Soft-mode spectroscopy: Experimental studies of structural phase transitions*

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This paper reviews the experimental studies of displacive phase transitions in solids. Primary emphasis is upon inelastic light scattering and neutron scattering; related infrared reflectivity measurements, as well as x-ray and EPR analyses are also summarized. Several prototype structures are considered in detail: (1) the rocksalt IV–VI semiconductors PbTe, SnTe, and GeTe; (2) the ferroelectric perovskites exemplified by $PbTiO_3$ and $BaTiO_3$; (3) perovskites which exhibit cell-doubling transitions, such as $LaAlO_3$, $SrTiO_3$, and $KMnF_3$; (4) crystals having the α-quartz structure, including GeO_2, SiO_2, and $AlPO_4$; (5) the "improper ferroelectrics" $Gd_2(MoO_4)_3$ and $Tb_2(MoO_4)_3$; (6) the V–VI–VII semiconductors typified by SbSI; (7) the hydrogen-bonded ferroelectrics of the KH_2PO_4 family; (8) Jahn–Teller systems such as $DyVO_4$ and $RbCoF_3$, in which structural distortions occur as secondary effects; (9) order–disorder systems such as $NaNO_2$ and the ammonium halides (NH_4Cl, NH_4Br), in which no "soft mode" occurs in the spectral region ($\omega > 10^{11}$ Hz) probed by ir, Raman, and neutron spectroscopy; (10) β-tungsten ($A - 15$) structures such as V_3Si and Nb_3Sn, which exhibit high-temperature superconductivity. These crystal categories are used to illustrate several phenomena of current physical interest: Specifically, we discuss harmonic and anharmonic mode coupling; "critical exponents" β differing from one-half in the temperature dependences of the order parameter $\varphi(T) = \varphi_0(T - T_0)^\beta$ and of the soft-mode frequency $\omega(T) = \omega_0(T - T_0)^\beta$; and the recently discovered "central" modes centered at zero frequency, which grow in intensity as the transition temperature T_0 is approached from above or below. The review covers the period 1940-1972. A few 1973 works are mentioned for which the author had preprints in 1972 or very early 1973. This review is in no sense a comprehensive survey of ferroelectricity. Readers are referred to the following earlier reviews on that subject: Silverman (1966, 1969), Cochran and Cowley (1967), Blinc (1968), Murzin *et al.* (1968), Nettleton (1970), and Blinc and Zaks (1972).

CONTENTS

I. INTRODUCTION

Over the last decade the experimental studies of structural phase transitions have been numerous. Various spectroscopic techniques have been employed, including infrared reflectivity, inelastic light and neutron scattering, EPR, NQR, x-ray, and ultrasonic analyses. At this stage we may say quite generally that for most transitions in which the crystal is ordered in both phases (i.e. possesses periodic transitional symmetry) the structural distortions are characterized by an unstable or "soft" optical phon-

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on, whose frequency decreases substantially as the transition temperature is approached from above or below.[1] This description comprises the now famous theory of Cochran (1960, 1961), which directly stimulated much of the experimental work of the last decade.

Several reviews have summarized progress in this field in recent years. The surveys by Cochran (1969, 1971) are especially good in discussing theoretical aspects. Barker (1967, 1970) has provided two useful papers which are more tutorial. Other summaries have had more specialized emphases: for example, the study of acousto-optic mode interactions by Fleury (1971).

By far the most useful review of work in this field is the proceedings of the 1971 NATO Advanced Study Institute in Geilo, Norway (Samuelsen *et al.*, 1971). In the present paper we hope to complement the Geilo book in several ways: First, we have summarized work crystal by crystal, rather than categorizing studies according to experimental technique; this may make it easier for nonspecialists to assess quickly the present level of understanding for each substance; second, at the time of the Geilo meeting several important experimental results—specifically, the occurrence of "central modes" centered at $\omega = 0$, and the failure of molecular field theories for structural transitions—were so new that it was very difficult to relate them to earlier measurements and theories. In the present review an attempt has been made to place such discoveries within the context of related work. For example, central modes whose intensities grew at transition temperatures were first predicted and analyzed from an anharmonic point of view by Cowley (1970). This paper was apparently unknown to the authors of the more recent inelastic neutron studies (Riste *et al.*, 1972) as was the study of central modes (diverging Rayleigh intensities) in NH_4Cl by Lazay *et al.* (1969). Even a very recent analysis of central modes in $SrTiO_3$ (Shapiro *et al.*, 1972), using a formalism which distinguishes between collision-free and collision-dominated phonon regimes, does not mention that an equivalent theory was experimentally confirmed by Cowley *et al.* (1971) for KH_2AsO_4 more than a year earlier. Each experiment showed that the soft-mode frequency remained finite at the transition temperature T_0, despite the second-order character of the transition; each paper employed the same theoretical explanation; yet the more recent $SrTiO_3$ paper made no mention of the KH_2AsO_4 work. Such anomalies provide a major motivation for reviews.

A second motive for the present paper has been to assess critically experimental work in the field. In some cases terminology has been misleading: Sakurai *et al.* (1970) have termed $\omega \approx 0$ scattering in $NaNO_2$ "critical," whereas it has no demonstrated connection with critical exponents (Stanley, 1971) analyzed in magnetic transitions (Heller and Benedek, 1962, 1965) or with critical opalescence (Andrews, 1869). We shall term phenomena discussed in this paper critical if they occur *very* near transition temperatures. By "very near" we mean, for T less than the transition temperature T_0, that range of T sufficiently close to T_0 that the rms value of the order parameter is several times its expectation value. Above T_0 the critical regime may be defined as temperatures for which the coherence length for the soft-mode fluctuations exceeds the length characterizing the interparticle potential (and where mean field theory is therefore invalid). The critical regime for structural transitions may exceed 20°K, whereas for magnetic systems a value of 0.01°K may be more typical; see the Ginzburg criterion, Eq. IV-5. Cowley (1972) and Barker (1970) have termed the 106°K transition in $SrTiO_3$ as "antiferroelectric"—yet $SrTiO_3$ is not antiferroelectric in terms of dielectric behavior and is only antiferroelectric if *every* crystal with two formula groups per primitive cell is also. Such semantic distinctions are not important to experts in the field who understand the detailed mechanisms in each crystal class, but they can severely confuse nonspecialists.

Of even greater consequence is work which is simply wrong. As an example of this, we may single out the Raman studies of soft modes in SbSI, where three independent experimental groups have evaluated three completely different temperature dependences; it would seem to follow that two of these are in error. A second example is afforded by the neutron studies on $KMnF_3$ by Minkiewicz *et al.* (1969) who concluded that a soft zone-boundary phonon *quadrupled* the primitive cell from a Pm3m to Pbnm structure. Other errors abound, especially in x-ray studies (e.g., Geller and Bala, 1956), which are relatively insensitive to small rotationlike distortions involving light ions (fluorine or oxygen, typically). In all of the cases considered, the errors have been made by very competent scientists, and by setting the record straight we imply no criticism; however, out of politeness, some workers fail to refute clearly earlier publications, and the resulting contradictions in the literature are not helpful.

A. Early experiments

One experimental study of structural phase transitions stands out as far ahead of its time. The only prewar spectroscopic investigation of a solid state structural phase transition was that of Raman and Nedungadi (1940) on quartz. In this pioneer effort the basic concept of a soft mode was put forth: An optical phonon whose eigenvector approximated the ionic displacements occurring at a crystallographic phase transition was observed to decrease in energy remarkably as the transition temperature was approached from below.

No related spectroscopic experiments were reported for crystallographic phase transitions for many years after Raman and Nedungadi's paper. And in fact their work appears to have been largely overlooked in Western Europe and the United States; it apparently was unknown to Cochran at the time he developed his lattice dynamical theory of structural phase transitions (1960, 1961). The early quartz measurements were perhaps of greater influence in the Soviet Union, where Ginzburg and Levanyuk produced a series of papers (1949a,b; 1955, 1958, 1960, 1962) clearly influenced both by Landau's theory of phase changes (1937) and by the experimental work of Raman and Nedungadi. Much of the emphasis in Russia at this period of time was focused upon the solid state analogue of critical opalescence—the divergence in light scattering cross sections observed in simple fluids a century earlier by Andrews (1869). Experimental efforts by Iakolev *et al.* yielded some indication of critical, quasielastic scattering with cross section divergent as $T \rightarrow T_0$ in quartz, and this was interpreted as solid state critical opalescence (Iakolev *et al.*, 1956a,b; 1957).

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[1] Exceptions are "reconstructive" transitions, such as zincblende–wurtzite, in which large ionic displacements are required.

However, as subsequent experiments by Shapiro and Cummins (1968) were to show, the scattering in quartz was due to microdomain formation in the hysteresis region between ~845 and 847°K characterizing the first-order phase transition in SiO_2.

As we shall discuss in the sections of this paper devoted to experimental studies of individual crystal classes, the first quantitative spectroscopic investigations of solid state displacive phase transitions were the inelastic neutron studies of Cowley (1962, 1964) and the infrared reflectivity analyses of Barker and Tinkham (1962) and Spitzer *et al.* (1962, 1963). All of these papers were subsequent to Cochran's stimulating theoretical work and represented a departure from earlier nonspectroscopic analyses. Prior to 1960, the interest in structural phase transitions (aside from the above-mentioned work on quartz) was very much centered upon ferroelectrics. Independent discovery of ferroelectric $BaTiO_3$ in several laboratories during World War II prompted renewed theoretical interest in the mechanisms of crystallographic distortions, as well as experimental efforts to produce practical technological devices from the new ferroelectric materials. Experimental work during this period was primarily on $BaTiO_3$ and on more complex hydrogen-bonded ferroelectrics known earlier, especially triglycine sulfate (TGS) and potassium di-hydrogen phosphate (KDP). As we shall discuss below, the experimental measurements were macroscopic; they consisted of bulk measurements of the low-frequency dielectric constants and of the spontaneous polarizations as functions of temperature. These macroscopic measurements were the only information available on the phase transition dynamics, and were correlated with x-ray structure data, which of course provided information about *static* properties of the crystals above and below the transition temperatures. For some systems, such as the hydrogen-bonded ferroelectrics, theoretical work (Slater, 1941) offered a microscopic description of the phase transitions, but the *dynamics* of transitions was treated theoretically only by macroscopic, thermodynamical concepts—specifically, by writing out expressions for the free energies, specifying a macroscopic order parameter (the spontaneous polarization in the case of ferroelectrics), and imposing certain stability conditions; namely, that the free energy be minimum with respect to the order parameter. We review this approach below. First, however, we will specify two definitions used in this paper. By ferroelectric we designate a crystal which exhibits hysteresis in its D/E relationship, where E is the macroscopic electric field across the crystal, and D is the electric displacement vector. For some highly conducting crystals, it is not possible to obtain a measurable field across the specimens, and this definition of ferroelectric must be generalized (see the discussions on GeTe and Na_xWO_3 in this paper). To include such cases we will specify that a ferroelectric is a crystal having a polar optical phonon whose eigenvector is the same as the ionic displacements required to transform the lattice to a centric structure with the same number of ions per primitive unit cell.[2] Such a definition is still "operative" and allows us to include GeTe and certain metallic compounds as ferroelectric. The second definition we wish to consider is antiferroelectric. Some years ago crystals were classified as antiferroelectric at a certain temperature if *at a higher temperature* the dielectric constant behaved in a specified, peculiar way. In particular, a crystal was termed antiferroelectric in Phase I if the transition to a higher temperature paraelectric Phase II evidenced a small peak in the dielectric constant at the transition temperature. The difficulty with this description is that a crystal without a phase transition cannot be antiferroelectric. Moreover, the highest temperature phase of any crystal cannot be antiferroelectric. And in general one cannot characterize a crystal at one temperature as antiferroelectric by *any* set of experimental measurements at that temperature. The opinion of this reviewer is that antiferroelectricity is an ill defined, almost useless concept. However, it continues to be used in the literature; if one wishes to define it in order to make comparisons with ferroelectrics, the definition most analogous to that given above for ferroelectric would be: An antiferroelectric is a crystal having a polar optical phonon whose eigenvector is the same as the ionic displacements required to transform the lattice to a centric structure having half[3] as many ions per primitive cell. With this definition an antiferroelectric may or may not be centric. Moreover, a crystal may be simultaneously ferroelectric and antiferroelectric at a given temperature. However, the phases of $SrTiO_3$, $KMnF_3$, and $LaAlO_3$ having two formula groups per primitive cell do *not* fall under the definition given above because the eigenvectors characterizing their transformations to simpler, single-formula-group primitive cells are those of *nonpolar* phonons. The above definitions are illustrated in Fig. 1 for a hypothetical two-dimensional structure. Another concept or definition which should be made explicit in this introduction is that of the "order" of a phase transition. We shall term a transition "first order" if the displacement parameter (or order parameter) φ changes discontinuously at the transition temperature T_0 For such systems, the soft-mode frequency $\omega(T)$ will also exhibit a discontinuity at T_0, and need not decrease to zero at T_0. By "second order" we designate those transitions in which the displacement parameter $\varphi(T)$ decreas-

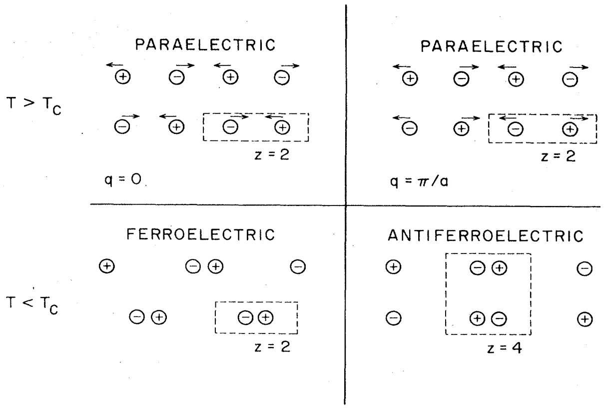

FIG. 1. Two-dimensional diagram of GeTe-structure ferroelectrics. Here z is the number of formula groups per primitive cell.

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[2] We thus include all pyroelectrics as ferroelectric. For device purposes, a ferroelectric is usually defined as a pyroelectric whose direction of spontaneous polarization can be reversed with an applied electric field.

[3] This number need not be half; it could be 1/4, 1/6, ..., $1/n$ for any even integer n.

es continuously to zero at T_0 is approached from above *and* below. The description of transitions as "third order" or higher is no longer popular; however, what would be meant by third order if the term were applied to displacive phase transitions is a transition in which the displacement parameter $\varphi(T)$ decreased to zero as $T \to T_0$ from above and below, and *in addition* has

$$\left.\frac{d\varphi}{dT}\right|_{T=T_0} = 0.$$

If we ignore the subleties of "central modes" for the moment, we may generally say that for second-order (*or any higher order*) displacive phase transitions, the soft-mode frequency will decrease to zero as T_0 is approached from above or below. This point has been understood by all workers in the field except Mooradian and Racah (1971), who erroneously concluded that the failure of their observed soft mode in Ti_2O_3 to decrease to zero indicated that the phase transition was third order or higher. The actual explanation for their data is that the phonon they observe is not a soft mode, i.e., has no direct relationship to the order parameter; and the order parameter for the Ti_2O_3 phase transition is electronic, not displacive.

Let us note also in discussing order parameters that the spontaneous polarization is *not* always the macroscopic order parameter for a ferroelectric. We shall term those for which it is not "improper ferroelectrics" and discuss such situations in the section devoted to gadolinium molybdate and its isomorphs.

B. Free energies: theories of Landau, Devonshire, and Ginzburg

Landau described in 1937 a theory of second-order phase transitions based upon symmetry criteria. In Fig. 2 we show a plot of charge density for a simple one-dimensional lattice. The solid line refers to $T > T_0$, and the dotted line to $T < T_0$. It can be seen that below T_0 the periodicity of the lattice has changed, and that the unit cell has doubled in length. If this kind of change is to occur continuously with temperature, Landau's first requirement is that the charge density can be written as

$$\rho(r) = \rho_0(r) + \Delta\rho(r), \tag{I.1}$$

where $\rho_0(r)$ is a function invariant under the operations of the high-symmetry space group; $\rho(r)$ is invariant under the operations of the low-symmetry space group; and the latter symmetry group is a subgroup of the former.

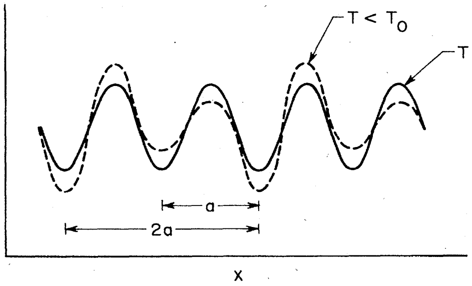

FIG. 2. Charge density $\rho(x)$ vs x above and below a phase transition temperature.

Landau expands the function $\Delta\rho(r)$ in terms of the irreducible representations for the structure considered:

$$\Delta\rho(r) = \sum_{i,j} c_{ij}\phi_{ij}(r), \tag{I.2}$$

where $\phi_{ij}(r)$ are the j-dimensional basis states for the ith irreducible representation. The second assumption of Landau's theory is that changes corresponding to two different representations will set in at the same temperature only by accident. Thus Eq. (I.2) is simplified to

$$\Delta\rho(r) = \sum c_j\phi_j(r). \tag{I.3}$$

The difference between Landau's theory and Cochran's (1959, 1960, 1961) is that Cochran assumes not only that $\Delta\rho(r)$ can be expanded in terms of the irreducible representations (only one of which characterizes the structural change), but in addition, that $\Delta\rho(r)$ can be expanded in terms of eigenvectors or normal coordinates of the lattice, and *only one of these* will characterize the symmetry change at T_0. Cochran's theory is more restrictive, since in general there will be more than one orthogonal normal mode of each symmetry class. For example, in quartz there are four modes of Γ_1 symmetry. Landau's theory says that the α–β transition, if second order, cannot involve distortions of two different symmetries; Cochran's theory adds that it cannot involve two modes of the same symmetry.

Cochran, Landau and Devonshire (1949) all assume that the free energy F near the transition temperature T_0, where the c_i in Eq. (I.3) are small, can be expanded in a power series, e.g.,

$$F = F_0 + \tfrac{1}{2}A\eta^2 + 1/3B\eta^3 + \tfrac{1}{4}C\eta^4 + \cdots, \tag{I.4}$$

where η is a normalized linear combination of the c_i.

The conditions for stability

$$\partial F/\partial\eta = 0 \quad\text{and}\quad \partial^2F/\partial\eta^2 > 0 \tag{I.5}$$

eliminate any linear term in η in Eq. (I.4) and require that the coefficient A in Eq. (I.4) be positive. The condition that F be a true minimum at $\eta = 0$, eliminated the η^3 term in Eq. (I.4). If this latter condition is not satisfied, the phase transition cannot be second order, for a finite η at $T = T_0$ implies finite c_i—which physically must be infinitesimal (Landau's third condition).

The above requirements yield (for all η),

$$0 = \partial F/\partial\eta = A\eta + C\eta^3 \tag{I.6}$$

or $\eta = 0$ for positive A and C; otherwise

$$\eta^2 = -A/C.$$

For $T > T_0$,

$$0 < \left.\frac{\partial^2F}{\partial\eta^2}\right|_{(\eta\,=\,0)} = A.$$

Thus, A is positive. Usually it has been assumed that

$$A = A_0(T - T_0), \tag{I.7}$$

and that C is independent of temperature. This leads to the prediction that the order parameter η varies as

$$\eta = \eta_0|T_0 - T|^{1/2}. \tag{I.8}$$

The assumption given in Eq. (I.7) is not just heuristic. This particular temperature dependence follows from the assumption of infinitely long-range forces, i.e., each particle can be treated as moving in an average potential or "mean field" of all the other particles. This has been done classically for fluids in the Van der Waals theory, and for spins in magnetic systems as well. In fluids and in magnetic systems, the mean field theory *fails* spectacularly, as shown by Heller and Benedek (1962, 1965) for ferromagnetic EuS and antiferromagnetic MnF_2. A theoretical derivation of the exponent $\beta = \frac{1}{2}$ in Eq. (I.8) is given by Stanley (1971). Other critical exponents are derived from mean field theory in this reference, as well. Because the interactions in fluids and magnetic solids are short range, we expect the assumptions leading to Eq. (I.7) to fail. By comparison, the forces in ferroelectrics are largely Coulombic, and therefore of very long range. Thus we expect Eq. (I.8) to hold for soft-mode phase transitions in ferroelectrics.[4] (Note that the α–β transition in quartz and the 106°K transition in $SrTiO_3$ are not of the ferroelectric type.) But in other systems we may find $\beta \approx 1/3$ typical of three-dimensional Ising and Heisenberg models.

The connection between the temperature dependence of the order parameter and a phonon frequency follows from the simple one-dimensional harmonic oscillator equation (η is a displacement; F, a potential) in linear response (Thomas, 1971).

$$m\omega^2 = \partial^2 F/\partial\eta^2 = A \tag{I.9}$$

[from Eq. (I.6)] or

$$\omega = \omega_0 |T - T_0|^{1/2}. \tag{I.10}$$

Thus we conclude that in ferroelectrics or other crystals in which the assumption of infinite range forces is reasonable, a mode having undamped frequency dependence given in Eq. (I.10) may be expected.

C. Cochran's theory

In addition to the macroscopic, thermodynamic approach to soft modes outlined above, two other models have been of great value. They are Cochran's (1960, 1961) lattice dynamical theory, discussed below, and a microscopic, anharmonic theory due primarily to Cowley (1963).

