 1 bar =  $10^5$  Pa.

For  $KD^*P$ , however, the soft mode frequency is comparable to that of the acoustic mode and the thermodynamic analysis is inadequate. A series of spectra of  $KD^*P$  illustrating the complicated lineshape produced by the interaction is shown in figure 4 from Reese *et al.* (1973). These spectra were successfully analysed with the coupled mode formalism described in § 3(c).

Note that although only the  $xy$  shear strain is linearly coupled to the polarization  $P_3$  and is thereby proportional to  $P_3$  in the F phase, other strains can couple to  $P_3$  quadratically via electrostriction and can thus be proportional to  $P_3^2$ . The predicted temperature dependence of both  $xy$  and  $zz$  strains in the vicinity of the transition have recently been observed by Bastie *et al.* (1978).

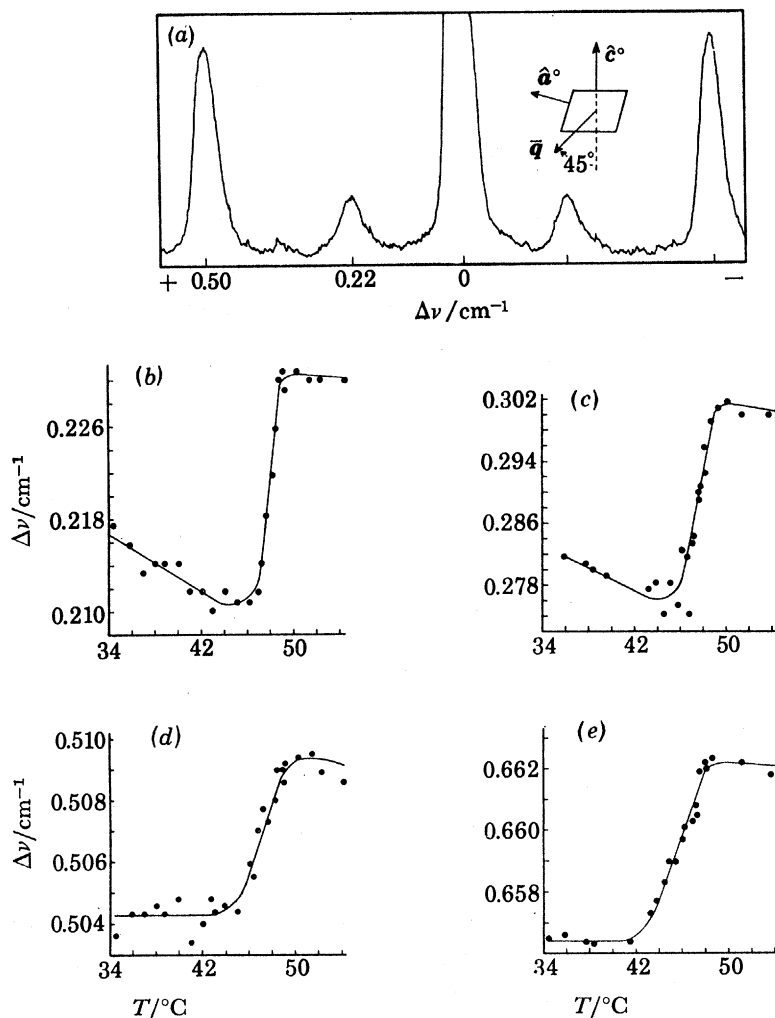


FIGURE 5. Brillouin spectrum and temperature dependence of the Brillouin shifts in TGS. (a) (010) plane,  $\theta = 90^\circ$ ; (b) transverse,  $\theta = 90^\circ$ ; (c) transverse,  $\theta = 135^\circ$ ; (d) longitudinal,  $\theta = 90^\circ$ ; (e) longitudinal,  $\theta = 135^\circ$ . (From Gammon (1967).)