Cochran (1960) points out that for a simple cubic monatomic lattice the stability requirements are that the elastic coefficients satisfy the following conditions:

$$C_{44} > 0, \tag{I.11a}$$

$$C_{11} > 0, \tag{I.11b}$$

$$C_{11}^2 - C_{12}^2 > 0, \tag{I.11c}$$

$$C_{11} + 2C_{12} > 0, \tag{I.11d}$$

and that for complex crystals these conditions are generalized to the requirement that

$$\omega_i > 0 \tag{I.11e}$$

for all i, where ω_i is the ith normal mode frequency. We see, therefore, that $\omega_i \to 0$ is equivalent to some generalized elastic coefficient becoming small. In the latter case, the crystal's restoring force against some shear deformation is weak—the crystal literally softens. This equivalence of ω_i with some generalized elastic coefficient C_{jk} is thus responsible for the term soft mode applied to the normal mode for which $\omega(T) \to 0$.

Cochran illustrates his lattice dynamical theory with a cubic diatomic crystal (see the discussion of GeTe and SnTe in Sec. II of this review). Using the shell model (Dick and Overhauser, 1958), he writes the equations of motion for the crystal as

$$m_1 \ddot{u}_1 = R_0(v_2 - u_1) + (4\pi/3)\mathrm{PZe}, \tag{I.12a}$$

$$m_2 \ddot{u}_2 = k(v_2 - u_2) + (4\pi/3)\mathrm{PXe}, \tag{I.12b}$$

$$0 = k(u_2 - v_2) + R_0(u_1 - v_2) + (4\pi/3)\mathrm{PYe}, \tag{I.12c}$$

where u_1, u_2, and v_2 are the displacements from equilibrium of the positive ions and the cores and shells, respectively, of the negative ions; Ze, Xe, and Ye are the corresponding charges in each case, so that $X + Y + Z = 0$ is required for the crystal to be macroscopically uncharged. Here P is the polarization, and R_0 is a short-range force; k is the intraion (shell-core) force constant for the negative ion. Sinusoidal substitutions for u_1, u_2, v_2, and P in Eqs. (I.12abc) yield

$$m_1 \omega^2 U_1 = R_0'(U_1 - U_2) - (4\pi/3)pZ'e, \tag{I.13a}$$

$$m_2 \omega^2 U_2 = R_0'(U_2 - U_1) + (4\pi/3)pZ'e, \tag{I.13b}$$

$$p(1 - [4\pi(Ye)^2/3v(k + R_0)]) = (Z'e/V)(u_1 - u_2), \tag{I.13c}$$

where $u_1 = U_1 \exp(-i\omega t)$; $u_2 = U_2 \exp(-i\omega t)$; V is the unit cell volume; $P = p\exp(i\omega t)$; $R_0' = kR_0/(k + R_0)$; $Z' = Z + YR_0/(k + R_0)$; and the definition of polarization

$$p = (e/V)(Zu_1 + Xu_2 + YV_2) \tag{I.13d}$$

has been employed.

Now when an effective field $E = E_0 e(-i\omega t)$ is applied to the crystal at a sufficiently high frequency ω_1 that the cores do not move appreciably, the equilibrium of the shell is determined by

$$E_0 \mathrm{Ye} = (k + R_0)V_2 \tag{I.14}$$

and the polarization is

$$p = \mathrm{Ye}V_2/V. \tag{I.15}$$

Thus the electronic polarizability of the negative ion is

$$\alpha_\infty = pV/E_0 = (\mathrm{Ye})^2/(k + R_0). \tag{I.16}$$

This polarizability is related to the high-frequency dielectric constant via the Clausius–Mossotti formula

$$4\pi\alpha_\infty/3V = (\epsilon_\infty - 1)/(\epsilon_\infty + 2) \tag{I.17}$$

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[4] Strictly speaking, the mean-field approximation assumes the interparticle force is independent of distance r; whereas, although Coulombic $1/r$ forces change very slowly with r, they do decrease, and no one has explicitly shown that a $1/r$ potential gives mean field results. See the Ginzburg criterion, Eq. (IV.5), however, which shows that long-range potentials such as $1/r$ have very small temperature ranges over which critical phenomena are manifest.

so that Eq. (I.13c) becomes

$$p = Z'e(\epsilon_\infty + 2)(u_1 - u_2)/3V \qquad (\text{I.18})$$

so that Eqs. I.13ab become, eliminating U_1 and U_2,

$$\mu\omega_T^2 = R_0' - \frac{4\pi(\epsilon_\infty + 2)(Z'e)^2}{3V}, \qquad (\text{I.19a})$$

where μ is the reduced mass, and the subscript T denotes transverse. The longitudinal mode frequency is derived in the same way, with the addition of the Lorentz field $4\pi P/3$, yielding

$$\mu\omega_L^2 = R_0' + 8\pi(\epsilon_\infty + 2)(Z'e)^2/9V\epsilon_\infty. \qquad (\text{I.19b})$$

From Eqs. (I.19ab) we see that ω_L can never be zero, since two positive quantities are added

$$[R_0' = kR_0/(k + R_0) \text{ with } k, R_0 > 0].$$

However, ω_T can be zero. In fact, for this to occur, it is not even necessary that $R_0' \to 0$. All that is required is for

$$R_0' = 4\pi(\epsilon_\infty + 2)(Z'e)^2/9V. \qquad (\text{I.20})$$

That is, the temperature dependences of short-range (R_0) and long-range (Z') parameters may lead to a subtle cancellation of the effective force constant. Thus, a soft transverse optical phonon, $\omega_T \to 0$, may lead to ferroelectricity without any bizarre anomalies in the temperature dependences of short-range forces.

D. Microscopic theory—Cowley

Anharmonic theory of lattice dynamics has been thoroughly reviewed by Cowley (1963). Here we shall summarize only a few of his results and proceed by a more sophomoric approach. If we consider the response of a damped harmonic oscillator to a sinusoidal driving force:

$$m\ddot{x} + \alpha\dot{x} + kx = e^* E_0 \exp(i\omega t), \qquad (\text{I.21})$$

where the damping term α is complex ($\alpha/m = \Gamma + i\Delta$), we find that the energy transferred to the oscillator at any frequency is given by

$$\sigma(\omega) \propto \tfrac{1}{2}m\langle[\dot{x}(\omega)]^2\rangle = \operatorname{Im}\left(\frac{\text{const.}}{\omega^2 + \omega(\Delta + i\Gamma) - \omega_0^2}\right), \qquad (\text{I.22})$$

where $\omega_0^2 = k/m$. This is just a special example of the fluctuation–dissipation theorem, which proves that at equilibrium, $\sigma(\omega)$ is proportional to the imaginary part of the susceptibility: $\chi(\omega) = x/E$. Students will find an explicit derivation of Eq. (I.22) from (I.21) in several mechanics textbooks, including Becker (1954, p. 151).

The cross section specified by Eq. (I.12) has its maximum at a frequency ω_m such that

$$\omega_m^2 + \omega_m\Delta = \omega_0^2 \quad \text{or } \omega_m^2 \approx \omega_0^2 - \omega_0\Delta. \qquad (\text{I.23})$$

Both Δ and Γ are anharmonic corrections (i.e., damping) to an otherwise harmonic oscillator equation. Consequently, we may write each as proportional to the density of final states into which the harmonic phonon is decaying. For the lowest order process in which one phonon of wave vector q and energy $\hbar\omega$ decays into two other phonons with energies $\hbar\omega_1 + \hbar\omega_2 = \hbar\omega$ and momenta $q_1 + q_2 = q$, we find

$$\Delta = A(\bar{n}_1 + \bar{n}_2 + 1), \qquad (\text{I.24})$$

where A is a constant, and $\bar{n}_1$ and $\bar{n}_2$ are the Bose–Einstein populations of the phonons produced in the decay: $\bar{n}_1 = [\exp(\hbar\omega_1/kT) - 1]^{-1}$. Similarly, if one phonon is created and another phonon annihilated, Δ will be proportional to $(\bar{n}_1 - \bar{n}_2)$. In either case, at high temperatures where $kT \gg \hbar\omega$, we may approximate Eq. (I.24) as

$$\Delta \cong A[(k_B T/\hbar\omega_1) + (k_B T/\hbar\omega_2)] \text{ or } \Delta = \omega_0^{-1}CT, \qquad (\text{I.25})$$

where C is a constant.

Now let us consider the special situation of a double-well potential $V(x) = -kx^2 + jx^4$ with k and j positive. Such a potential will have real frequencies, but in the harmonic approximation $\omega_0 = (k/m)^{1/2}$ is imaginary. We may consider such a potential as characterizing an unstable harmonic oscillator which is stabilized by anharmonic decay. Since in the harmonic approximation $\omega_0^2 = k/m$ is negative, let us set

$$\omega_0^2 = -CT_0, \qquad (\text{I.26})$$

where C and T_0 are positive quantities. Equations (I.25) and (I.26) may then be substituted in Eq. (I.23), yielding

$$\omega^2(T) = C(T - T_0) \text{ or } \omega(T) = C'(T - T_0)^{1/2}. \qquad (\text{I.27})$$

The coefficient $\beta = \frac{1}{2}$ occurring in the temperature dependence of the measured phonon frequency $\omega(T)$ is a characteristic exponent appearing in all "molecular field" or "mean field" theories in which forces of infinite range are assumed (Stanley, 1971). The value of $\beta = \frac{1}{2}$ in Eq. (I.27) shows that our theory assumes each phonon may be considered as in equilibrium with the average or mean field produced by all the other phonons in the lattice.

Obviously, Eq. (I.27) describes a soft mode whose frequency $\omega(T)$ decreases to zero as a transition temperature T_0 is approached. We have thus obtained Cochran's soft-mode equation from a more microscopic approach.

E. The LST relation

Lyddane, Sachs, and Teller (1941) derived a simple expression relating phonon frequencies to the dielectric properties of crystals.

We may write an expression for the dielectric constant of a lattice in terms of a phonon harmonic oscillator as

$$\epsilon(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)\omega_0^2/(\omega_0^2 - \omega^2), \qquad (\text{I.28})$$

where ϵ_∞ is the $\omega \to \infty$ value of the dielectric constant, and ω_0 is the value of the transverse phonon frequency. The longitudinal phonon frequency ω_{LO} occurs where $\epsilon(\omega) = 0$ (This follows from Maxwell's equations; a tutorial derivation is given by Scott, 1971c). From this it follows that

$$\epsilon(0)/\epsilon_\infty = [\omega_{\text{LO}}/\omega_0]^2. \qquad (\text{I.29})$$

This equation is the result of harmonic oscillator theory. In practice it accurately describes systems in which anharmonicity is included, since the quantities ω_{LO} and ω_0 are the *observed* values—not the harmonic values. This point is discussed in greater detail by Barker (1964).

Fröhlich observed in 1949 that the occurrence of ferroelectricity [$\epsilon(0) \rightarrow \infty$ as $T \rightarrow T_0$] should produce an equivalent anomaly in $\omega_0(T)$, as indicated in Eq. (I.29). This is of course the content of Cochran's soft-mode theory.

The generalization of the LST relation in Eq. (I.29) was given by Cochran and Cowley (1963), who found for a crystal with n modes having polarization along direction j, that

$$\frac{\epsilon_j(0)}{\epsilon_\infty} = \prod_{i=1}^{n} \left[\frac{\omega_{\mathrm{LO},i}}{\omega_{0,i}} \right]^2 . \tag{I.30}$$

Central modes

Cowley (1970) provided a microscopic description of the spectrum expected for a crystal approaching a structural transition temperature. In addition to the soft modes at frequencies $+\omega(T)$ and $-\omega(T)$, Cowley predicted a third peak in the response (or scattering intensity) centered at $\omega = 0$.

Physically, Cowley's description distinguishes between responses measured on a time scale over which the soft mode reaches equilibrium with acoustic phonon density fluctuations ($\tau > 10^{-11}$ sec.), and shorter time scales over which equilibrium is not established.[5] This corresponds to the distinction between "collision-dominated" and "collision-free" regimes of first and zeroeth sound propagation.

Algebraically, the treatment given by Cowley involves a frequency-dependent relaxation time. The response function of the system must be calculated in terms of the proper self-energy Σ. This kind of phenomenon was first analyzed by Mountain (1966), who described quasielastic scattering from fluctuations in liquids from this point of view. The effect of frequency-dependent damping on the quasielastic spectra of solids was first pointed out by Cowley (1970). The relation between Cowley's work on soft modes and Mountain's analysis of density fluctuations in liquids has been made explicit in a very readable review by Fleury (1972).

The algebraic descriptions of this complex phenomenon are given in the sections of this paper dealing with KH_2PO_4, $SrTiO_3$, and Nb_3Sn. In this introduction we wish to emphasize two physical points. First, part of the anharmonic response near the phase transition temperature T_0 is contained in the central mode; for this reason the soft mode need not soften all the way to $\omega = 0$ at $T = T_0$, *even* for second-order phase transitions. This was first shown experimentally by Cowley *et al.* (1971). Second, the central mode may occur even for systems or temperature regimes which are not "critical," i.e., where mean field theory applies. In order to show that the central modes are "critical" it is necessary to show that the integrated intensity of the central mode behaves as

$$I = I_0(T - T_0)^{-2\beta}, \tag{I.31}$$

with β *not* equal to $\frac{1}{2}$. Thus far, such behavior has been shown for $SrTiO_3$ by inelastic neutron scattering (Riste *et al.*, 1971; Shapiro *et al.*, 1972), and for NH_4Cl by inelastic light scattering (Lazay *et al.*, 1969). However in the latter case, Bartis (1973) has shown that the exponential anomaly occurs due to effects of impurities and dislocations. NH_4Cl, then, is not viewed as exhibiting intrinsic self-energy amonalies of the kind described by Cowley.

The discussion appropriate to central modes is much more extensive than we shall have room for in this experimental review. Readers are referred to a very readable paper by Wehner and Klein (1972) for further details, and to the analogous effects predicted in magnetic systems by L'vov (1968) and Moriya (1968). We should emphasize even in this introduction that while Cowley's 1970 theory was explicitly illustrated by a three-phonon interaction appropriate only for noncentric crystals, Silberglitt (1972) has made a direct extension of Cowley's theory to the four-phonon interaction applicable to centric lattices such as $SrTiO_3$. The basic physical idea of differing high-frequency and low-frequency responses to a dynamical system is the same in each case. Interested readers are referred to Schwabl (1972, 1973), Feder (1971), and Coombs and Cowley (1973) for a fuller discussion of this topic.

Note that NH_4Cl, unlike $SrTiO_3$, is an order–disorder system. Discussions of NH_4Cl diverging Rayleigh intensities (Bartis, 1973) are therefore not closely related to $SrTiO_3$ central modes.

II. ROCKSALT-STRUCTURE IV–VI SEMICONDUCTORS

A. Neutron scattering in PbTe and SnTe

Attention from a lattice dynamical point of view was first paid to IV–VI semiconductors by Cochran (1964), who determined the static dielectric constant of PbTe by measuring the $q = 0$ transverse and longitudinal phonon frequencies and invoking the Lyddane–Sachs–Teller relation

$$\epsilon(0)/\epsilon(\infty) = [(\omega_{\mathrm{LO}}/\omega_{\mathrm{TO}})]^2 . \tag{II.1}$$

Here $\epsilon(0)$ was determined to be 310 ± 19 at room temperature. In addition, the temperature coefficient of $\omega_{\mathrm{TO}}(T)$ was found to be $5 \times 10^{-4} (^\circ\mathrm{K})^{-1}$; thus the 0°K to frequency could be estimated from the 32 cm^{-1} room temperature value as $\sim 27\ \mathrm{cm}^{-1}$. While this measurement indicates that PbTe does not have a ferroelectric phase, it does reveal an anomalous temperature dependence, i.e., the *TO* phonon energy *decreases* with decreasing temperature. This behavior is in contrast with that of "normal" crystals in which

$$\omega^2(T) \approx \omega^2(0) - AT \tag{II.2}$$

is observed over a wide temperature range (here A is a positive constant). Cochran's work also served to focus attention on the prospect of simple diatomic ferroelectrics. The difficulty in determining the existence of ferroelectricity in this class of materials via usual techniques (application of external electric fields to measure hysteresis) is that the crystals are too highly conducting to sustain even a small electric field. Consequently, verification of ferroelectricity is best provided by indirect means, i.e., measurement of the temperature dependence of transverse $q = 0$ phonon frequencies to show that such frequencies soften or decrease to zero at some temperature T_0. Such endeavors were pursued by Cochran, Pawley *et al.* at Chalk River, using SnTe (Pawley *et al.*, 1966).

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[5] Also designated "adiabatic" and "isothermal" regimes by Feder (1971).

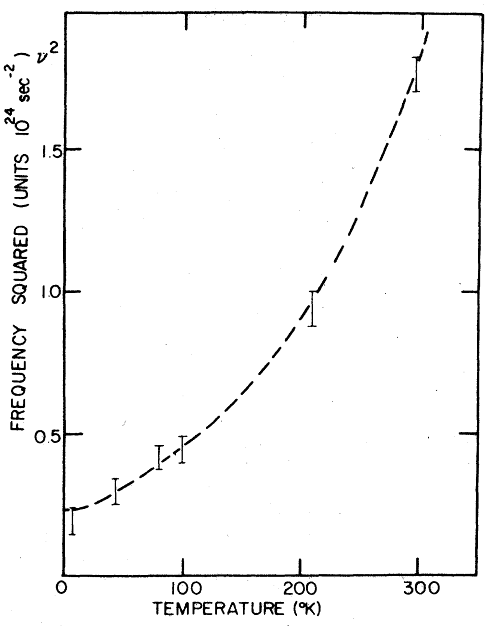

FIG. 3. ω vs T in SnTe (experiment) (Pawley *et al.*, 1966).

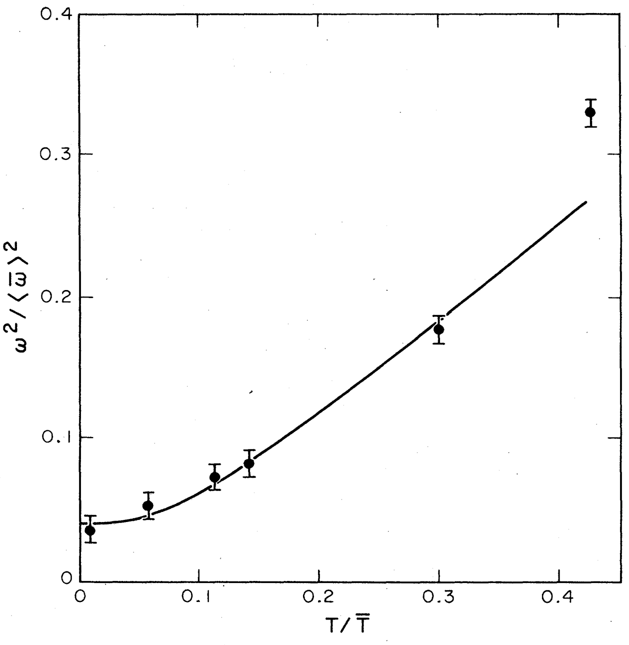

FIG. 4. ω vs T in SnTe (theory) (Gillis, 1969).

Their results are shown in Fig. 3. It can be seen from this graph that SnTe remains paraelectric at all temperatures, but undergoes a decrease in $\omega_{\mathrm{TO}}^2(T)$ of more than tenfold as T is lowered from room temperature to 4°K. Hence $\epsilon(0)$ increases by ~ 10 but does not diverge as $T \to 0$.

B. Self-consistent phonon field theory (Gillis and Nettleton)

The inelastic neutron scattering data on $\omega_{\mathrm{TO}}(T)$ were fitted by Gillis (1969) to a microscopic force constant model in which the forces were treated self-consistently. The use of self-consistent phonon theory had been made earlier by Hooton (1958), Koehler (1966), and others, and concurrently by Nettleton (1969) who applied it to the $q = 0$ soft mode in SrTiO$_3$. As can be seen in Fig. 4, a good fit to $\omega_{\mathrm{TO}}(T)$ is obtained in Gillis' calculation. There are, however, several minor criticisms of his analysis. The key equation in Gillis' work is given below:

$$\omega_{\mathrm{TO}}^2(T) \approx \omega_{\mathrm{TO}}^2(0) + A \exp[-\hbar\omega_{\mathrm{TO}}(0)/KT] \quad \text{(II.3)}$$

Below we compare this expression with that derived from the general theory discussed in Sec. I [see especially Eq. (I.13)]:

$$\begin{aligned} \omega_{\mathrm{TO}}^2(T) &\approx \omega_{\mathrm{TO}}^2(0) + \int_0^\infty B(\omega)\bar{n}(\omega, T)\rho(\omega)\,d\omega \\ &\approx \omega_{\mathrm{TO}}^2(0) + \bar{n}(\omega_0, T)\int_0^\infty B(\omega)\rho(\omega)\,d\omega \\ &\approx \omega_{\mathrm{TO}}^2(0) + A\bar{n}(\omega_0, T) \\ &\approx \omega_{\mathrm{TO}}^2(0) + A/[\exp(\hbar\omega_0/KT) - 1]. \end{aligned} \quad \text{(II.4)}$$

Here $\rho(\omega)$ is the $T = 0$ density of states; $\bar{n}$, the Bose population factor; $B(\omega)$, the anharmonic matrix element; and ω_0, the frequency of the mean final state. We see that Gillis has made the low-temperature approximation $[\exp(\hbar\omega_0/KT) - 1] \approx \exp(-\hbar\omega_0/KT)$. This is a good approximation only for $T \ll \omega_0$ (in this case, $T < 40$°K). However, there is a more serious error in Eq. (II.3). Note in particular that Gillis assumes $\omega_0 = \omega_{\mathrm{TO}}$ in Eq. (II.4). This means, physically, that the only anharmonic decay processes considered are those in which $q = 0$ TO phonons decay into other $q \approx 0$ on the same TO branch.

Normally, anharmonic processes would include many channels involving higher energy phonons. It is not expected that ω_0 have any relation to ω_{TO}. It is especially curious to equate ω_0 with ω_{TO} in the case of SnTe, which is centric in the paraelectric phase; in centric crystals the anharmonic decay of $q = 0$ TO phonons into other $q \approx 0$ phonons on the same branch is forbidden in lowest order. Thus, we conclude that Gillis' calculation yields good numerical agreement with experiment only because of a coincidence: that $\omega_{\mathrm{TO}} \approx \omega_0$ in SnTe. To show how unlikely this equivalence is, in general, we point out here that $\omega_{\mathrm{TO}}(0) = 9$ cm^{-1} in SrTiO$_3$, whereas $\omega_0 \cong 70$ cm^{-1} (Worlock 1971). Thus ω_0 and $\omega_{\mathrm{TO}}(0)$ may disagree by *an order of magnitude*.

C. GeTe

At about the same time Cochran's work on PbTe revealed a soft mode, GeTe was under extensive study. Bierly *et al.* (1963) had shown earlier that GeTe distorted from the SnTe rocksalt (cubic) structure above 670°K to a rhombohedral structure below, and that Sn$_{1-x}$Ge$_x$Te solutions had transition temperatures which increased approximately linearly with x. This observation, together with the work of Pawley *et al.* (1966) is sufficient to conclude that Sn$_{1-x}$Ge$_x$Te and pure GeTe are ferroelectric in the low-temperature phase. However, the situation was muddied-up considerably by conflicting x-ray studies of Goldak *et al.* (1966), Zhukova and Zaslavskii (1967), and Kabalkina *et al.* (1966); the latter study concluded that GeTe is centric below $T_0 = 670$°K, but this view can now be disregarded.

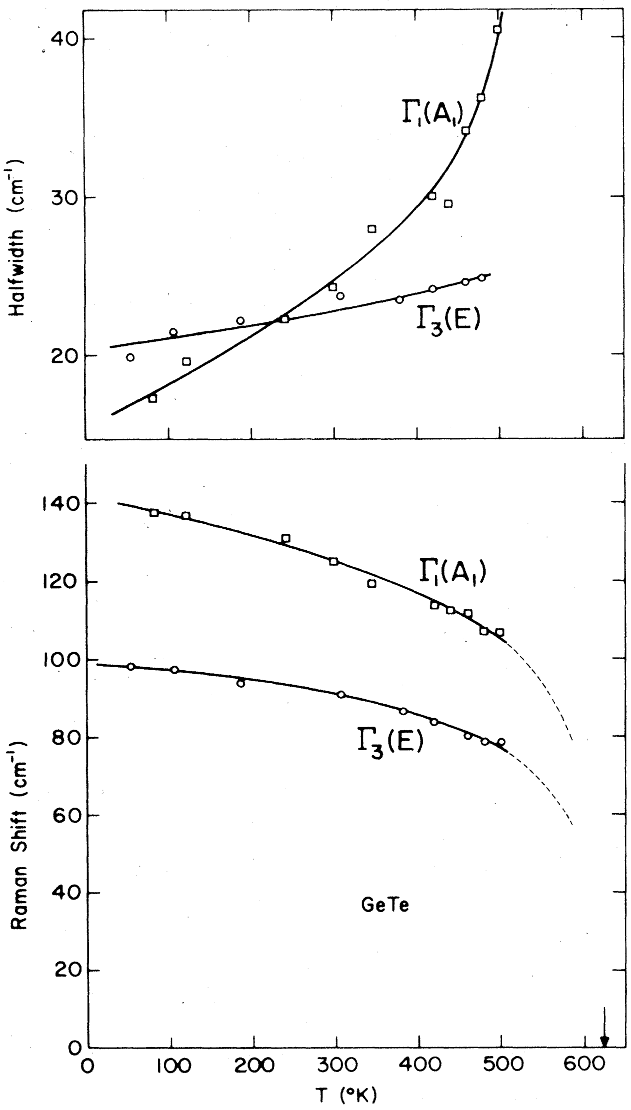

FIG. 5. ω vs T in GeTe, (Steigmeier and Harbeke, 1970).

Finally, in the last three years Harbeke and Steigmeier (1970) measured the A_1 and E transverse phonons in GeTe by light scattering and showed that these polar modes do soften considerably at $T \rightarrow T_0$ from below. The nondegenerate mode lies at the higher frequency, as shown in Fig. 5. This measurement therefore directly confirms that α-GeTe is ferroelectric. The cubic and rhombohedral modifications of GeTe are diagrammed in Fig. 6, following Pawley (1969). It should be noted that the extrapolation of phonon frequencies to zero in Fig. 5 is not justified, since the transition is now thought to be first order.

Neither inelastic neutron scattering nor light scattering has yet been successful at analyzing soft phonons in $Sn_xGe_{1-x}Te$ solutions. Cowley (private communication) reports that for $x \lesssim 1$ the solutions exhibit very broad phonon features. It is not clear whether such phonon broadening is due to sample inhomogeneity; but if that is the case, light scattering—which requires $\sim 10^3$ smaller scattering volume—might be more profitable than neutron spectroscopy.

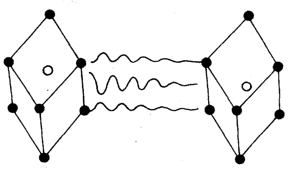

FIG. 6. Rhombohedral distortion of GeTe (Pawley, 1969).

Several other IV–VI's have been studied by x-ray techniques. Malevskii (1966) showed that solutions of form $Pb_{2x}(Tl, Bi)_{1-x}S$ are cubic for $x \geq 0.2$, and rhombohedral for $x < 0.2$. No soft-mode studies have yet been made on this series, however. Nor is it known what the low-symmetry space group is.

Finally, among the IV–VI semiconductors, SnSe, SnS, and SnTe have been singled out by Pawley (1969) as diatomic antiferroelectrics. Kafalas and Mariano (1964) have shown that at about 18 kbar SnTe undergoes a cell-doubling transition to the SnS structure. At ambient pressures SnTe exhibits an abrupt decrease in frequency for one optical phonon branch at the $[(\pi/a)00]$ boundary (Pawley, 1969) which is presumably an indication of the instability manifest at 18 kbar. Thus far no measurements of zone-boundary phonon frequency as a function of pressure have been reported. Raman measurements would, of course, be possible only above 18 kbar, where the cell-doubling creates reciprocal lattice points at $[\pi/a, 0, 0]$ and renders the $q = \pi/a' = 2\pi/a$ soft mode Raman-allowed.

III. MODE COUPLING THEORY

The interaction between two excitations has been subject to many different algebraic descriptions over the years in the technical literature associated with different branches of physics. The two extreme limits of approximation assume that either: (1) the linewidth associated with each excitation is much smaller than the energy separation of the two "modes;" in this case the modes may be treated as coupled, nearly harmonic oscillators; or (2) the linewidth of at least one of the excitations is much larger than the energy separation of the two modes; in this case, the broad mode may be approximated as a featureless continuum.

The case of a well-defined excitation interacting with a continuum has been treated in a now classic paper by Breit and Wigner (1936), and the asymmetric line shapes resulting from such an interaction are usually described as satisfying the Breit–Wigner single-level formula.

In addition to Breit and Wigner's work, Fano (1935) attempted an early description of interactions between discrete levels and continua. Unfortunately, Fano's paper completely missed the point: He failed to consider the interference term due to addition and subtraction of scattering amplitudes. Many years later Fano (1961) corrected this oversight and obtained formulas for asymmetric line shapes very similar to those of Breit and Wigner; however, the labeling of such shapes as "Fano lineshapes," as Rousseau and Porto (1968) termed them, in a gross injustice.

The physical interpretation of Breit and Wigner's theory is shown in Fig. 7. There are two scattering

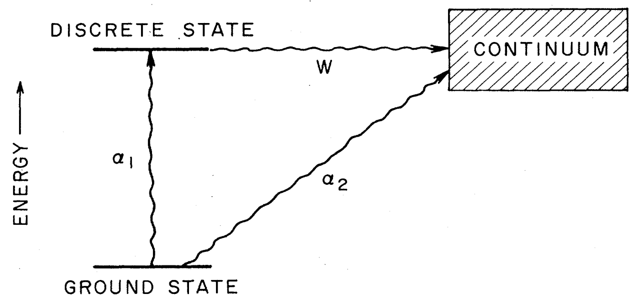

FIG. 7. Energy level diagram for Breit–Weigner interference. Here W is the matrix element for a nonradiative decay.

channels into the same heavily damped final state: one direct

$$\langle 2|\alpha_2|0\rangle \tag{III.1}$$

and one indirect, via the discrete state

$$\langle 2|W|1\rangle\langle 1|\alpha_1|0\rangle, \tag{III.2}$$

where W is a matrix element describing a nonradiative transition from the discrete state to the continuum.

The line shape resulting from this kind of interaction is given by

$$\sigma(\epsilon) = (q+\epsilon)^2/(1+\epsilon^2), \tag{III.3}$$

where q is a dimensionless constant given by

$$q = \langle 1|\alpha_1|0\rangle/\pi\langle 1|W|2\rangle\langle 2|\alpha_2|0\rangle, \tag{III.4a}$$

and ϵ is a normalized energy:

$$\epsilon = \pi^{-1}(E-E_1)[\langle 1|W|2\rangle]^{-2}. \tag{III.4b}$$

Carruthers (1962) was the first to suggest that this kind of interference shape should exist for phonons in solids. And such line shapes were first reported experimentally by Rousseau and Porto (1968), who described their data in terms of the formula given in Equation (III.3). Rousseau and Porto misidentified the broad feature in their $BaTiO_3$ data as a two-phonon excitation; it actually is a heavily damped one-phonon state. Scott (1970a) has explained how the one-phonon interactions in $BaTiO_3$ and other crystals may correctly be described within the context of Breit–Wigner or Fano formalism.

In the opposite limit of approximation in which damping is very small, no line shape distortions are manifest. In this case, we may describe the mode interactions by diagonalizing the Hamiltonian below:

$$\mathcal{H} = \begin{bmatrix} \hbar\omega_1(T) & W \\ W & \hbar\omega_2 \end{bmatrix}, \tag{III.5}$$

where $\hbar\omega_1$ and $\hbar\omega_2$ are the energies of the first and second uncoupled modes, and W is the matrix element for decay from the unperturbed first state $|1\rangle$ into the second state $\langle 2|$. In cases of interest in the present review, $\omega_1(T)$ is the temperature-dependent frequency of the soft mode, and passes through ω_2 at some temperature near the phase transition temperature T_0.

The above formalism was applied to coupled soft modes in $SrTiO_3$ by Worlock *et al.* (1969).

A. Barker–Hopfield reflectivity analysis

A theoretical description which is sufficiently general to encompass both extremes discussed above has been given by Barker and Hopfield (1964). Barker and Hopfield consider two damped harmonic oscillators with frequencies ω_1 and ω_2 and reciprocal lifetimes Γ_1 and Γ_2. The kinetic energy for each oscillator may be written as $\frac{1}{2}m_i\omega_i^2q_i^2$, where m_i is the effective mass for the ith normal mode q_i, plus an imaginary term characterizing the anharmonic decay; the potential energy is given by $\frac{1}{2}k_iq_i^2$, where k_i is a force constant equal to $m_i\omega_i^2$.

We may write the spectral distribution function for scattering from either uncoupled mode as

$$\sigma(\omega) = [\bar{n}(\omega,T)+1]A\chi''_j(\omega), \tag{III.6}$$

where the susceptibility χ_j is the jth mode is given by

$$\chi_j(\omega) = \omega_j^2/(\omega_j^2-\omega^2+i\Gamma_j\omega) \tag{III.7}$$

which follows from the driven, damped harmonic equation

$$m_j\ddot{x} + m_j\Gamma_j\dot{x} + k_jx = E_0\exp(i\omega t), \tag{III.8}$$

where $\omega_j^2 = k_j/m_j$, and from the definition of susceptibility

$$\chi(\omega) \equiv x/E(\omega). \tag{III.9}$$

Equation (III.6) is simply a statement of the Nyquist theorem, or the fluctuation dissipation theorem, which states that the energy transferred at frequency ω into any system at equilibrium is proportional to the imaginary part of the susceptibility. For the special case of a damped harmonic oscillator this theorem is especially easy to prove: the energy transferred, $\sigma(\omega)$, is equal to the average value of $\frac{1}{2}m_j(\dot{x}_j)^2$. This may be obtained directly by solving Eq. (III.8) with $x(t)$ assumed sinusoidal. The result is

$$\sigma(\omega) = \omega\Gamma_j\omega_j^2/[(\omega_j^2-\omega^2)^2+\Gamma_j^2] \tag{III.10}$$

which differs from Eq. (III.6) only by the factor $\bar{n}+1$, due to phonon populations at different frequencies. Note that $\sigma(\omega)$ times a population factor $kT/\hbar\omega$ is given by a Lorentzian line shape.

The generalization of the above to two coupled modes is obtained by summing the individual susceptibilities χ_j, and by allowing mode coupling. Specifically, a response function $G_{ij}(\omega)$ is defined such that

$$G_{jj}(\omega) = \chi_j(\omega), \tag{III.11}$$

with $\chi_j(\omega)$ defined above. However, $G_{ij}(\omega)$ also has nonzero off-diagonal elements

$$G_{12}(\omega) = k_{12}^2 + i\Gamma_{12}\omega, \tag{III.12}$$

thus

$$G_{ij}(\omega) = \begin{bmatrix} \omega_1^2-\omega^2+i\Gamma_1\omega & k_{12}^2+i\Gamma_{12}\omega \\ k_{12}^2+i\Gamma_{12}\omega & \omega_2^2-\omega^2+i\Gamma_2\omega \end{bmatrix}, \tag{III.13}$$

where k_{12} is the force constant of a "spring" which connects the oscillators having unperturbed frequencies ω_1 and ω_2; and Γ_{12} is the damping constant of a "dashpot" connecting the two modes. The perturbed normal mode frequencies for the system are obtained by diagonalizing the matrix in Eq. (III.13). Physically, the effect of either k_{12} or Γ_{12} is to produce asymmetries in the otherwise Lorentzian line shapes characterizing the energy transfer to damped harmonic oscillators. In fact, as emphasized by Barker and Hopfield, any given spectrum may be reproduced with either a nonzero k_{12} or a nonzero Γ_{12}; since the real and imaginary parts of the matrix in Eq (III.13) may be independently diagonalized, it is not algebraically necessary to include both k_{12} and Γ_{12}. The choice one makes in fitting observed data is largely a heuristic one. Barker and Hopfield made one choice in the case of $BaTiO_3$ and $SrTiO_3$ which put all the damping in one oscillator, namely, the soft mode, i.e., in Eq. (III.13), $\Gamma_2 \cong 0$; Γ_1 large. This choice amounts to a choice of *phase* for the interacting modes; Barker and Hopfield's choice for the ABO_3 perovskite ir spectra is physically appealing. However, Barker and Hopfield did not test their choice by fitting spectra at more than one temperature.

Most recent experimental work on coupled modes has employed a formalism analogous to that of Barker and Hopfield. The theoretical analyses of Zawadowski and Ruvalds (1970) for $AlPO_4$, of Katiyar *et al.* (1971) for KH_2AsO_4, and of Fleury and Lazay (1971) for $BaTiO_3$ are all quite similar. In KH_2AsO_4 Katiyar *et al.* were able to determine that k_{12} was large ($\sim 100\,\mathrm{cm}^{-1}$), and Γ_{12} nearly zero; this was inferred by fitting lineshapes at many different temperatures and requiring that all parameters appearing in Eq. (III.13) have very simple temperature dependences or be completely independent of temperature. The same physically motivated choice of phase for the mode couplings was employed subsequently by Fleury and Lazay (1971).

As Zawadowski and Ruvalds have emphasized, the theory of Barker and Hopfield is essentially equivalent to that obtainable from a more elegant Green's function approach. This way of attacking the problem has been employed in earlier work by Maradudin and Fein (1962), whose theory was directed toward inelastic neutron studies.

To relate the coupled, damped harmonic oscillator theory described above to the earlier theory of Breit and Wigner, it is necessary only to allow Γ_1 or Γ_2 to increase toward infinity; in this case, the Breit–Wigner line shape formula is recovered asymptotically.

Fleury (1972) has summarized mode coupling mechanisms in a particularly succinct and readable review. He points out that the spectral distribution function $\sigma(q,\omega)$ given in Eq. (III.6) may be given directly either in terms of $\chi_j^0(q,\omega)$, the complex susceptibility for the uncoupled, noninteracting mode j, or in terms of $\chi_j^1(q,\omega)$, the susceptibility for the interacting system. These two susceptibilities are related by Eq. (III.14)

$$\chi_j^1(q,\omega) = \chi_j^0(q,\omega)/(1 - \chi_j^0(q,\omega)\Sigma_j(q,\omega)), \qquad \text{(III.14)}$$

where Σ_j is called the proper self-energy (see Wehner, 1966) of mode j.

In the specific cases of linear and anharmonic mode coupling we discuss in this review, we shall be concerned with the various forms which $\Sigma_j(q,\omega)$ may take. For the preceding discussion (Barker and Hopfield, 1964) of linear mode coupling summarized in Eqs. (III.6–III.13), we have

$$\Sigma_j(q,\omega) = \text{const.} \times \chi_{j'}^0(q,\omega), \qquad \text{(III.15)}$$

where $\chi_{j'}^0(q,\omega)$ is the susceptibility for a second mode j'. This leads to the response function given in matrix form in Eq. (III.13).

The second general case of mode coupling is that of anharmonic interactions, exemplified by Akhieser damping (Akhieser, 1939). In Akhieser damping, the local temperature of a given "mode" j is modulated by the presence of mode j'. Thermal equilibrium is therefore established over a time T where

$$\mathrm{T} \ll (1/\omega_{j'}). \quad \text{If } \mathrm{T} \gg 1/\omega_{j'},$$

the effects of mode j' are averaged out. These are the isothermal and adiabatic time regimes discussed by Feder (1971). This mechanism of mode coupling may be described by a self-energy function

$$\Sigma_j(q,\omega) = \frac{i\omega\alpha}{1 - i\omega\mathrm{T}}, \qquad \text{(III.16)}$$

where α and T are, respectively, q-dependent strengths and relaxation times due to j'.

The coupled susceptibility for such an interacting system is given from Eq. (III.14) as

$$\chi_j^1(q,\omega) = \{\omega_j^2 - \omega^2 - [i\alpha\omega/(1 - i\omega\mathrm{T})]\}^{-1}. \qquad \text{(III.17)}$$

When both Akhiezer-type damping and frequency-independent terms are considered, one obtains

$$\chi_j^1(q,\omega) = \{\omega_j^2 - \omega^2 + i\gamma_j\omega - i\alpha\omega/(1 - i\omega\mathrm{T})\}^{-1} \qquad \text{(III.18)}$$

which is the general form employed by Cowley (1970) and by Cowley *et al.* (1971) in the analysis of soft modes in KDP structures (see Sec IX of this review).

It is notable that the susceptibility given in Eq. (III.17) was first employed by Mountain (1966) to describe quasielastic central mode scattering from density fluctuations in liquids. Cowley (1970) was the first to point out that this should lead to observable central modes in solids near phase transition temperatures, where $\omega_j \to 0$. Such modes have been observed directly or indirectly in $SrTiO_3$, Nb_3Sn, SbSI and KDP-isomorphs, and are discussed in sections of this review devoted to those crystal classes.

B. Fermi resonance in solids

Fermi resonance is of course the coupling between two excitations in a molecule, one of which is a one-quantum level, and the other of which is a two-quantum state. Such a coupling is due to cubic anharmonic terms of form $c_{ijj}q_iq_j^2$ in the vibrational Hamiltonian. These terms are especially large in molecules such as CO_2 and H_2O, where the two-quantum level of one vibrational state is nearly coincident in energy with a one-quantum level for a different normal mode. This strong "resonance" between the two states yields a large energy repulsion between the unperturbed states; the interaction constant c_{ijj} may be shown by perturbation theory to have the form

$$c_{ijj} \cong (\omega_i - 2\omega_j + i\Gamma_i)^{-1}. \qquad \text{(III.19)}$$

The idea that Fermi resonance would exist between phonons in ionic crystals was first put forth by Scott (1968), who analyzed the soft mode in quartz on this basis. This work is discussed in a subsequent section of the present review. Scott described the coupling between one- and two-phonon states in a quasiharmonic way. Damping was ignored, and the coupled-mode energies were obtained by diagonalizing

$$\mathcal{H} = \begin{bmatrix} h\omega_1(T) & W \\ W & h\omega_2 \end{bmatrix}, \tag{III.20}$$

where $h\omega_2$ is the energy of a two-phonon density-of-states peak, and $h\omega_1(T)$ is the soft-mode energy. This yields

$$\omega_\pm(T) = \{[\omega_1(T) + \omega_2]/2\} \pm \tfrac{1}{2}[\omega_1(T) - \omega_2^2 + 4W^2]^{\frac{1}{2}} \tag{III.21}$$

for the coupled mode frequencies. This expression differs slightly from the more rigorous (but still phenomenological) anharmonic theory employed by Ruvalds and Zawadowski (1970). Typically the difference is the squaring of all frequencies involved; compare Eq. (III.13) and (III.20). Since

$$(\omega_1^2 - \omega_2^2) = (\omega_1 - \omega_2)(\omega_1 + \omega_2) \approx 2\omega_2(\omega_1 - \omega_2) \tag{III.22}$$

for $\omega_1 \approx \omega_2$, it is not a bad approximation to use the formalism with unsquared frequencies for the $\omega_1 \approx \omega_2$ region of maximum interest. This point has been emphasized by Scott (1971b).