#### (b) Class 2 materials

Triglycine sulphate (TGS) is an example of class 2 materials, the nonpiezoelectric ferroelectrics. O'Brien & Litovitz (1964) first explored the temperature-dependent acoustic properties of TGS with ultrasonic techniques. Subsequently Gammon & Cummins (1966) and

Gammon (1967) performed Brillouin scattering experiments which revealed the behaviour predicted by the analysis of § 3(b) with a rounded upward step occurring below the transition at  $T_c = 49^\circ\text{C}$ .

Figure 5, from Gammon (1967), shows the temperature dependence of the Brillouin shifts of longitudinal and transverse acoustic modes at scattering angles of  $90^\circ$  and  $135^\circ$ . Each curve can be analysed by following equation (28) or (29), or else simply used to find one value of  $\tau(T)$  since  $\omega\tau \approx 1$  at the temperature where  $\Delta\nu$  passes through the midpoint of the dispersion curve. The resulting four points were found to agree well with the Landau–Khalatnikov prediction with

$$\tau = (2.9 \pm 0.3) \times 10^{-11} (T_c - T)^{-1} \text{ s.} \quad (31)$$

Note that both the upward (rounded) step in the velocity and the peak in the linewidth occur at a temperature lower than the transition temperature, in marked contradiction to the thermodynamic analysis.

(c) *Class 3 materials*

We now turn to the materials whose properties we are primarily interested in investigating, the improper ferroelectrics. In 1967, Borchardt & Bierstedt discovered that a group of rare earth molybdates undergo ferroelectric phase transitions at or near  $159^\circ\text{C}$ . Cross *et al.* (1968) found that the dielectric anomaly in gadolinium molybdate (GMO) disappears if the crystal is mechanically clamped, suggesting that the polarization is not the true order parameter but is instead an indirect result of the spontaneous strain induced by piezoelectric coupling.

Subsequently, several theoretical papers appeared, suggesting that the transition was associated with a doubly degenerate soft mode at the edge of the Brillouin zone in the P phase. In 1972, Dorner *et al.* (1972) studied the neutron scattering spectrum of terbium molybdate (TMO) and observed a soft mode which is doubly degenerate and lies at the M point of the Brillouin zone for  $T > T_0 = 159^\circ\text{C}$ . A summary of the earlier experimental and theoretical work on these materials can be found in their paper.

For  $T > T_0$ , they found that the soft mode frequency exhibits the familiar temperature dependence

$$\omega_M^2 = A(T - T_c)$$

with  $T_c = 149^\circ\text{C}$  and  $A = 0.0165 \text{ (meV)}^2/^\circ\text{C}$ .

Their results also showed that the static antiferroelectric displacement resulting from the condensation of the soft mode at the zone boundary constitutes the order parameter which couples anharmonically to the shear strain  $u_{xy}$ . Both the spontaneous strain  $u_{xy}$  and the spontaneous polarization were found to be proportional to  $\eta_0^2$ .

Since ferroelectricity in these crystals is thus a tertiary effect, it can, to first approximation, be ignored and the acoustic properties can be discussed in terms of the simple free energy we introduced in § 2. A more detailed analysis of the thermodynamics with additional terms kept in the free energy is given in Dorner *et al.* (1972) and in several of the references cited there.

Cross *et al.* (1968) showed that the elastic constant  $C_{66}$  of GMO exhibits a strong anomaly in the F phase but is almost constant in the P phase in marked contrast to ‘proper’ piezoelectric ferroelectrics like KDP. Subsequently, other studies of the elastic properties of these crystals appeared, in particular an ultrasonic study of GMO by Höchli (1972) and Brillouin scattering measurements by Luspín & Hauret (1974) and Busch (1974).