In the self-energy language discussed above, Fermi resonances such as those in SiO_2 or $AlPO_4$ may be described as if the two-phonon state were a second "mode" j', characterized by a frequency $\omega_{j'}$ and an inverse lifetime or width $\Gamma_{j'}$. Equations (III.14) and (III.15) would still apply, with

$$\Sigma_j = \text{const.} \times \chi_{j'}^0 = \frac{\text{const .}}{[(2\omega_k)^2 - \omega^2 + i\Gamma_{j'}\omega]}, \tag{III.23}$$

and where the mode frequency $\omega_{j'} = 2\omega_k$ (ω_k is the frequency of the phonon whose overtone is the two-phonon energy $\omega_{j'}$).

IV. α-QUARTZ STRUCTURES

A. SiO_2

1. *α-phase*

In January of 1940, Raman and Nedugadi reported the study by inelastic light scattering of the trigonal-hexagonal phase transition in quartz at ~ 573°C. They observed that, "the 220 cm^{-1} line behaves in an exceptional way, spreading out greatly towards the exciting line ··· as the transition temperature is approached. It therefore appears reasonable to infer that the increasing excitation of this particular mode of vibration with increasing temperature and the deformation of the atomic arrangement resulting therefrom are in a special measure responsible for ... inducing the transformation from the α to the β form." This is a remarkably good description of a soft mode, a full twenty years before Cochran's famous papers. In the same year, Saksena (1940) presented a lattice dynamical model of quartz which demonstrated the instability of one particular normal mode as the α–β transition from $D_3^4(P3_12)$ to $D_6^5(P6_12)$ structure developed.

Over the next two decades very little interest in the dynamics of the quartz phase transition was manifest in the literature. In fact, the only experimental work reported was from the Soviet Union, where Iakovlev *et al.* (1956, 1957) observed very strong scattering of light from quartz near $T_0 = 573°C$. This was unfortunately misinterpreted as critical opalescence (Ginzburg and Levanyuk, 1958, 1960, 1962), analogous to that first observed in fluids by Andrews a century earlier (1869). Subsequent work by Gammon (1968), Shapiro, and Cummins (1968) showed that the intense elastic light scattering near T_0 in quartz is static and hence not due to critical fluctuations. It apparently arises from microdomain formation in the ~3°K hysteresis region found (Shapiro and Cummins, 1968) to characterize this first-order phase transition. Höchli and Scott (1971) and Höchli (1970) have interpreted these microdomains as due to the coexistence of α- and β-quartz structures in the hysteresis region. The idea that such a coexistence region should exist in quartz was suggested earlier by Semenchenko and Baskakova (1969).

The possible existence of "critical opalescence" in displacive solid state phase transitions is an idea which has raised its head many times over the years. As is

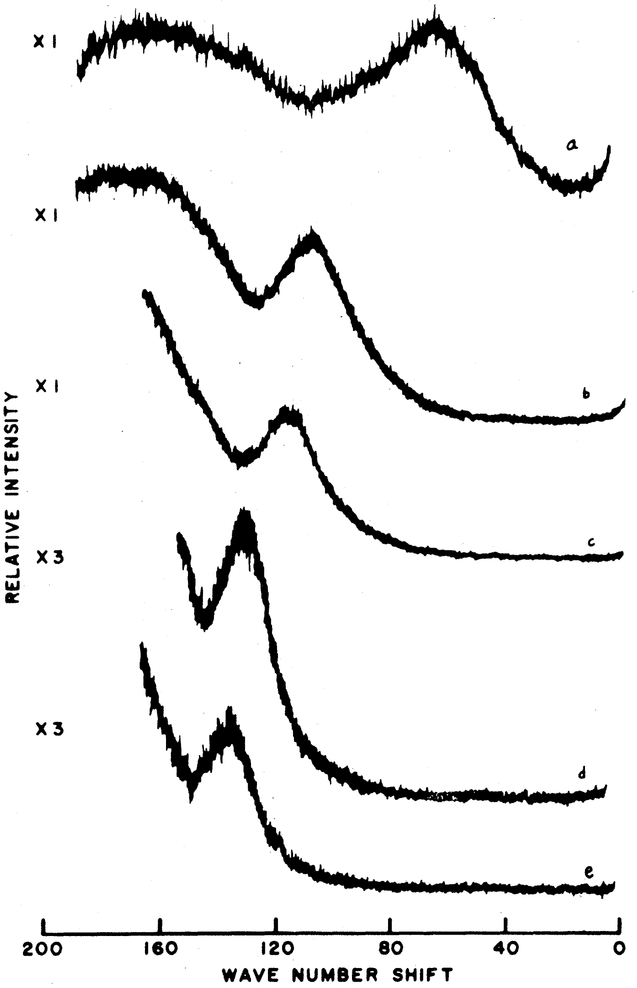

FIG. 8. Spectra of α-quartz for Γ_1 symmetry modes: a, 800K; b, 700K; c, 600K; d, 400K; e, 300K (Unpublished data of the author).

discussed in several sections of this review, there is no evidence to support this notion for most crystals yet studied. Whereas a quasielastic response at $\omega \approx 0$ does grow in intensity near displacive phase transitions in some crystals ($SrTiO_3$, Nb_3Sn, lead germanate, and SbSI) this phenomenon can apparently be described in terms of anharmonic effects *within the mean field approximation.* Nothing "critical" has yet been demonstrated about such behavior, except in $SrTiO_3$, where exponents describing the central mode intensity have been evaluated.

In addition to the "red herring" of critical opalescence in quartz, there was a second facet of the phonon data which delayed the eventual straightforward analysis of the transition dynamics: The polarized α_{zz} Raman spectrum revealed five sharp, symmetric features rather than the four group-theoretically predicted. The "extra" feature had been reported as early as 1945 by Krishman, but at that time the phonon characteristics of piezoelectrics were not sufficiently well understood to allow identification of transverse and longitudinal modes, etc. It was not until 1967 that unambiguous assignment of all one-phonon lines in the quartz spectra was made (Scott and Porto, 1967) This work allowed the assignment of the "extra" mode at 147 cm^{-1} as second order (a two-phonon process) to be made. Such an interpretation was compatible with the lattice dynamical models of Elcombe (1967) and of Kleinman and Spitzer (1962), who agreed on the assignments of the four Γ_1 or A_1 fundamental (one-phonon) $q = 0$ frequencies.

This simple interpretation was brought into question by the work of Shapiro *et al.* (1967), whose Raman measurements at elevated temperatures showed that the "soft mode" decreased from $\sim$220 cm^{-1} to only $\sim$165 cm^{-1} at $T \approx T_0$, while the "extra" feature grew in intensity and decreased from $\sim$147 cm^{-1} to $\sim$40 cm^{-1} over the same temperature range, as shown in Fig. 8.

This apparent complexity was reconciled by Scott (1968), who invoked the idea of Fermi resonance from molecular spectroscopy to explain the newly observed solid state phenomenon. Fermi resonance is well known in such simple molecules as CO_2 and H_2O: a one-quantum vibrational level for one normal mode lies very near the energy of a two-quantum vibrational level for a second normal mode. There is an anharmonic interaction between the levels (assuming the symmetries are the same), resulting in a level repulsion and a "no-crossing" rule.

In this interpretation, the soft mode is the feature at $\sim$220 cm^{-1} at low temperatures, and the feature at $\sim$40 cm^{-1} at high temperatures. At intermediate temperatures, the soft mode is thoroughly mixed with the Γ_1-symmetry two-phonon state. This behavior is indicated in Fig. 9, where the inferred *uncoupled* mode temperature dependences are shown as solid lines.

Most of the intensity of both features in the 160 cm^{-1} region of the quartz spectrum is first order, i e., due to a one-phonon response. That this one-phonon response should exhibit a peak at the two-phonon density of states maximum was first explained by Ruvalds and Zawadowski (1970), via a many-body calculation.

Once the Fermi resonance has been adequately taken into account, one can proceed to extract the temperature dependence of the uncoupled soft mode.

This was originally done by Scott (1968), who obtained

$$\omega = A(T_0 - T)^{0.30}, \qquad \text{(IV.1)}$$

via a mode decoupling of the form given below

$$\langle \Psi_2 | \mathcal{H} | \Psi_f \rangle \;=\; \begin{array}{ccc} & \Psi_1 & \Psi_2 \\ \Psi_1 & \hbar\omega_1(T) & W \\ \Psi_2 & W & \hbar\omega_{2}., \end{array} \qquad \text{(IV.2)}$$

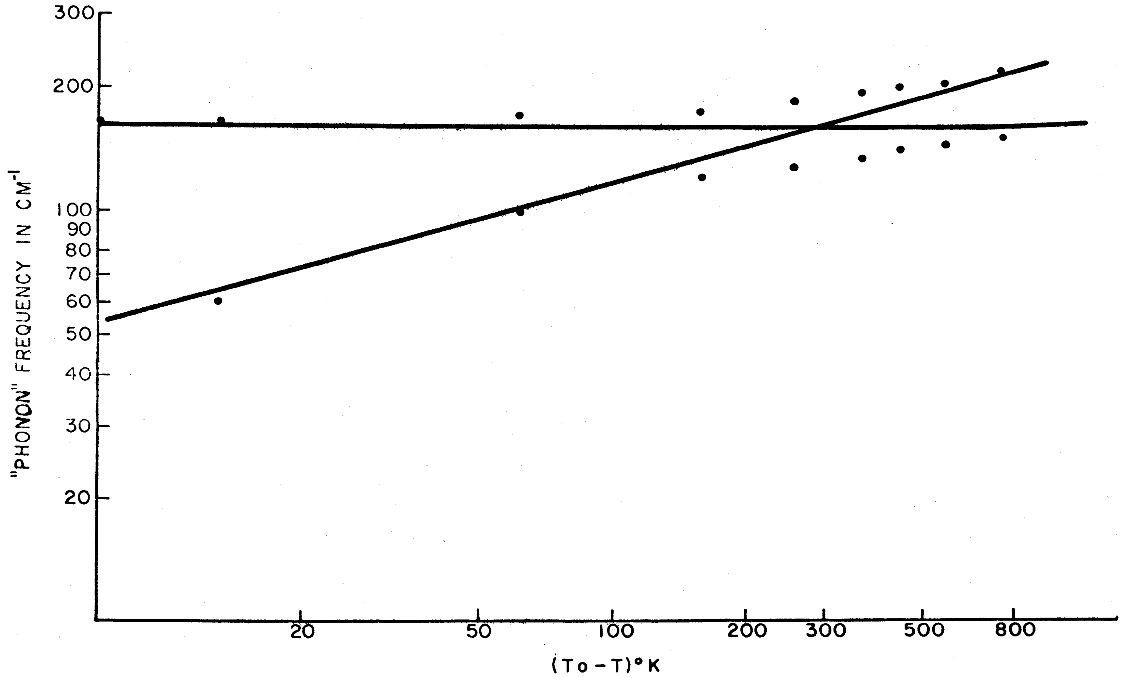

FIG. 9. ω vs T for soft modes in α-quartz (Scott, 1968).

where W is the third-order anharmonic matrix element connecting the one- and two-phonon states; and $\hbar\omega_2$ is the temperature-independent two-phonon energy.

A more exact treatment discussed in a previous section replaces ω_1 and ω_2 by $\omega_1^2 + i\Gamma_1\omega$ and $\omega_2^2 + i\Gamma_2\omega$ in Eq. (IV.2), and permits both real and imaginary matrix elements connecting the states. As discussed by Ruvalds and Zawadowski (1970) and Höchli and Scott (1971), the two formalisms give very nearly the same results in the case of quartz: $\omega = A(T_c - T)^{0.31}$ was obtained from the latter analysis, with $T_c \approx T_0 + 5°\mathrm{C}$.

The exponent 0.30 appearing in Eq. (IV.1) may be significant inasmuch as values of $\sim \frac{1}{3}$ are expected for systems in the critical regime in which mean field theories fail due to the large fluctuations not incorporated in linear response theories; i.e., regions where $\langle\varphi^2\rangle^{1/2} \gg \langle\varphi\rangle$, where φ is the order parameter. Höchli and Scott (1971) have shown that the behavior of an elastic constant in α-quartz is also describable by the formula

$$C(T) = B(T_c - T)^{0.33}, \qquad \text{(IV.3}a\text{)}$$

with $T_c \approx T_0 + 5°\mathrm{C}$.

Shapiro and Cummins (1968) had earlier pointed out the anomalous temperature dependence of the soft-mode frequency, but their inferred exponent was inaccurate due to their neglect of mode coupling.

The evaluation of critical exponents for first-order phase transitions, such as those in quartz or SbSI, is a matter of current theoretical investigation. Although quartz exhibits temperature dependences for many parameters—soft-mode frequency, elastic coefficients, thermal expansion—which may be fitted over a range of $T_0 - T = 80°\mathrm{K}$ by a single $\beta = 0.33$ exponent, Banda *et al.* (1973) have very recently shown that this may be explained within mean-field theory for any system exhibiting a first-order transition. By including a cubic term in the free energy (absent for second-order transitions), they obtain an expression for the order parameter as a function of T_0, the actual transition temperature (strictly, where the high- and low-temperature-phase free energies are equal; roughly, the average of the transition temperatures encountered upon heating and cooling), and T_C, the temperature at which the order parameter extrapolates to zero.

Banda *et al.* find

$$\eta(t) = \text{const.}\left\{1 + \tfrac{1}{3}\left[1 + \frac{8(T_0 - T)}{T_0 - T_C}\right]^{\frac{1}{2}}\right\}. \qquad \text{(IV.3b)}$$

This expression is functionally very different from a simple 1/3 exponential in $(T_0 - T)$, but when graphed it yields remarkably similar values. Indeed, we are forced to agree with the conclusions of Banda *et al.*, that "the observation of a critical-like exponent for the behavior of the long-range order parameter does not, in itself, imply critical behavior."

We do note, however, that the thermal expansion data of Banda *et al.* do agree better with a simple 1/3 exponent than with the mean-field formula. Thus, phenomena in quartz may still be "critical" (or fluctuation-dominated) near T_0. If this is the case, it would be explained by the fact that T_0 and T_C differ by only a few degrees, whereas the single-exponent regime is about 80°K. Such systems have been described as "slightly first-order." The existence of critical phenomena in such systems is a moot question. In contrast, first order systems such as $\mathrm{PbTiO_3}$, where T_0 is not at all close to T_C, present no possibility of critical phenomena whatsoever, in the opinion of this reviewer. [Dorner *et al.*, *Ferroelectrics* (in press) have also very recently given a mean field analysis of first-order transitions like that in quartz, which yields approximately exponential dependences, like the treatment of Banda *et al.*]

We should point out that the elastic coefficient anomaly in quartz cannot be due to piezoelectric coupling between the soft optic mode and an acoustic phonon: Since the soft mode is nonpolar, this interaction vanishes in lowest order (Miller and Axe, 1967). This implies that a higher-order interaction is operative, and Axe and Shirane have shown that the interaction in quartz is of form

$$\mathcal{H}_i = Au^2\varphi, \qquad \text{(IV.4)}$$

where u is the elastic strain (acoustic phonon amplitude), and φ is an order parameter associated with the $q = 0$ soft optic phonon displacements. A survey of other linear and nonlinear opto-acoustic mode couplings has been given in a review by Fleury (1971).

While the $\beta \approx 1/3$ exponent obtained in fitting soft-mode frequencies and elastic coefficients is not in itself compelling evidence that critical phenomena are manifest over a large temperature range, such a conclusion is more plausible than in the case of ferroelectrics (such as SbSI). The reason is that the fluctuations near T_0 involve nonpolar phonons; hence, the interactions may be of very short range, in contrast to the long-range Coulomb fields in a ferroelectric. The range or coherence length for fluctuations near T_0 has been related to the temperature regime over which "critical" $\beta \approx 1/3$ exponents might be expected. The formula below is due to Ginzburg (1960).

$$\left(\frac{T_0 - T}{T_0}\right)_{\mathrm{crit}} = \left(\frac{k}{\rho\Delta C_p}\right)^2 \frac{1}{l^6}, \qquad \text{(IV.5)}$$

where k is the Boltzman constant; ρ, the density; and ΔC_p, the specific heat jump at T_0 in the classical description. In quartz, Czaja has pointed out (1970) that if l, the coherence length at $T = 0°\mathrm{K}$, is taken as one unit cell length (in the basal plane), ΔT_{crit} is estimated as 150°K!! This value agrees very well with the temperature region below T_0 over which the specific heat exhibits a logarithmic singularity. Thus, a critical temperature range several orders of magnitude larger than those commonly found in magnetic systems may be crudely justified in structural phase transitions involving short-range forces.

It is of special interest in this context to point out that in $\mathrm{SrTiO_3}$, where the EPR data of Müller and Berlinger (1971) convincingly show a critical regime of $\Delta T \approx 20°\mathrm{K}$, the transition also involves nonpolar phonons, *and* the 0°K coherence length deduced via Eq. (IV.5) was also one or two unit cell diameters.

2. β-phase

It remained for inelastic neutron scattering experiments to elucidate the dynamical behavior in the β-phase of quartz: the soft mode is of B_1 symmetry in β-quartz

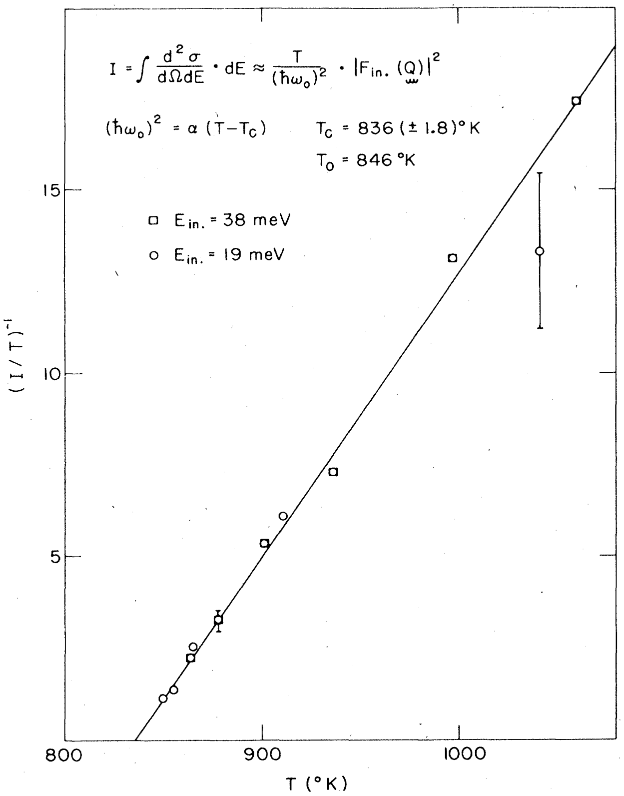

FIG. 10. ω_0^2 vs T in β-quartz (Axe and Shirane, 1970).

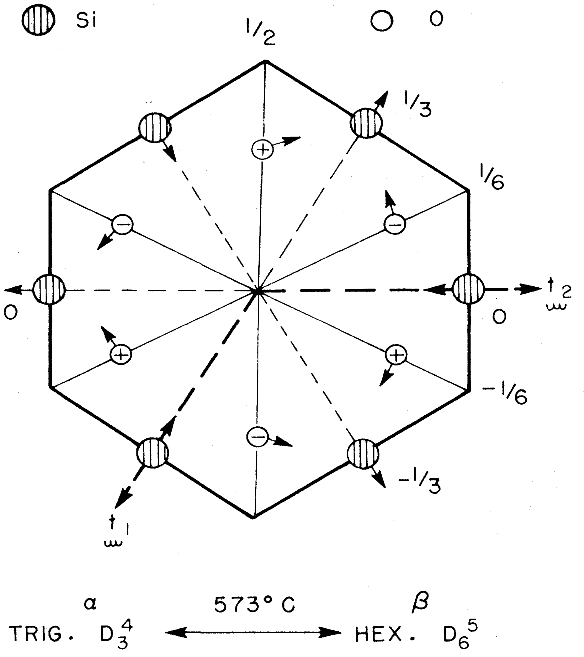

FIG. 11. Soft-mode eigenvector in quartz (Axe and Shirane, 1971).

and is neither ir nor Raman-active. In a publication typical of the fine work emerging from Brookhaven on the subject of phase transitions, Axe and Shirane (1970) measured the temperature dependence and eigenvector of the soft mode in the β-phase. Their results for $\omega_0^2(T)$ are shown in Fig. 10. The undamped frequency $\omega_0(T)$ was determined indirectly from the integrated intensities, according to the equation

$$I = \int \frac{d^2\sigma}{d\Omega dE} dE \approx \frac{T}{(\hbar\omega_0)^2}|F(Q)|^2. \tag{IV.6}$$

Note that T_c is ~10°C less than T_0, as expected for a first-order transition. This ΔT is of the same size as extrapolated from the α-phase Raman and elastic coefficient data. The actual mode was observed to be overdamped. It could not be underdamped even by going to temperatures much above T_0, for at higher temperatures other transitions (e.g., to tridymite) occur. The soft-mode frequency in β-quartz was also found to be extremely anisotropic, forming a low-frequency "trough" to large q in certain directions in momentum space.

The ionic displacements in the soft mode and for the α–β structural distortion are shown in Fig. 11. The silicon motion is described as symmetric "breathing" perpendicular to the D_3 c axis. This is in accord with Saksena's early (1940) model. In addition, the SiO_2 triangles undergo a rotation about the C_2 axes normal to c. It is this $Si-O_2$ rotation which is largely responsible for the instability in the shear wave (acoustic phonon) measured by Höchli (1970). The soft-mode eigenvector determined by Axe and Shirane differs by only a few percent from the actual ionic displacements occurring to T_0; the difference is that the soft mode includes a small amount of displacements transforming as A_1 in the β phase, whereas the static displacements at T_0 have exactly B_1 symmetry. It is likely that this A_1 part of the soft-mode eigenvector reduces to zero as $T \to T_0$, although that is not rigorously necessary, since the transition is first order.

Finally, some information concerning the zone-boundary phonons which comprise the ~147 cm^{-1} two-phonon peak in α-quartz exists in the neutron study and lattice dynamical calculation of Elcombe (1967). Her dispersion curves show that the most likely origin of the 147 cm^{-1} peak is due to two transverse acoustic phonons at critical point $K = (2\pi/a)$ $(2/3, 0, 0)$. The fact that the two-phonon peak is an overtone (i.e., two of the same phonon), and not a combination, is apparent from Leadbetter's (1969) time-of-flight neutron measurements on polycrystalline quartz, which revealed a sharp peak in the one-phonon density of states at 70 ± 5 cm^{-1}.

B. $AlPO_4$

Aluminum phosphate is one of several ternary compounds of formula III – V – O_4 which is isomorphic to α-quartz at normal temperatures. Because the Al and P ions are nonequivalent, the primitive unit cell is twice as large along the [001] c axis as is quartz or GeO_2. Hence, phonons which would be described as lying at critical point $A = (0, 0, \pi/a)$ in quartz lie at $(0, 0, \pi/a) = (0, 0, \pi/\frac{1}{2}a') = (0, 0, 2\pi/a') = \Gamma$ in $AlPO_4$, and are Raman-allowed. One such mode lies at 158 cm^{-1} in $AlPO_4$ and is of the same Γ_1 symmetry as the soft mode (Scott, 1971).

When the soft mode decreases from its ~220 cm^{-1} low-temperature value as $T \to T_0 (T_0 = 853°K)$ in $\alpha AlPO_4$, it interacts very strongly with the phonon at

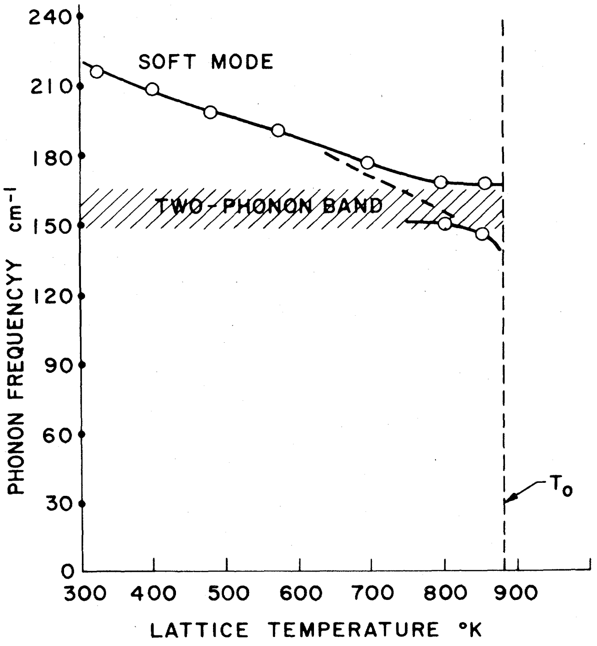

FIG. 12. ω vs T in $AlPO_4$ (Scott, 1970a).

158 cm^{-1}. This interaction is in addition to the soft-mode "Fermi resonance" coupling with the $2TA$ state at ~ 147 cm^{-1} (both SiO_2 and $AlPO_4$ exhibit this interaction). Figure 12 shows a plot of soft-mode frequency versus temperature in $AlPO_4$. Note that, as in SiO_2, the transition is first order, and $\omega(T)$ does not reach zero at $T = T_0$ (Scott, 1970a).

The one-phonon couplings between the soft-mode and the 158 cm^{-1} state leads to dramatic lineshape anomalies, as shown in Fig. 13. Figure 14 shows the Fermi resonance hybridization of one- and two-phonon levels, as well.

The line asymmetries illustrated in Fig. 13 have been explained by Scott (1970a), who employed a modification of the old Breit–Wigner theory from nuclear physics, and by Zawadowski and Ruvalds (1970), who employed many-body techniques.

In treating the $AlPO_4$ data, Zawadowski and Ruvalds have employed the anharmonic formalism discussed in Sec. I of this paper:

$$S(\omega) = (\bar{n} + 1)\chi''(\omega) \tag{IV.7}$$

where $S(\omega)$ is the Raman intensity at ω; $\bar{n}$ is the Bose population; and $\chi''(\omega)$ is the imaginary part of the susceptibility:

$$\chi(\omega) = \sum_{i,j} P_i P_j G_{ij}(\omega), \tag{IV.8}$$

with $G_{ij}^{-1}(\omega)$ given as

$$G_{ij}^{-1}(\omega) = \begin{bmatrix} \omega_1^2 - \omega^2 + i\Gamma_1\omega & \Delta^2 + i\Gamma_{12}\omega \\ \Delta^2 + i\Gamma_{12}\omega & \omega_2^2 - \omega + i\Gamma_2\omega \end{bmatrix}. \tag{IV.9}$$

Zawadowski and Ruvalds further assumed that $\Delta \ll \Gamma_{12}$, since it was known that the imaginary term $i\Gamma_{12}\omega$, in Eq. (IV.9) was dominant in the "Fermi resonance" coupling in the same crystal. Their resulting theoretical spectra are shown in Fig. 14 and are in excellent agreement with the experimental data of Fig. 13.

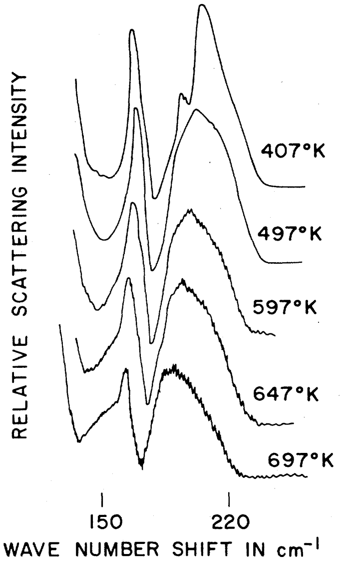

FIG. 13. Mode coupling in $AlPO_4$ (Scott, 1970a).

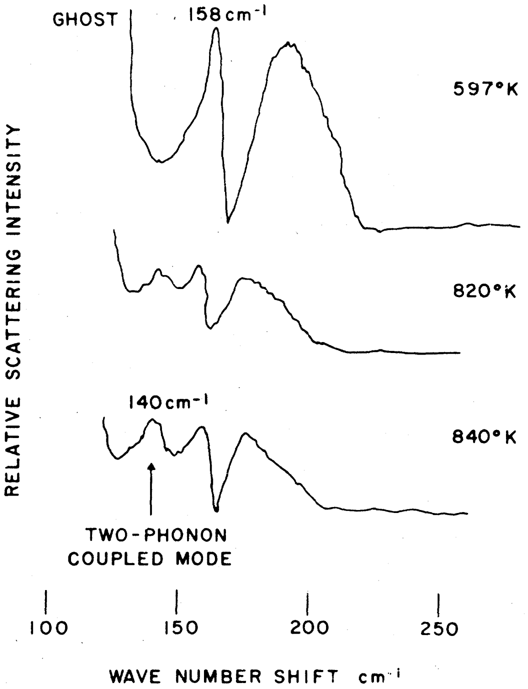

FIG. 14. Fermi resonance in $AlPO_4$ (Scott, 1970a).

In Figs. 15 and 16 the calculation of these same authors (Ruvalds and Zawadowski, 1970) for the line shapes in SiO_2 or $AlPO_4$ in the vicinity of the Fermi resonance are compared with experimental data. As in the case of the one-phonon couplings, their description of one- and two-phonon interactions are in good accord with experiment.

C. GeO_2

Germanium dioxide has received considerably less attention than have isomorphic SiO_2 and $AlPO_4$. The

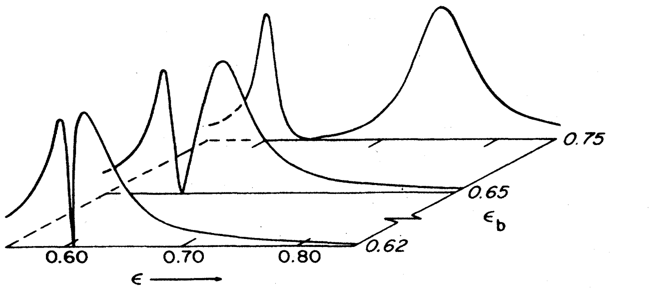

FIG. 15. AlPO₄ spectral theory (Zawadowski and Ruvalds, 1970). Here ε_b is the soft-mode energy for zero coupling; ε is the phonon energy.

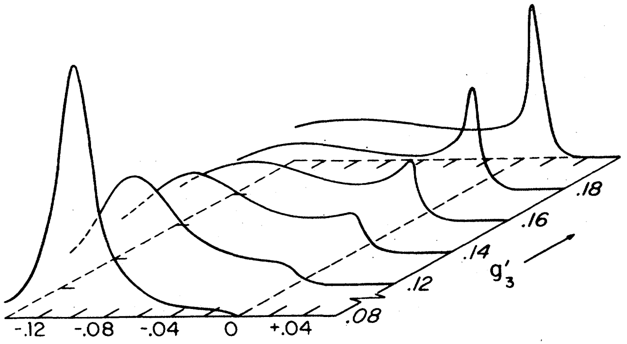

FIG. 16. SiO₂ spectral theory (Ruvalds and Zawadowski, 1970). Here g_3' is the coupling constant due to cubic anharmonicity.

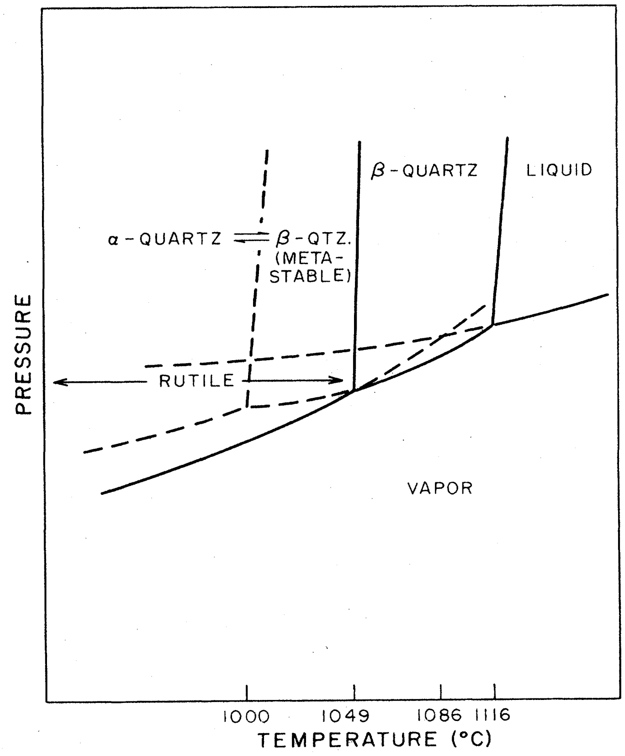

FIG. 17. GeO₂ phase diagram (Sarver and Hummel, 1960).

Raman spectra of both rutile (D_{4h}^{14} or $P4/mnm$) and α-quartz (D_3^4 or 32) structures of GeO₂ have been published by Scott (1970b). The α-quartz form of GeO₂ has the same Γ_1 symmetry optical phonon (at ~166 cm^{-1} in GeO₂; see Mirgorodskii 1973 for correct assignment of the mode) as do SiO₂ and AlPO₄, but whereas this mode softens dramatically with increasing temperature in the latter crystals, no decrease in frequency is observed for GeO₂. This may be understood with the aid of the phase diagram in Fig. 17. This diagram is quite schematic (Sarver and Hummel, 1960), but illustrates the important point: at low pressures, the rutile structure is stable, but the α-quartz form is metastable with a long conversion time. Under pressure, there is a stable β-quartz phase between 1049° and 1116°C. The rutile to α-quartz and rutile to β-quartz transitions are both necessarily first order. The α–β quartz transition is probably first order. Thus, at ambient pressures α-GeO₂ would not be expected to exhibit very dramatic softening of its Γ_1 mode at about 166 cm^{-1}; the β-quartz phase cannot be reached at such low pressure. The phase diagram of Fig. 17 indicates that further Raman experiments on the α–β transition in GeO₂ might reveal information concerning soft modes, but would have to be made at high temperatures and pressures.

V. FERROELECTRIC PEROVSKITES

Whereas Rochelle Salt and other complex hydrogen-bonded crystals were known to exhibit ferroelectricity for some time prior to the second world war, the discovery of ferroelectric BaTiO₃ during the war years stimulated considerably more interest in the phenomenon, on the basis of the simple, highly symmetric O_h^1 (or $Pm3m$) structure of ABO₃ perovskites, shown in Fig. 18, and the absence of hydrogen in the crystal—previously thought to be essential for ferroelectricity. Although BaTiO₃ was the first crystal of this class studied, it has remained more enigmatic than its isomorphs, owing to very short phonon lifetimes and extreme phonon anisotropy. However cloudy the quantitative understanding of BaTiO₃ transition dynamics may have been in the past, there is now a wealth of information on SrTiO₃, PbTiO₃, KNbO₃, KTaO₃ and mixed crystals of the ABO₃ perovskite structure, and it seems unlikely to this reviewer that any of the theories or interpretations which singled out BaTiO₃ as unique or qualitatively different from its isomorphs is correct.

Spectroscopically, the first important studies of BaTiO₃ and SrTiO₃ were ir reflectivity measurements of Barker and Tinkham (1962) and Spitzer *et al.* (1962), each of whom found that the low-frequency dielectric response in each crystal was due to a temperature-dependent, low-

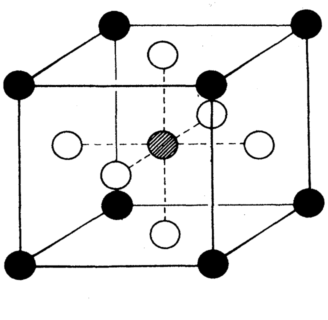

FIG. 18. ABO₃ perovskite structure.

frequency optical phonon, i.e., a mode which could be characterized by a damped harmonic oscillator rather than a Debye relaxation. These two experiments on $BaTiO_3$ and $SrTiO_3$ may be viewed as confirming the soft-mode description of ferroelectricity in the ABO_3 perovskites. This interpretation was further strengthened by the concurrent inelastic neutron scattering studies of Cowley (1962, 1964).

A. KTaO₃ and SrTiO₃

Several years later, Fleury and Worlock (1967a,b, 1968) performed a series of light scattering experiments on $SrTiO_3$ and $KTaO_3$ which improved the quantitative information available on temperature dependences of soft-mode energies and linewidths. The ir linewidths were in error due to an extrapolation made to long wavelengths.

$SrTiO_3$ and $KTaO_3$ are known to remain paraelectric at all temperatures; however, the $q = 0$ optic mode which consists of Ti or Ta motion along a [100] axis against the oxygen octahedra becomes very nearly unstable as absolute zero is approached. The energies decrease by more than an order of magnitude as the lattice temperature is lowered from ~300°K. The $\omega(T)$ dependence for $KTaO_3$ is shown in Fig. 19. The soft mode in $KTaO_3$ (and $SrTiO_3$) remains underdamped at all temperatures, facilitating accurate measurement of $\omega(T)$. These same soft modes (F_{1u} $q = 0$ in the cubic phase) cause transitions in $PbTiO_3$ and $BaTiO_3$. If a small percentage of Ba is substituted for Sr in $SrTiO_3$, or a small percentage of Nb is introduced into $KTaO_3$ (replacing Ta), these crystals are observed to exhibit ferroelectricity, with transition temperature approximately proportional to Ba (or Nb) concentration.

B. PbTiO₃, BaTiO₃ and ferroelectric ceramics

The soft ferroelectric modes have been studied via Raman spectroscopy in a large number of perovskites by this time. Work on $PbTiO_3$ (Burns and Scott, 1970a), $K_xNa_{1-x}TaO_3$ (Davis, 1970), $PbTi_{1-x}Zr_xO_3$ (Burns and Scott, 1970b), $Pb_{1-x}Ba_xTiO_3$ (Burns and Scott, 1971), and $Pb_xLa_{1-x}Zr_yTi_{1-y}O_3$ ceramics (Brya, 1971) have all confirmed the soft-mode picture of ferroelectricity in this class of compounds.

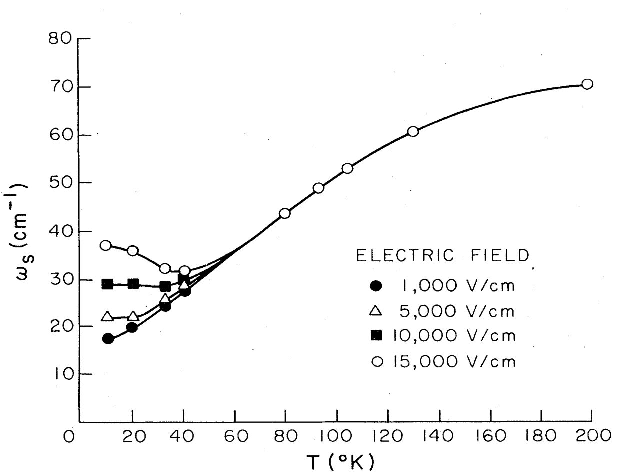

FIG. 19. ω vs T in $KTaO_3$ (P.A. Fleury and J. M. Worlock, Phys. Rev. **174**, 613 (1968).

The inelastic neutron studies of $PbTiO_3$ (Shirane *et al.*, 1970), $KNbO_3$ (Nunes *et al.*, 1971), and $BaTiO_3$ (Harada *et al.*, 1971) have been even more important. In analyzing the soft mode in the high-temperature cubic phase of each crystal, the Brookhaven group has shown that there is a soft mode associated with the first-order phase transition in each crystal; that it exhibits $\omega = A(T - T_c)^{1/2}$ Curie–Weiss dependence; that it is overdamped at temperatures well above T_0 in $BaTiO_3$ and $KNbO_3$, but underdamped in $PbTiO_3$; that in both $BaTiO_3$ and $KNbO_3$ the damping of the soft mode is extremely anisotropic; and that strong coupling between acoustic phonons and the soft optic mode is observed in each case. Since this acousto-optic mode coupling vanishes in lowest order for centrosymmetric crystals such as the cubic perovskites, the analysis in each case involves a nonlinear coupling of form $c_{ijj}q_iq_j^2$, where q_i is the acoustic phonon displacement, and q_j is the optic mode displacement. Such couplings in centric lattices were first analyzed by Axe *et al.* (1970).

The soft-mode measurements at Brookhaven suffice to explain the anomalous x-ray results on perovskites. Harada and Honjo (1967) and Comes *et al.* (1968, 1969, 1971) have reported distinct sheets of diffuse x-ray scattering in planes perpendicular to [h00] reciprocal lattice vectors in $BaTiO_3$ and $KNbO_3$. Comes *et al.* have interpreted these sheets as evidence of *static* disorder and have proposed a specific model for chainlike disorder in these crystals. However, the neutron studies discussed above show that the diffuse x-ray patterns of Harada and Honjo or Comes *et al.* are due not to *static* displacements, but to the rms soft-mode amplitudes; the fact that these amplitudes are extremely anisotropic (very large in the [100] directions) explains the specific x-ray patterns observed. Cochran (1968) first made this point explicitly, and discussed the rms soft-mode amplitudes $\langle u^2\rangle^{\frac{1}{2}}$ quantitatively for $BaTiO_3$ and $KNb_{0.4}Ta_{0.6}O_3$. In the same paper, Cochran pointed out that the Curie constant C defined as

$$\epsilon_0(T) = 4\pi C/(T - T_c) \tag{V.1}$$

is related (Cochran, 1960) to the rms soft-mode displacements by the equation

$$C = VP^2/A \sum_k M_k\langle u_k^2\rangle, \tag{V.2}$$

where V is the unit cell volume; k designates the kth atom in each primitive cell; P is the polarization induced by the ionic displacements u_k; and A is the temperature coefficient for the $q = 0$ soft optic mode

$$\omega^2(T) = A(T - T_c) \tag{V.3}$$

in the cubic phase.

For $BaTiO_3$, Eqs. (V.1) and (V.2) are in good agreement, yielding $c = 1.0 \times 10^4$ °K from Eq. (V.2) (Barker, 1967), and $C = 1.2 \times 10^4$ °K from Eq. (V.1) (Jona and Shirane, 1962).