In figure 6 we see the elastic constants and Brillouin linewidths in GMO found by Luspín & Hauret (1974). Note that the step in the elastic constants as well as the maximum in the

linewidth occurs at the transition temperature in marked contrast to the case of TGS discussed in the preceding section. The elastic constants deduced from Brillouin scattering were also found to be in good agreement with the ultrasonic results of Höchli (1972) who, furthermore, found no dispersion in sound velocities between 10 and 70 MHz.

The absence of dispersion effects in GMO of the sort observed in TGS is probably due to the fact that the transition is of first rather than second order. Indeed, the neutron scattering results of Dorner *et al.* (1972) indicate that at the transition, the soft mode frequency is still about  $3 \text{ cm}^{-1}$ , which is sufficiently high that the thermodynamic approximation is at least roughly valid. However, other improper ferroelectrics may turn out to have transitions which are closer to second order, making dispersion effects observable. Furthermore, it is possible that the order of the transition may be modified by hydrostatic stress as in the cases of  $\text{NH}_4\text{Cl}$  and KDP, both of which become second order under moderate stress.

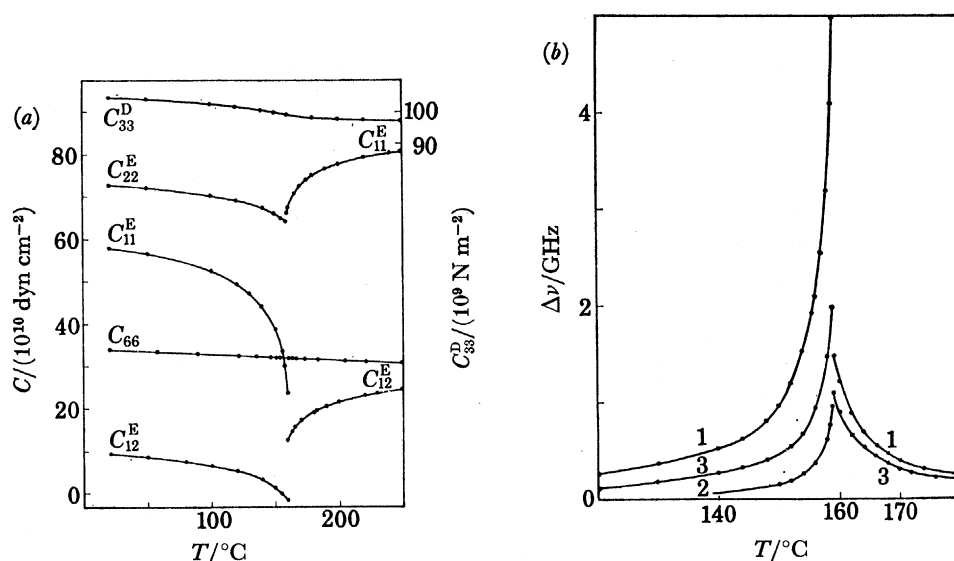


FIGURE 6. Results of Brillouin scattering measurements of GMO. (a) Temperature dependence of the elastic constants. (b) Temperature dependence of the linewidth of longitudinal Brillouin components for directions of propagation [100] (1), [010] (2) and [110] (3) (from Luspin & Hauret (1974)).

Finally, there is the problem of the rounding of the elastic constants observed in both the F and P phases as can be seen in figure 6. Höchli (1972) has shown how this rounding effect can be interpreted as anharmonic coupling between the acoustic mode and pairs of optic modes, following the theoretical work of Pytte and Axe & Shirane (1970). In this analysis, one must include the entire branch of modes containing the soft mode rather than only pairs of isolated soft modes so that the predicted effects are not included in either the thermodynamic theory or the simplified coupled mode theories we have discussed. The computational method is very similar to that employed in the mode-mode coupling theories of Kawasaki and Kadanoff and Swift where anomalous behaviour of long wavelength hydrodynamic modes is evaluated by integrating over all pairs of intermediate states to which the mode can couple.