By comparison, a tunneling model having small tunneling integral yields a theoretical Curie constant

$$C = Vp^2/k_B = 2.8 \times 10^3 \text{ °K} \tag{V.4}$$

which is much smaller than observed. Thus, the experimental data are not in accord with a static disorder

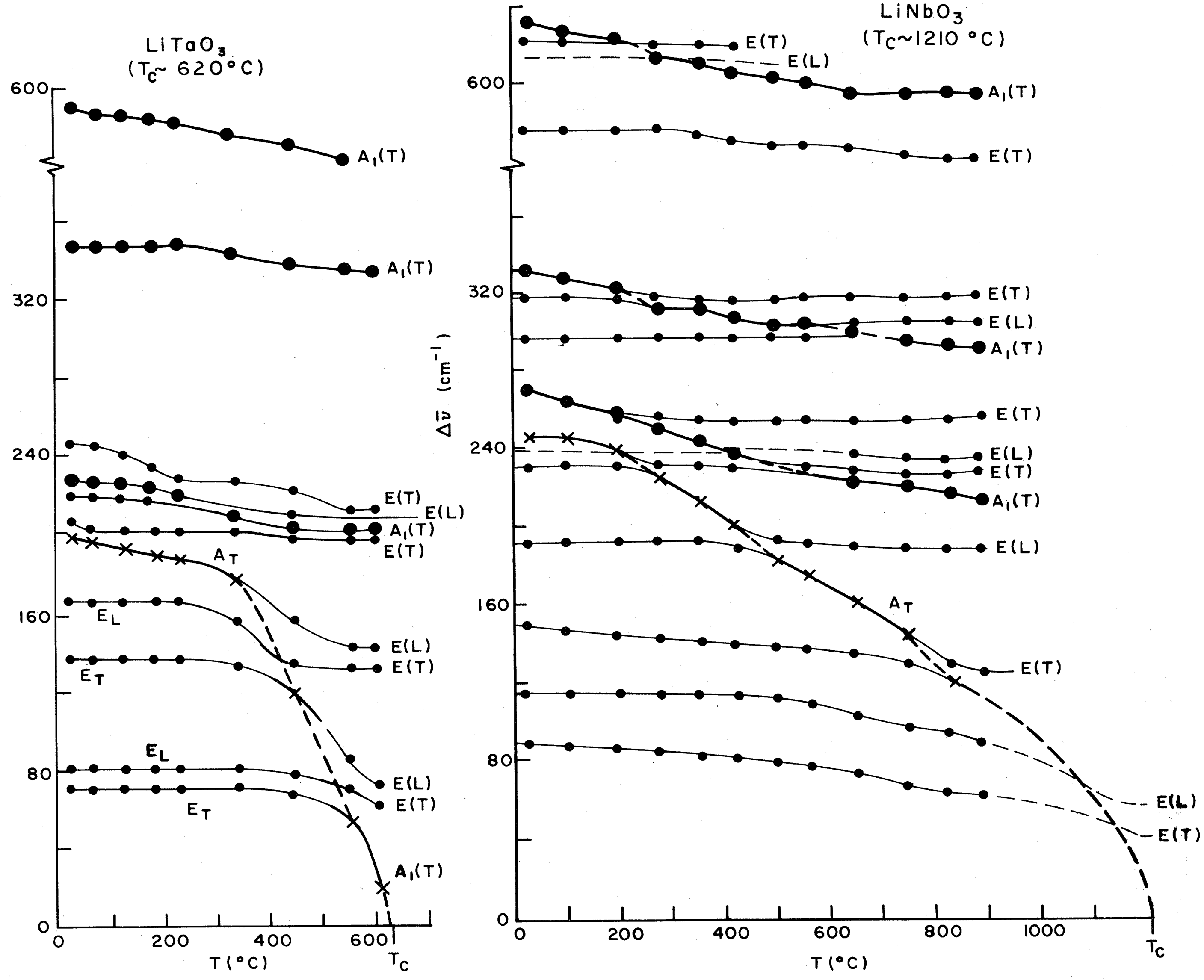

FIG. 20. (a) ω vs T: in LiTaO$_3$ (Johnston and Kaminow, 1968); (b) ω vs T: in *LiNbO$_3$* (Johnston and Kaminow, 1968).

model of ABO$_3$ ferroelectrics, nor with the idea of tunneling, as opposed to large amplitude motion in shallow double-well potentials.

C. Other ABO$_3$ ferroelectrics: LiNbO$_3$ and LiTaO$_3$

Although lithium niobate and lithium tantalate do not have the perovskite structure, they are ABO$_3$ lattices with oxygen octahedra, and they exhibit many macroscopic similarities with the perovskite ferroelectrics. The space group of both crystals is $R3c$ (or C_{3v}^6) at ambient temperatures, with two formula groups per primitive cell. Above T_0 (~900°K for LiTaO$_3$ and ~1480°K for LiNbO$_3$), the structures have $R\bar{3}c$ (or D_{3d}^6) symmetry. Johnston and Kaminow (1967) have shown that each crystal exhibits an underdamped soft mode having approximate Curie–Weiss dependence over the region $0.1 \leq T/T_0 \leq 0.75$. Plots of their data for LiNbO$_3$ and LiTaO$_3$ are shown in Fig. 20a and b.

Also of interest in regard to Johnston and Kaminow's measurements on LiTaO$_3$ is their report of a maximum in the Rayleigh scattering intensity at $T = T_0$. An increase of about twofold was observed in the unresolved Rayleigh-plus-Brillouin spectral intensity as temperature increased from ~775°K to $T_0 \cong 905$°K. Although the authors interpreted these data as "critical" Rayleigh scattering, there is certainly nothing demonstrably "critical" in their observations (As discussed in other sections of this paper, "central modes" or growing scattering intensities at $\omega \approx 0$ may be critical or noncritical, that is, describable within the context of mean field theories). Moreover, there is no evidence that they are measuring Rayleigh scattering, since the Brillouin intensities are expected to increase sharply near T_0, due to piezoelectric coupling between optic and acoustic phonons; the resolution in Johnston and Kaminow's experiment was more than twenty times too poor to resolve Rayleigh and Brillouin components.

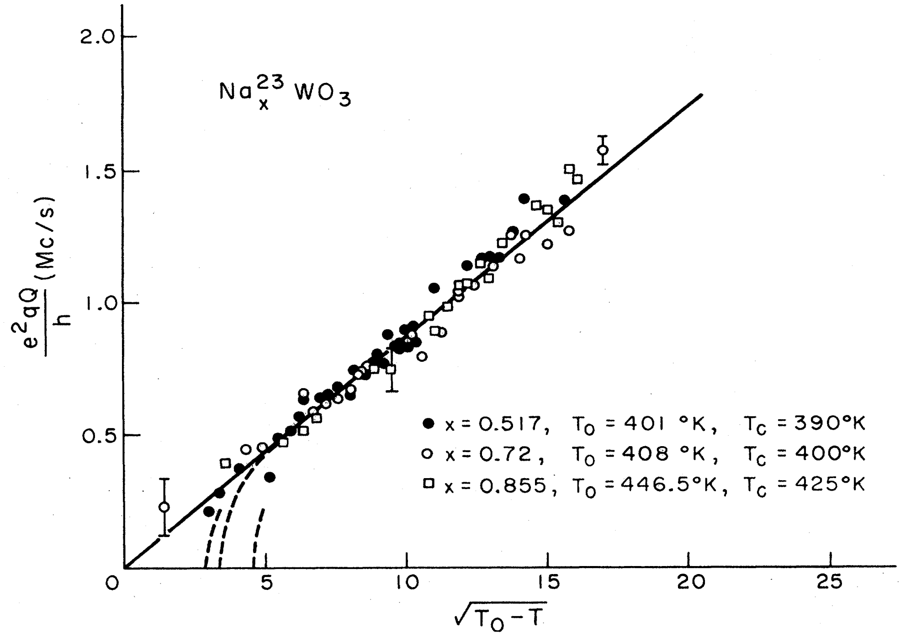

FIG. 21. NQR quadrupole coupling constant vs T in Na_xWO_3. The phase transition in these ferroelectric metals was first analyzed by Brown and Banks, (1954).

D. M_xWO_3

The tungsten bronzes have disordered cubic perovskite structures at high temperatures. The best studied of these compounds is Na_xWO_3, which Brown and Banks (1954) observed to undergo a cubic-tetragonal phase transition at ~400°K, with the exact value of T_0 depending upon the sodium concentration. Brown and Banks proposed that this cubic-to-tetragonal distortion was identical to that in $BaTiO_3$. Following their cue, Matthias has often referred to the tungsten bronzes as "ferroelectric metals," and as we havd seen in the case of highly conducting GeTe, ferroelectricity can be defined in a lattice dynamical way when high conductivities prevent the usual D-E hysteresis measurements.

The most quantitative measurements on the cubic-tetragonal transitions in Na_xWO_3 are the NQR measurements of Borsa (1971). His results are shown in Fig. 21.

The principle involved in assessing the nuclear quadrupole coupling constant is that the constant $e^2qQ/h \equiv eqV/h$ is dominated by the electric field gradient V produced by the rms soft-mode amplitude, and that e^2qQ/h is proportional to $\omega(T)$, where ω is the soft-mode frequency. This point is discussed in greater detail in section IX of this paper, in the KH_2AsO_4 analysis.

Less work has been reported on the hexagonal tungsten bronzes, such as Rb_xWO_3; Scott *et al.* (1970) were successful in obtaining a Raman spectrum of metallic $Rb_{0.3}WO_3$, but no low-frequency modes were observed.

VI. PEROVSKITES WITH CELL-DOUBLING TRANSITIONS

A. $SrTiO_3$

The idea that crystals could double their primitive unit cells in a continuous way by means of a soft optical phonon at the Brillouin zone boundary was contained in one of Cochran's early discussions of ADP [$NH_4H_2PO_4$] (Cochran, 1961). It was not until 1968, however, that the Raman study of Fleury *et al.* directly revealed such behavior for the second-order displacive transition in $SrTiO_3$ at ~106°K. The existence of such a phase transition was shown by Müller (1958), by Bell and Rupprecht (1963), and by Rimai and deMars (1962), but incorrect space group determination in the low-temperature phase (Lytle, 1964) delayed the understanding of the transition dynamics for several years. As shown subsequently by the Raman studies of Fleury *et al.* (1968), x-ray diffraction experiments, as done by Lytle, are not a good probe of the static configuration of $SrTiO_3$ below T_0, for the transition involves only a small rotation of the oxygen octahedra; and the oxygen x-ray scattering is very weak compared with that of the heavy metal ions Moreover, the rotation angle for the oxygen octahedra varies from ~2° of arc at ~0°K down to zero (the transition is second order) at $T_0 \approx 106$°K; at liquid nitrogen temperature, φ is about 1.4° and the linear displacement of the O ions about their high-temperature equilibrium positions is less than 0.03 Å, which would make x-ray detection difficult.

The space group of $SrTiO_3$ in the low-temperature, tetragonal phase was first correctly determined by the EPR studies of Unoki and Sakudo (1967), who determined it as D_{4h}^{18} (or $I\ 4/mcm$) with two formula groups per primitive cell. The distortion at $T_0 = 106$°K consists of an out-of-phase "rotation" of adjacent oxygen octahedra in the (100) planes as shown in Fig. 22. This oxygen octahedron motion can be described as a rotation only as a first approximation: The O ions actually remain on the faces of each cube and therefore increase in separation from the titanium. Because the [100] planes are equivalent in the cubic phase, the distortion produces domains below T_0 in which the [100], [010], or [001] axis becomes the unique tetragonal c axis.

The unraveling of the static structure of $SrTiO_3$ came about from dynamical measurements on the crystal. In most crystals the complete space group determination has been made unambiguously, and the dynamical behavior can be predicted by comparing positions in the highand low-temperature phases. In $SrTiO_3$, the reverse was possible: Since the positions and symmetries of the

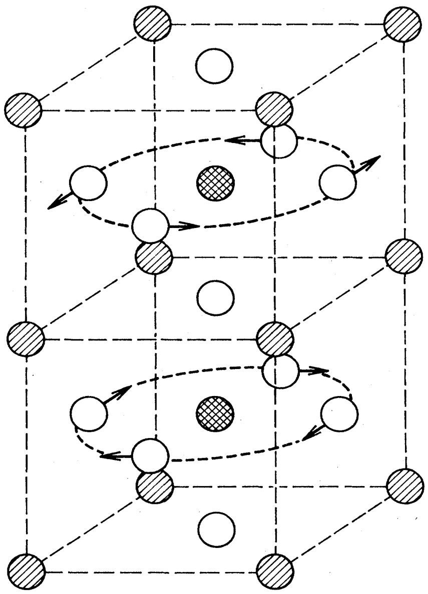

FIG. 22. $SrTiO_3$ soft-mode eigenvector.

Raman lines observed below T_0 were compatible only with a B_{2u} (one component of F_{2u}) symmetry distortion (a B_{2u} distortion is an odd-parity inhomogeneous shear strain) from the ideal cubic perovskite structure, *and* since there is only one optical phonon with that symmetry in the cubic phase, the structure could unambiguously be determined from the Raman spectrum below T_0. This is explicitly shown in Table VI.1, where the symmetries listed in Column I are those at the Brillouin zone corner; the frequencies in Column II are estimated from Cowley's 1964 neutron scattering data.

Figure 23 shows the dependence of soft-mode frequencies upon T in the tetragonal phase (Fleury *et al.*, 1968). These data indicate that the transition is second order, i.e., $\omega(T)$ extrapolates smoothly to zero at $T = T_0$.

Most of the theoretical formalism for the discussion of the $SrTiO_3$ phase transition applies equally well to the rare-earth aluminates which are also O_h^1 structure cubic perovskites at high temperatures. We therefore review the experimental data on these materials before summarizing the theoretical descriptions in the literature.

TABLE VI.I. S.T.O_3 Zone-Corner Modes [III].

Cubic phase symmetry	Energy (estimated from Cowley's 1964 [001] data)	Tetragonal symmetry	Energy observed	ir/Raman
$A_{2u}(\Gamma_2')$	800 cm^{-1}	A_{2g}		silent
$F_{2g}(\Gamma_{25}')$	500 cm^{-1}	E_u		*ir*
		A_{1u}		silent
$F_{1u}(\Gamma_{15})$	400 cm^{-1}	E_g	. . .	*xx,yz*
		B_{1g}	460	*xx-yy*
$E_u(\Gamma_{12}')$	200 cm^{-1}	B_{2g}	235?	*xy*
		A_{2g}	. . .	silent
$F_{1u}(\Gamma_{15})$	110 cm^{-1}	E_g	143	*xx,yz*
		B_{1g}	. . .	*xx–yy*
$F_{2u}(\Gamma_{25})$	soft	E_g	15	*xx,yz*
		A_{1g}	48	*xx,zz*

B. $LaAlO_3$

$LaAlO_3$, lanthanum aluminate, was first characterized structurally by Geller and Bala (1956), who determined that its space group at ambient temperatures is D_{3d}^5 (or $R\bar{3}m$), and that it undergoes a transformation from rhombohedral to cubic at 435 ± 25°C. Unfortunately, both of these conclusions are wrong. The correct space group is D_{3d}^6 ($R\bar{3}c$), as determined by Derighetti *et al.* (1965). And the transition temperature is 527 ± 10°C as determined independently by x-ray (Plakhty and Cochran, 1968) and EPR (Müller *et al.*, 1968) techniques.

The physical connection between this rhombohedral distortion from the $Pm3m$ high-temperature structure and that occurring in tetragonal $SrTiO_3$ is shown in Fig. 24. It can be seen that the oxygen octahedra in $LaAlO_3$ distort in a way which can also be approximated by a rigid rotation; only in $LaAlO_3$ the rotation is about the [111] body-diagonal of the cube. (And, as in $SrTiO_3$, it is not truly a rigid rotation, since the O ions remain on the cube faces.) This picture of the $LaAlO_3$ transition is due

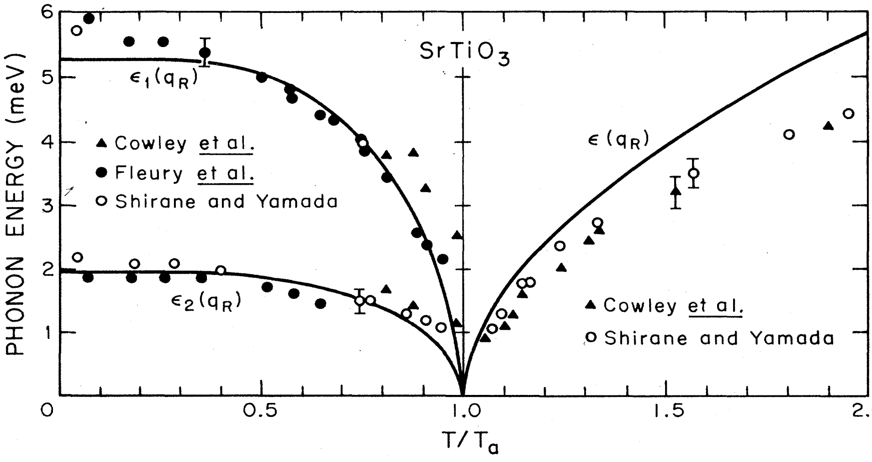

FIG. 23. ω vs T, $SrTiO_3$ (theory and experiment) (Feder and Pytte, 1970).

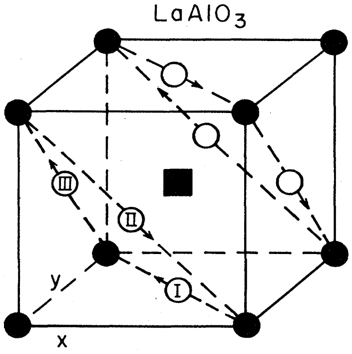

FIG. 24. $LaAlO_3$ soft-mode eigenvector (Cochran and Zia, 1968).

originally to deRango *et al.* (1964) and to Cochran and Zia (1968).

The microscopic order parameter in each case is the angle of octahedron rotation; mean field theory predicts a soft-mode frequency proportional, therefore, to $\varphi(T)$, as will be shown.

The rotations in $LaAlO_3$ and $SrTiO_3$ involve the same soft Γ_{25} (F_{2u}) optic phonon at the same place, $R = [1, 1, 1]$ corner, in the Brillouin zone. Since this mode is threefold degenerate in the cubic phase, three independent linear combinations of displacements are possible: These correspond to rotationlike distortions of oxygen octahedra about [100], [111], and [110] axes, resulting in tetragonal, rhombohedral, and orthorhombic lattices, respectively, below T_0—each with a doubled primitive cell. The tetragonal distortion occurs in $SrTiO_3$; the rhombohedral distortion in $LaAlO_3$; the orthorhombic distortion does not occur in nature, for while it is group-theoretically permitted, it does not minimize the free energy, and is therefore thermodynamically unstable (Thomas and Müller, 1968). The latter comment reminds us that in general we must consider thermodynamics and not just group theory in determining what stable structures are permitted when degenerate soft modes are involved.

The simplicity of the soft-mode eigenvectors in both $SrTiO_3$ and $LaAlO_3$—i.e. the fact that only the oxygen ions move—has allowed Pytte and Feder (1970, 1971) to analyze all of the dynamical variables in these two crystal classes via a simple microscopic Hamiltonian having only five independent parameters. Their very successful theory is discussed below, following the more phenomenological descriptions of Thomas *et al.*, which preceded Pytte and Feder's work.

C. Theory of Thomas and Müller

Thomas and Müller have written down a phenomenological potential describing the oxygen octahedron motion in ABO_3 perovskites:

$$V(T) = \frac{1}{2}a(T)(\Phi_x^2 + \Phi_y^2 + \Phi_z^2) + \frac{1}{4}b(T)(\Phi_x^4 + \Phi_y^4 + \Phi_z^4) + \frac{1}{2}c(T)(\Phi_x^2\Phi_y^2 + \Phi_y^2\Phi_z^2 + \Phi_z^2\Phi_x^2). \qquad \text{(VI.1)}$$

Only terms through quartic are included, and the coefficients a, b, c are assumed to be slowly varying functions of T. The variables Φ_x, Φ_y, Φ_z are the amplitudes of rotationlike displacement of oxygen octahedra about the x, y, or z axes, respectively, where $x = [100]$, $y = [010]$, and $z = [001]$.

By minimizing this potential with respect to the displacements Φ_i, Thomas and Müller have shown that there exist two stable phases below T_0: a tetragonal phase if $c > b > 0$; and a rhombohedral phase if $b > c > 0$ and $b > -2c$ (c may be negative). Their phase diagram is shown in Fig. 25.

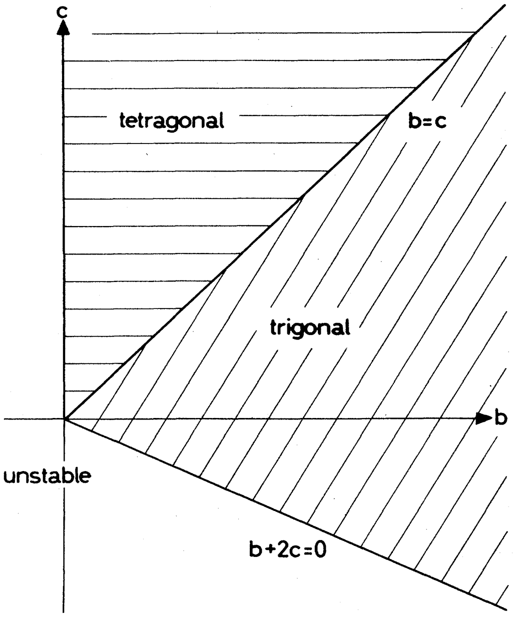

FIG. 25. $SrTiO_3$ phase diagram (Thomas and Muller, 1968).

For the tetragonal distortion, the ratio of frequency for the nondegenerate component of the soft mode (rotation of oxygens about the tetragonal axis) to that of the doubly degenerate component (rotation perpendicular to the unique axis) is given by

$$\omega_E^2(T)/\omega_A^2(T) = (c - b)/2b \qquad \text{(VI.2)}$$

and is approximately independent of T. This is confirmed experimentally (Fleury *et al.*, 1968), where the ratio in Eq. (VI.2) is approximately 0.1; thus $c \approx 1.2b$. Note in Fig 24 that this value $c \approx b$ is the instability region for the tetragonal–rhombohedral transition. Thus, under normal conditions $SrTiO_3$ is nearly unstable against the rhombohedral (or trigonal) distortion.

The transition into the trigonal phase of $SrTiO_3$ from both cubic and tetragonal structures has been accom-

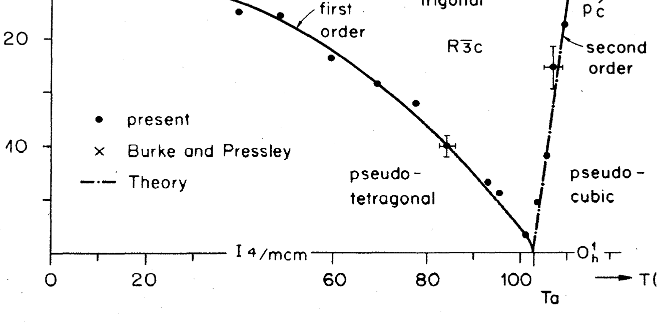

FIG. 26. $SrTiO_3$ phase diagram (Müller *et al.* 1970).

TABLE VI.2. Model parameters giving best fit to experimental results. (Appropriate factors of h have been supplied to convert all dimensions to energy.)

Model parameter		$SrTiO_3$	$LaAlO_3$
Ω_0^2	(meV^2)	202	447
$\omega_0^2(q_R)$	(meV^2)	-68	-118
J_1	(meV^3)	246	99
J_2	(meV^3)	255	285
C_1	(meV^3)	50	139

plished independently by three groups. The cubic–trigonal transition is second order, while the tetragonal–trigonal is necessarily first-order (group theoretically). These transitions can be induced by applying a few kg/mm^2 uniaxial stress along the [111] cube axes. The distortions have been measured by Burke and Pressley (1969), Burke *et al.* (1970), Wall *et al.* (1970), and Müller *et al.* (1970).

The complete *PT* phase diagram is shown in Fig. 26.

An extension of the phenomenological theory of Thomas and Müller has been given by Slonczewski and Thomas (1970). The latter work includes the effect of soft-mode interaction with elastic strain. The results are in good accord with the ultrasonic and Brillouin data (Bell and Rupprecht, 1963; Rupprecht and Winter, 1967; Kaiser and Zurek, 1966) and with the *c*/*a* data (Lytle, 1964; Alefeld, 1969).

D. Theory of Pytte and Feder

The elastic strain interactions have also been included in the microscopic theory of Feder and Pytte (1970). In the first part of their work (Pytte and Feder, 1969), a model Hamiltonian of form

$$\begin{aligned}\mathcal{H}_R = {} & \frac{1}{2}\sum \mathbf{P}(l)\cdot \underset{\approx}{\theta}^{-1}(ll')\mathbf{P}(l') \\ & + \frac{1}{2}\sum \mathbf{\Phi}(l)\cdot \underset{\approx}{k}(ll')\cdot \mathbf{\Phi}(l') \\ & + \frac{1}{2}\sum\sum J_{\lambda\lambda'}(ll')[\Phi_\lambda(l)-\Phi_\lambda(l')]^2[\Phi_{\lambda'}(l)-\Phi_{\lambda'}(l')]^2 \end{aligned} \tag{VI.3}$$

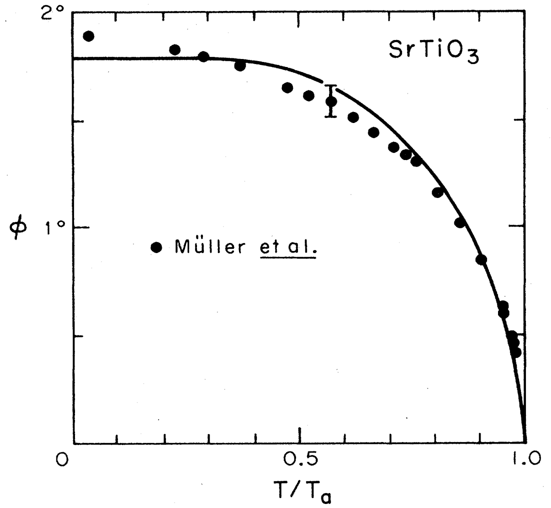

FIG. 27. φ vs T, $SrTiO_3$ (Müller *et al.* 1968).

was employed, where $\Phi_\lambda(l)$ is the amplitude of oxygen rotation about axis $\lambda = x, y$, or z, and l designates the lth unit cell; θ is an effective mass tensor; $\underset{\approx}{k}$ is a generalized spring constant; and J is an anharmonic (quartic) potential coefficient. This Hamiltonian was treated self-consistently and in the mean-field approximation by Pytte and Feder, and yielded good results in comparison with experiment. It was further expanded to include elastic strain interactions, resulting in a total of five independent parameters: ω_0^2, the soft-mode frequency in the harmonic approximation (this will be negative, corresponding to $\omega_0^2 = k/m$, where $V(X) = -kx^2 + jx^4$); Ω_0^2, the harmonic frequency for the oxygen rotation if ions in all adjacent cells were held rigid; J_1 and J_2, the anharmonic constants appearing in Eq. (VI.3); and C_1, a strain interaction term.

These five parameters are greatly overdetermined by the available data on $SrTiO_3$, and to a lesser degree, on $LaAlO_3$. Pytte and Feder's derived values are shown in Table (VI.2). The theoretically generated curves for the rotation angle $\varphi(T)$, the soft-mode frequencies $\omega(T)$, and the lattice elongation $\Delta c(T)/a$, are shown in Figs. 27–30.

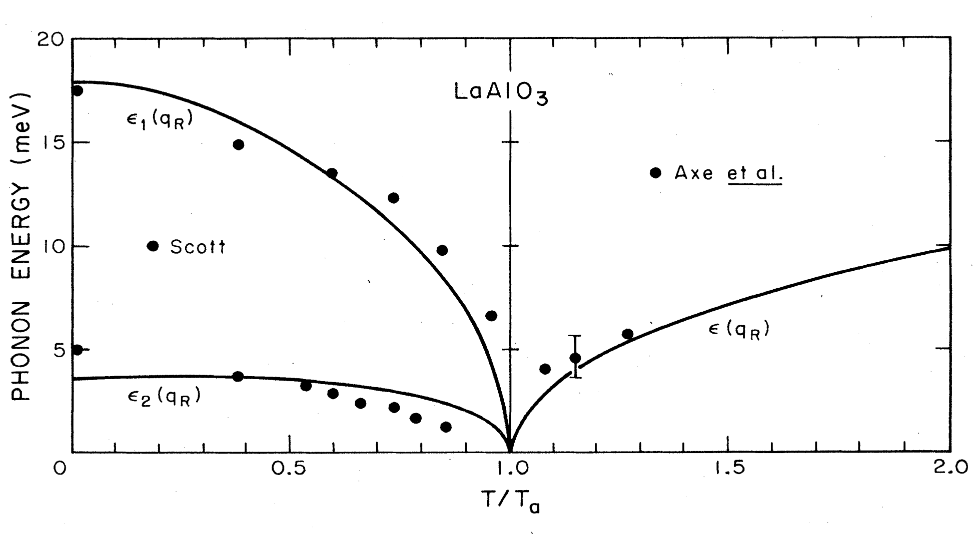

FIG. 28. ω vs T, $LaAlO_3$ (theory and experiment) (Feder and Pytte, 1970).

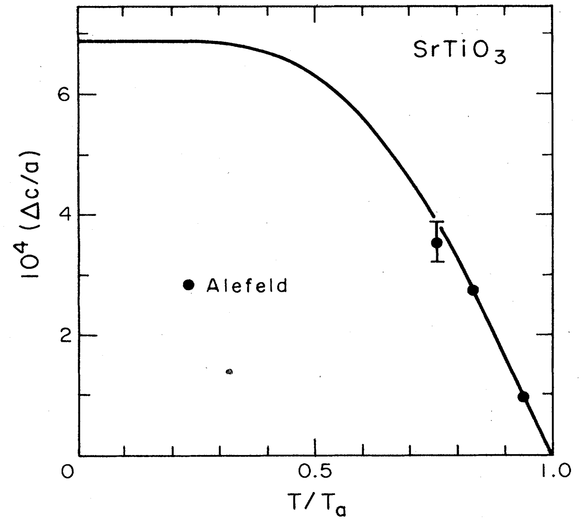

FIG. 29. Δc vs T, SrTiO$_3$ (Alefeld, 1969).

The theory successfully accounts for all aspects of the transition dynamics except the central mode and critical exponents near T_0, to be discussed below.

In addition to the EPR determination of $\varphi(T)$ in LaAlO$_3$ discussed above, NQR techniques have yielded $\varphi(T)$ independently.

Borsa (1971) and Borsa *et al.* (1971) have shown both theoretically and experimentally that the quadrupole coupling constant e^2qQ/h in LaAlO$_3$ is quadratic in the order parameter φ *below* the transition temperature T_0, where φ is a *static* oxygen octahedron rotation. This follows from a point charge calculation where the quadrupole at Al^{27} or La^{139} site due to oxygen displacements is calculated directly. The experimental results are shown in Fig. 30b. Equating the quadrupole coupling constant e^2qQ/h with $\langle\varphi^2\rangle^{1/2}$ *above* T_0, where $\langle\varphi\rangle = 0$ involves some subtleties and is discussed in the section of this review under KH$_2$PO$_4$.

E. Critical exponents—EPR studies of Müller

The first direct evidence that something was amiss with the mean-field descriptions of the SrTiO$_3$ phase transition

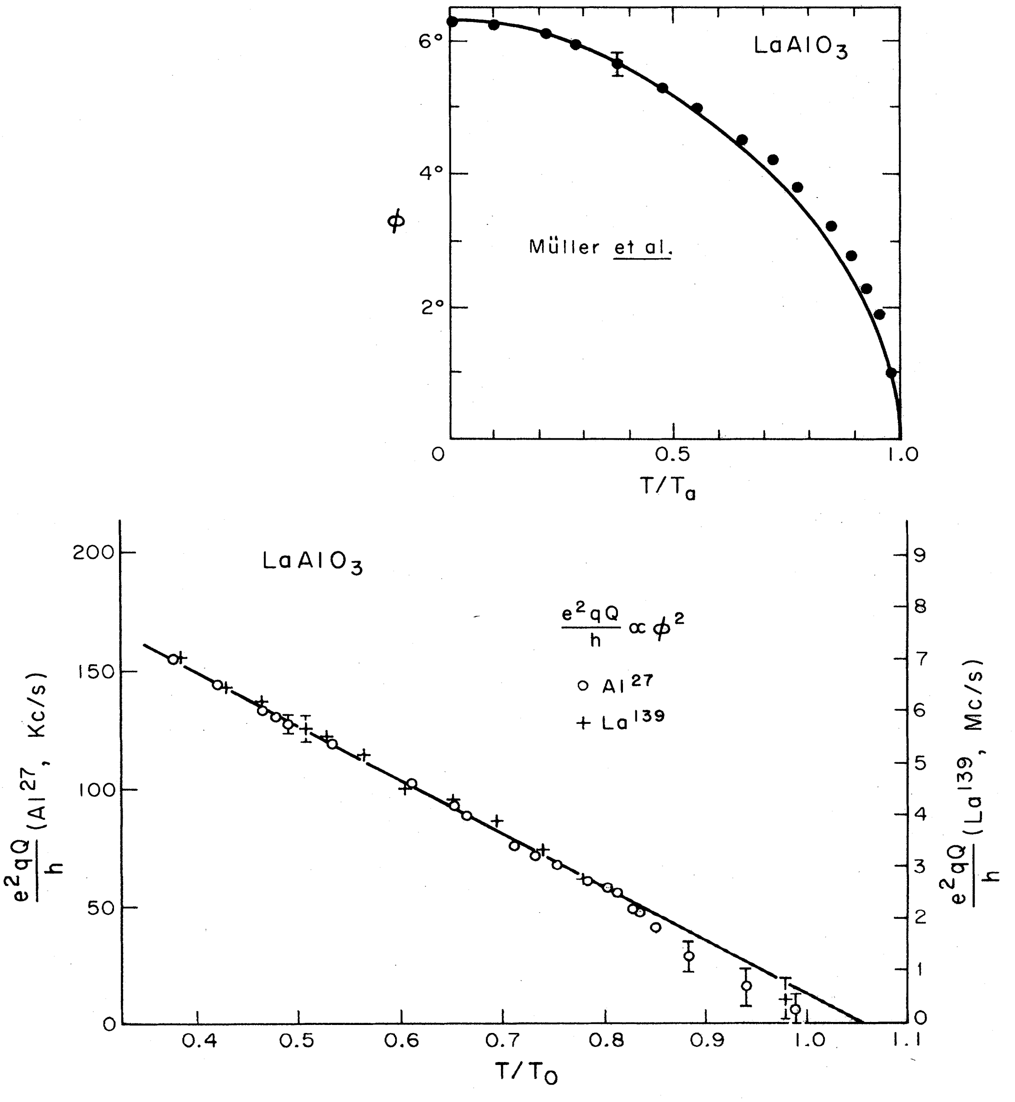

FIG. 30. (a) φ vs T, LaAlO$_3$ (Müller *et al.* 1968). (b) φ vs T, LaAlO$_3$ (Borsa, 1971).

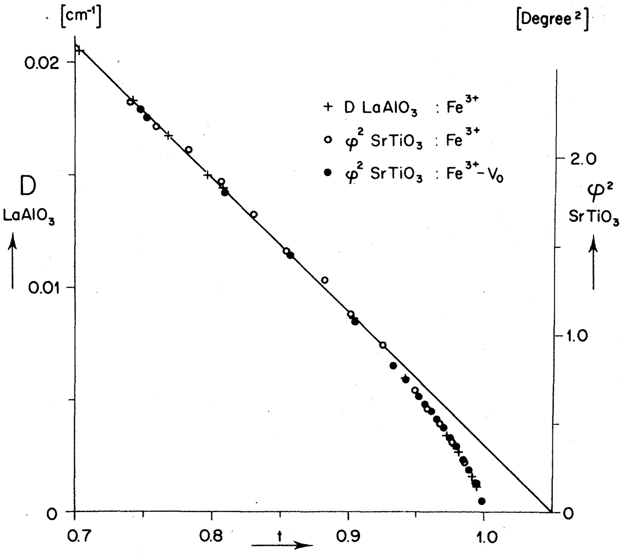

FIG. 31. $\omega = A(T_0 - T)^{1/3}$ dependence in SrTiO₃ (Müller and Berlinger, 1971).

dynamics was provided by Müller and Berlinger (1971), whose EPR data showed a continuous change from the classically predicted T dependence of the order parameter

$$\varphi(T) = A(T_0 - T)^{1/2} \tag{VI.4}$$

to a dependence

$$\varphi(T) = B(T_0 - T)^{1/3} \tag{VI.5}$$

within a temperature range $\Delta T \approx 0.1T_0$ in both SrTiO₃ and LaAlO₃. This dependence is illustrated in Fig. 31. In relating their observations to similar 1/3 exponents encountered in magnetism (Heller and Benedek, 1962, 1965) and in fluid phase transitions (Stanley, 1971), Müller and Berlinger have placed solid state phase transitions under the same "universality" framework (Kadanoff *et al.*, 1967) categorizing other phase changes. The basic physical idea embraced in this universality concept is that near T_0, when fluctuation amplitudes become very large and fluctuation coherence lengths become very long, the statistical mechanics should become independent of the exact nature of the interaction between the particles—i.e., as long as the average interaction length is much less than the coherence length, the form of the interaction is unimportant.

The divergence of fluctuations in the critical region should produce effects other than the change in exponent β discussed above. One such change is a divergence in linewidth for the EPR signal over the critical region as the inequality

$$\langle\varphi^2\rangle^{1/2} \gg \langle\varphi\rangle \tag{VI.6}$$

becomes satisfied. Müller (1971) has directly observed this broadening. A second change is in the exponent characterizing the intensity of a central mode in the Raman and neutron scattering response, to be discussed below.

F. Central modes

1. Experiments of Riste et al.

The first observation of central modes via inelastic neutron scattering was that of Riste *et al.* (1971), who reported a sharp peak at the R point in cubic SrTiO₃ (i.e. above $T_0 = 106°\mathrm{K}$) which grew in intensity as T_0 was approached from above. As discussed elsewhere in this review, specifically under the Nb₃Sn and KH₂PO₄ sections, the mere occurrence of a central mode centered at zero frequency which arises as $T \to T_0$ is not indicative of anything critical (Cowley, 1970; Cowley and Coombs, 1972). Quantitative measurements of the intensity and/or width of the central mode are required to establish deviation from the classical or molecular field theory.

2. Cowley's theory

The basic content of both Cowley's formalism (Cowley *et al.*, 1971) and that of Dorner *et al.* (1971) is that the soft-mode frequency $\omega_\infty(T)$ should decrease to a *finite* nonzero value as $T \to T_0$, while the central mode $\omega \approx 0$ response should grow. The different algebraic treatments of Cowley and of Dorner, Axe and Shirane are discussed in the KDP and Nb₃Sn sections of this paper.

Shapiro *et al.* introduce a frequency $\omega_0(T)$ which is related to the integrated intensity by the relation

$$\int_{-\infty}^{+\infty} S(\omega, q)\,d\omega = \frac{kT}{\omega_\infty^2(q,T) - \delta^2(T)} = \frac{kT}{\omega_0^2(q,T)}, \tag{VI.7}$$

where $\omega_\infty^2(T)$ is the soft-mode frequency, and δ is the matrix element for a certain anharmonic decay channel. Here ω_0 is essentially the frequency of the soft mode as measured by a low-frequency probe ($\omega \ll \delta$); whereas ω_∞ is the soft-mode frequency as measured by a high-frequency probe. The phase transition occurs when $\omega_0 = 0$, which may happen for ω_∞ and δ both finite. That this is the case in SrTiO₃ is shown in Fig. 32. Shapiro *et al.* have also determined that KMnF₃ exhibits the same behavior. In SrTiO₃ the value of δ^2 deduced experimentally at $T = T_0$ is $0.3 \pm 0.1\ (\mathrm{meV})^2$, in remarkably good agreement with Silberglitt's (1972) theoretical estimate of $\delta^2 = 0.1\ (\mathrm{meV})^2$.

Most important, Shapiro *et al.* have shown that $\omega_0(T)$ does not vary according to the $\beta = \frac{1}{2}$ prediction

$$\omega_0(T) = A(T - T_0)^\beta \tag{VI.8}$$

of mean-field theory, but exhibits $\beta = 2.0 \pm 0.5$ above T_0. This confirms directly the critical interpretation of Müller and Berlinger. Note that the value of the latter authors' β is 0.33. Thus, $\beta = 2.0 \pm 0.5$ above T_0, and 0.33 ± 0.01 below T_0. These values should be compared with those of Lazay *et al.* (1969) on NH₄Cl, whose Rayleigh intensities should be given by

$$I(T) = B|T - T_0|^{-2\beta}. \tag{VI.9}$$

Since NH₄Cl is an order–disorder system, the theoretical interpretation is basically different from that in SrTiO₃. An explanation of Lazay's exponents has been very recently given by Bartis (1973).

G. PrAlO₃, NdAlDO₃ and other perovskites

In addition to SrTiO₃ and LaAlO₃ discussed above, several other perovskites are now known to exhibit the

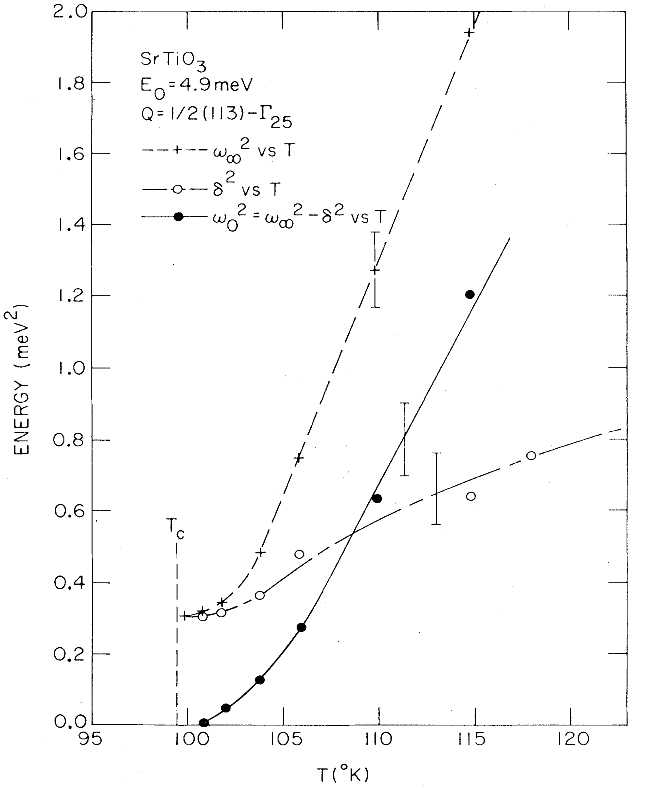

FIG. 32. ω vs T, SrTiO$_3$ showing finite ω at $T = T_0$ (Shapiro *et al.* 1972)

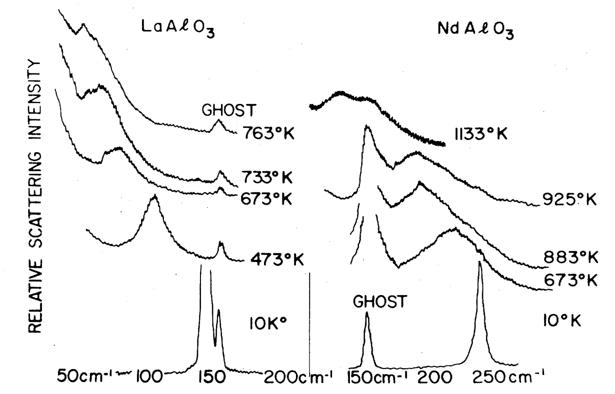

FIG. 33. Soft-mode data in LaAlO$_3$ and NdAlO$_3$ (Scott, 1969a).