Although we have considered only a few particular examples of structural phase transitions involving interactions with acoustic modes, many other cases have been studied and we mention a few briefly. First, there are some crystals which undergo structural transitions in which strain

is the actual order parameter; the best known example is  $\text{Nb}_3\text{Sn}$ . Recently Toledano *et al.* (1976) has observed a soft acoustic shear mode in lanthanum pentaphosphate by Brillouin scattering which may also be an example of strain as the order parameter. Second, there are examples of coexisting ferroelectric and ferroelastic behaviour in which the two effects are uncoupled, such as barium sodium nitrate (Toledano 1975). Finally, a very interesting transition was recently investigated by Sawada *et al.* (1977). Lithium ammonium tartarate resembles KDP in that a zone centre polar optic mode, which condenses at the ferroelectric phase transition, is linearly coupled piezoelectrically to an acoustic mode so that spontaneous strain is proportional to spontaneous polarization. In contrast to KDP, however, these authors find that it is the strain that is the primary order parameter while the dielectric anomaly occurs as a consequence of the coupling. The analysis proceeds very much in the spirit of our discussion of class 1 materials, except that the role of polarization and strain are reversed.

I wish to thank the École Normale Supérieure and the CNRS for their generous hospitality. I am also happy to acknowledge a stimulating discussion about improper ferroelectrics with J. C. Toledano of the CNET.

## REFERENCES (Cummins)

- Aizu, K. 1969 *J. phys. Soc. Japan* **27**, 387–396.  
 Axe, J. D. & Shirane, G. 1970 *Phys. Rev. B* **1**, 342–348.  
 Bastie, P., Vallade, M., Vettier, C. & Zeyen, C. M. E. 1978 *Phys. Rev.* (In the press.)  
 Brody, E. M. & Cummins, H. Z. 1968 *Phys. Rev. Lett.* **21**, 1263–1266.  
 Brody, E. M. & Cummins, H. Z. 1974 *Phys. Rev. B* **9**, 179–196.  
 Busch, M. 1974 Thèse, Université de Paris (Document de CNET no. PEC 190). *Opt. Commun.* **10**, 273–276.  
 Cross, L. E., Fouskava, A. & Cummins, S. E. 1968 *Phys. Rev. Lett.* **21**, 812–814.  
 Dorner, B., Axe, J. & Shirane, G. 1972 *Phys. Rev. B* **6**, 1950–1968.  
 Dvorak, V. 1971 *Phys. Status Solidi B* **46**, 763–772.  
 Gammon, R. W. & Cummins, H. Z. 1966 *Phys. Rev. Lett.* **17**, 193–195.  
 Gammon, R. W. 1967 Ph.D. thesis, Johns Hopkins University, Baltimore, Maryland (unpublished).  
 Höchli, U. T. 1972 *Phys. Rev. B* **6**, 1814–1823.  
 Jona, F. & Shirane, G. 1962 *Ferroelectric crystals*. Oxford: Pergamon Press.  
 Landau, L. D. & Khalatnikov, L. M. 1954 *Dokl. Akad. Nauk SSSR* **96**, 469–475.  
 Luspín, Y. & Hauret, G. 1974 *J. de Phys. Lett.* **35**, L193–195.  
 O'Brien, E. J. & Litovitz, T. A. 1964 *J. appl. Phys.* **35**, 180–186.  
 Reese, R., Fritz, I. J. & Cummins, H. Z. 1973 *Phys. Rev. B* **7**, 4165–4185.  
 Sawada, A., Udagawa, M. & Nakamura, T. 1977 *Phys. Rev. Lett.* **39**, 829–832.  
 Schmidt, V. H., Western, A. B. & Baker, A. G. 1976 *Phys. Rev. Lett.* **37**, 839–842.  
 Toledano, J. C. 1975 *Phys. Rev. B* **12**, 943–950.  
 Toledano, J. C., Errandonéa, G. & Jaguin, J. P. 1976 *Solid St. Commun.* **20**, 905–907.