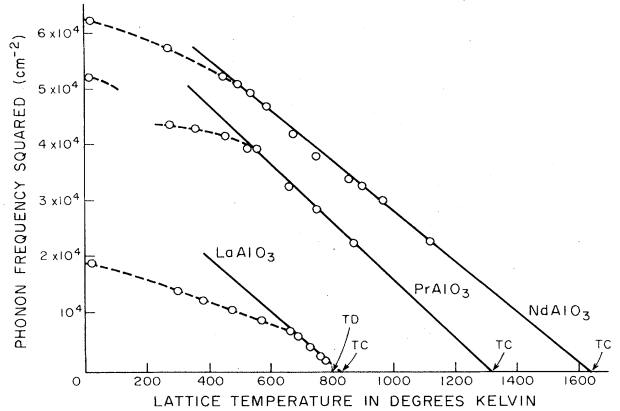

FIG. 34. ω^2 vs T in PrAlO$_3$, NdAlO$_3$, LaAlO$_3$ (Scott, 1969a). The plotted points are *peak* frequencies ω_p. Correction for damping $\omega_0^2 = \omega_p^2 + (\Gamma^2/2)$ gives higher frequencies ω_0 and leads to extrapolation transition temperatures about 200° K higher in PrAlO$_3$ and NdAlO$_3$. See Geller and Racah, 1970.

same structural phase transitions. Scott (1969) has shown that PrAlO$_3$ and NdAlO$_3$ exhibit the same soft-mode behavior as does LaAlO$_3$, with extrapolated transition temperatures high, but below the melting point. Typical data are illustrated in Fig. 33, and in Fig. 34 the T_0 values are estimated from the $\omega^2(T)$ linear extrapolation (mean field or Curie-Weiss theory). The plots in Fig 34 contain a small systematic error: whereas the peak frequencies ω_m are plotted vs T, the correct representation is to plot the harmonic frequency

$$\omega_0^2 = \omega_m^2(T) + (\Gamma^2(T)/2) \qquad \text{(VI.10)}$$

(Γ is the linewidth) vs T. This yields extrapolated T_0 values about 300°K higher than shown in Fig. 34, and in good accord with the value directly measured in PrAlO$_3$ via thermal techniques (Geller and Racah, 1970).

SmAlO$_3$ also manifests some soft-mode instabilities, but unlike PrAlO$_3$ and NdAlO$_3$ discussed above, the extrapolated transition temperature is above the known melting point (Scott and Remeika, 1969). This work on SmAlO$_3$ discussed one important idea explicitly: that the transition temperature in LaAlO$_3$, PrAlO$_3$, NdAlO$_3$, and SmAlO$_3$ varies inversely and monotonically with the radius of the rare-earth ion (which decreases as the inner shell is filled). Physically, the large radius La ion most effectively stabilizes the lattice, so that the cubic structure is obtained at a lower temperature. For Pr, Nd, or Sm, a higher temperature is required for them to have the same effective radius—consisting of r_0 plus the thermal rms displacement due to phonons. This picture of transition temperatures relating directly to ionic size was considered a long time ago for the SrTiO$_3$, BaTiO$_3$, PbTiO$_3$ series, but it is perhaps best applied to the rare-earth aluminates; in Pr, Nd, and Sm only the ionic radius changes appreciably, whereas in Sr, Ba, and Pb the masses and force constants also change appreciably.

As discussed above, the decrease in size of the A ion of an ABO$_3$ perovskite increases the instability of the cubic structure. This instability reaches the ultimate in WO$_3$, where the A ion is completely missing. The WO$_3$ structure *is* extremely unstable, as predicted from these considerations, and exhibits five different phases. The highest temperature phase is tetragonal, with two formula groups per unit cell. The lowest temperature phase is ferroelectric; and the transition to this phase is first order. A broad, temperature-dependent feature was reported in the WO$_3$ Raman spectra by Scott (1969), but no quantitative or detailed work has been published.

KMnF$_3$ is now known from inelastic neutron studies to be isomorphic to tetragonal SrTiO$_3$ ($I\ 4/mcm$) at temperatures below T_0 = 186°K (Minkiewicz *et al.*, 1970). The soft mode is overdamped. Earlier work by the same authors (Minkiewicz and Shirane, 1969) erroneously concluded that the zone-boundary phonon instability was compatible with *Pbnm* orthoferrite structure.

In addition to the inelastic neutron studies of Minkiewicz *et al.*, Raman studies of $KMnF_3$ soft modes below $T_0 = 186°K$ have been published by Eremenko *et al.* (1971).

VII. IMPROPER FERROELECTRICS

By the term "improper ferroelectric" we shall refer to any crystal which exhibits hysteresis in its E–D relationship below a structural transition temperature T_0, and for which the spontaneous polarization is *not* the order parameter characterizing the phase transition at T_0.

A. $Gd_2(MoO_4)_3$ experiments

Gadolinium molybdate $Gd_2(MoO_4)_3$ is an excellent example of such a system. Ferroelectricity in this material was discovered by Borchardt and Bierstedt (1967). At low ($< 159°C$) temperatures the spontaneous polarization is 2×10^{-3} C/m² (this is a very small value). In this ferroelectric β phase the crystal structure is orthorhombic, with space group $Pba2$ (Jeitschko, 1970), or C_{2v}^{8} The orientations of the MoO_4-tetrahedra are shown in Fig. 35. There are three nonequivalent MoO_4 orientations: one with apex along the crystallographic $+c$ axis; one along $-c$; and one with tetrahedron $\bar{4}$ axis along c.

As $T_0 = 159°C$ is approached from below, the MoO_4 tetrahedra rotate to a configuration midway between the two domain structures shown as solid and dotted lines in Figure 35. Above T_0 the structure is tetragonal, with space group $P\bar{4}2m$ (or D_{2d}^{3}). As Keve, Abrahams *et al.* have shown (1970, 1971, 1972) via a point charge calculation, the spontaneous polarization is entirely due to the MoO_4 ion rearrangement; the Gd^{3+} ions play no essential role.

The anomalous nature of the ferroelectric transition in this crystal was first pointed out by Cross *et al.* (1968), who measured the clamped and unclamped dielectric constants as functions of temperature near T_0. Their results are shown in Figure 36. It can be seen that the clamped dielectric constant ϵ_{33}^{X} is small and independent of temperature, whereas the unclamped constant ϵ_{33}^{x} exhibits a small, discontinuous anomaly at $T = T_0$. In contrast, ferroelectrics usually show large increases in both ϵ^{x} and ϵ^{X} at T_0. Of special interest is the T-dependence of the elastic constant $C_{66}(T)$, shown in the bottom curve of Figure 36. It decreases slowly and continuously as $T \rightarrow T_0$ from above. This behavior is identical to that exhibited by $SrTiO_3$ near $T_0 = 106°K$ and can be understood in the latter case as follows: Above T_0 there is a $q \neq 0$ soft optice mode at the Brillouin zone boundary, and no coupling with $q = 0$ acoustic phonons is operative; at $T = T_0$ the soft optic mode becomes $q = 0$ by virtue of the additional reciprocal lattice points created by cell-doubling phase transitions, i.e.,

$$q = \frac{\pi}{a'} \rightarrow q = \frac{\pi}{a/2} = \frac{2\pi}{a} \equiv 0 \qquad \text{(VII.1)}$$

This "new" $q = 0$ low-frequency optic mode depresses the acoustic phonon frequency (and thus lowers C_{66}) at T_0. Below T_0, the optic mode frequency increases again, and the acoustic phonon renormalities to approximately its $T > T_0$ value.

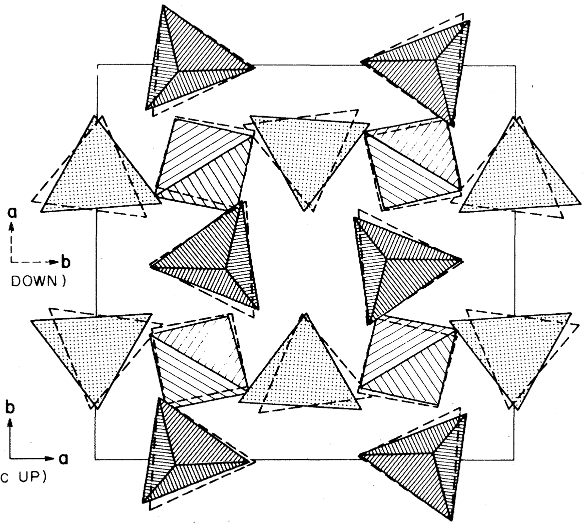

FIG. 35. Structure of $(MoO_4)^{=}$ ions in $Gd_2(MoO_4)_3$, after Abrahams (1972).

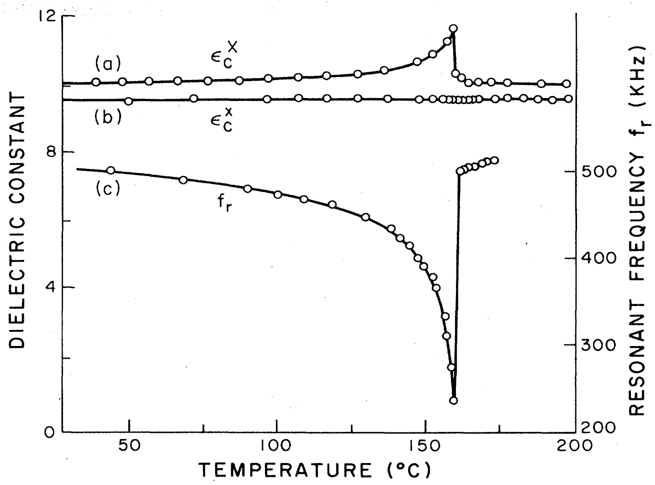

FIG. 36. $C_{66}(T)$ in $Gd_2(MoO_4)_3$, (Cross *et al.*, 1968).

B. Pytte's theory

This picture is completely compatible with all the information we have presently about $Gd_2(MoO_4)_3$ and isomorphic $Tb_2(MoO_4)_3$. The unit cell *does* double at T_0 (Dorner et al., 1972). However, earlier x-ray studies were very unclear on this point; Kvapil and John (1970) inferred a doubling along c, whereas Drobyshev et al. (1969) deduced a doubling of both a and b lattice parameters at T_0. Part of the confusion arises from the failure of x-ray crystallographers to specify *primitive* cell parameters. Fortunately, Pytte (1970) was able to interpret correctly the $Gd_2(MoO_4)_3$ situation and to explain, at least qualitatively, its dynamics even before the Brookhaven neutron studies of the soft optic mode at the Brillouin zone boundary were mlde. Independently, Levanyuk and Sannikov (1970) and Aizu (1970) arrived at the same conclusions as Pytte.

C. Experiments on $Tb_2(MoO_4)_3$ experiments

The work at Brookhaven (Axe *et al.* 1971; Dorner *et al.*, 1972) confirmed Pytte's hypothesis of a soft zone-boundary phonon. It further showed that this mode at critical point $\eta = (\pi/a)(1,1,0)$ had temperature dependence which obeyed Curie–Weiss law

$$\omega_M^2 = A(T - T_c), \qquad \text{(VII.2)}$$

with $T_c = 149°\mathrm{C}$, about 10°K less than the transition temperature T_0. This behavior is shown in Fig. 37.

This $q \cong \pi/a$ soft-mode description provided for $Gd_2(MoO_4)_3$ by Pytte (1970) explicitly pointed out why the spontaneous polarization, lattice distortion and birefringence (Smith and Burns, 1969; Cummins, 1970) behaved almost continuously through T_0 (not quite continuously; the transition is first-order), whereas the variation of $C_{66}^E(T)$ was very discontinuous. Pytte's theory of strain coupling has been extended by Dorner *et al.* (1972), to which interested readers are referred.

Pytte writes for the interaction Hamiltonian describing $q = (\pi/a)(1,1,0)$ soft optic mode and $q = 0$ acoustic mode (i.e. elastic strain),

$$\mathcal{H}_{Re} = \sum G_{ii} e_{ii} R^2 + \sum_{i \geq j} g_{1ij} e_{ii} e_{jj} R^2, \qquad \text{(VII.3)}$$

where e_{ij} are the strains; R is the optic mode order parameter [proportional to $\omega_M(T)$]; and G_{1i}, g_{1ij} are temperature-independent constants. The coupling of polarization to strain and soft optic modes may be written as

$$\mathcal{H}_{pe} = \tfrac{1}{2} a P_3^2 + d_{13}(e_{11} - e_{22})_{P_3} + b_{113} P_3 R^2 + d_{133}(e_{11} + e_{22}) P_3^2 + d_{333} e_{33} P_3^2, \qquad \text{(VII.4)}$$

where P_3 is the polarization.

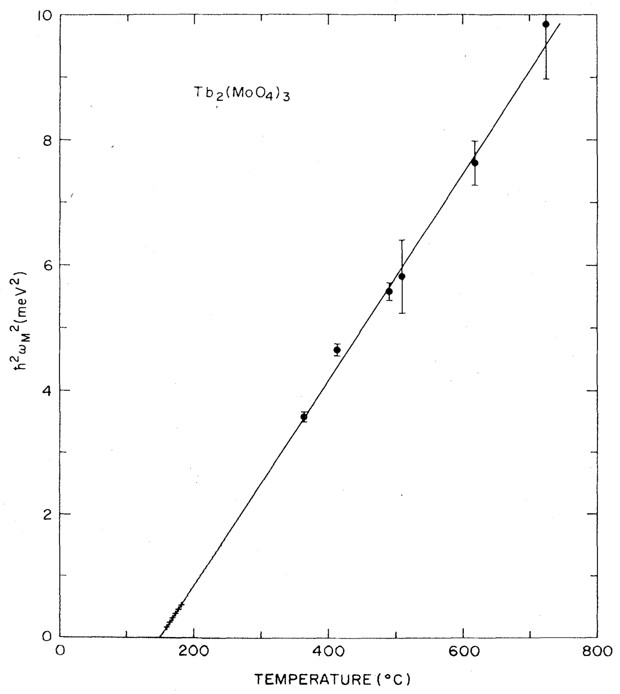

FIG. 37. ω vs T for soft mode in $Tb_2(MoO_4)_3$ (Dorner *et al.*, (1972).

When we minimize the energy specified in Eq. (VII.4) with respect to P_3, we obtain

$$P_3 = b_{113} R^2 + \text{const.} \qquad \text{(VII.5)}$$

which shows that the spontaneous polarization will vary as the *square* of the order parameter R. Thus, if R varies as $(T_0 - T)^{1/2}$, P_3 will vary as $(T_0 - T)$.

Similarly, by minimizing the energies specified in Eq (VII.3,4) with respect to the e_{ii}, Pytte shows that the change in elastic coefficient $\Delta C_{66}(T)$ is given (for $T < T_0$) by

$$\Delta C_{66}(T) = A + BR^2, \qquad \text{(VII.6)}$$

where A and B are constants independent of temperature. This temperature dependence is in good accord with that given in Fig. 36 if $R(T)$ is assumed to vary approximately as $(T_0 - T)^{1/2}$ near T_0 and $R(T) \sim$ constant at very low temperatures.

D. Description by Cochran and Dvorak

A similar free-energy description has been given by Cochran (1971) [and independently by Dvorak (1971)]who writes

$$F = \tfrac{1}{2} A_1 \eta_1^2 + \tfrac{1}{4} C_1 \eta_1^4 + \tfrac{1}{2} A_2 \eta_2^2 + H \eta_1^2 \eta_2, \qquad \text{(VII.7)}$$

where η_1 is the order parameter related to the soft zone-boundary optic mode, and η_2 is the polarization. As in simpler phase transitions, the mean-field approximation $A_1 = a(T - T_0)$ is assumed; other coefficients are independent of temperature. Minimizing F with respect to η_2 yields

$$0 = \partial F/\partial \eta_2 = A_2 \eta_2 + H \eta_1^2 = 0 \qquad \text{(VII.8)}$$

$$\text{or} \quad \eta_2 = -(H/A_2)\eta_1^2 \qquad \text{(VII.9)}$$

Whence, substituting back in (VII.7),

$$F = \tfrac{1}{2} A_1 \eta_1^2 + [\tfrac{1}{4} C_1 - \tfrac{1}{2}(H^2/A_2)]\eta_1^4. \qquad \text{(VII.10)}$$

Then, minimizing F with respect to η_1, we find

$$0 = \partial F/\partial \eta_1 = A_1 \eta_1 + [C_1 - (2H^2/A_2)]\eta_1^3 \qquad \text{(VII.11)}$$

$$\text{or } A_1 = [(2H^2/A_2) - C_1]\eta_1^2 \qquad \text{(VII.12)}$$

which leads to a second-order phase transition at T_0 if $2H^2 > C_1 A_2$. For this case, η_1 varies as $(T - T_0)^{\frac{1}{2}}$, and η_2, the polarization, varies as $(T - T_0)$, just as obtained by Pytte.

Cochran (1971) applies this kind of free-energy analysis to a very simple prototype system He considers a hypothetical zincblende structure with the c axis elongated, as diagrammed in Fig. 38, and supposes that there is an instability in a transverse mode at the zone boundary along c (as diagrammed). For the mode considered at $q = 2\pi/c$ only one type of atom moves. We may therefore specify the order parameter as η_x for displacement of the sublattice along x. Let us further denote the spontaneous polarization along the c axis as P_3. Then we may rewrite the free energy of Eq. (VII.7) as

$$F = \tfrac{1}{2} A(\eta_x^2 + \eta_y^2) + \tfrac{1}{4} C(\eta_x^4 + \eta_y^4) + \tfrac{1}{2} E \eta_x^2 \eta_y^2 + \tfrac{1}{2} A_0 P_3^2 + J P_3 \eta_x \eta_y, \qquad \text{(VII.13)}$$

where terms of form $J P_3 \eta_x^2$ and $J P_3 \eta_y^2$ have been dropped

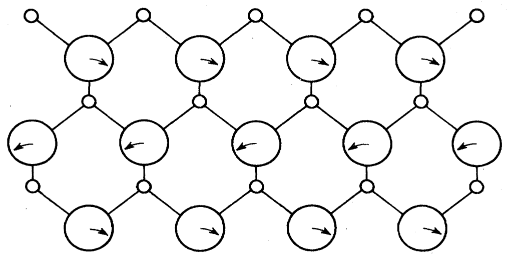

FIG. 38. Two-dimensional model illustrating $Gd_2(MoO_4)_3$-type phase transition (Cochran, 1971). The structure of ZnS projected on a [110] plane. When atoms of one type have displacements appropriate to a transverse mode with wave vector at the Brillouin zone boundary in the c direction, as shown by the arrows, anharmonic forces result in a secondary displacement of those atoms along $-c$, as indicated by the curvature of the arrows. If, however, the primary displacements were out of the plane of the diagram, and thus appropriate to a transverse mode degenerate in frequency with that already mentioned, the 'secondary' or induced displacements would be along $+c$. That is, change of direction of antipolarization by $\pi/2$ reverses the direction of induced polarization.

in going from Eq. (VII.7) to (VII.13). The stability requirement $\partial F/\partial P_3$ yields

$$P_3 = -\frac{J}{A_0}\eta_x\eta_y, \tag{VII.14}$$

and substituting back in (VII.13), we obtain

$$F = \tfrac{1}{2}A(\eta_x^2 + \eta_y^2) + \tfrac{1}{4}C(\eta_x^4 + \eta_y^4) + \tfrac{1}{2}[E - (J^2/A_0)]\eta_x^2\eta_y^2. \tag{VII.15}$$

This free energy can produce two kinds of second-order phase transitions: one in which $\eta_x = 0$, $\eta_y \neq 0$ (or vice versa); the second in which $\eta_x = \pm\eta_y \neq 0$. Which case actually occurs depends upon whether $[E - (J^2/A_0)]$ is greater than C or less than C. If J is small, then $\eta_x = \pm\eta_y \neq 0$ is obtained, and from Eq. (VII 14), this produces a ferroelectric state with $P_3 \neq 0$. This is the case in $Gd_2(MoO_4)_3$ or $Tb_2(MoO_4)_3$. These crystals are actually more complicated (Cochran, 1971) than discussed here, because the coupling of η_x, η_y and P_3 is not direct via $\eta_x\eta_y P_3$ terms in the free energy, but indirect via $\eta_x\eta_y\eta_s$ and $P_3\eta_s$ terms, where η_s is a shear strain—see Pytte (1971) and Dorner *et al.* (1972). This is shown in Eq. (VII.4) of this review.

$NH_4H_2PO_4$ (ADP) is an equally interesting case in which the theory of Eq. (VII.13)–(VII.15) applies. In ADP, however, $E - (J^2/A_0) < C$ and the stable state below T_0 is $\eta_x = 0$, $\eta_y \neq 0$, which (from Eq. VII.14) yields $P_3 = 0$. Thus, the antiferroelectric phase of ADP is not also ferroelectric.

Several aspects of the $Gd_2(MoO_4)_3$ phase transition are not yet understood. The soft mode has not been identified by neutron, infrared, or Raman spectroscopy in the ferroelectric phase. And the anomalous broadening of a 40 cm^{-1} optical phonon in the paraelectric phase analyzed by Raman spectroscopy (Fleury, 1970) is a complete mystery, since this mode can play no possible direct role in the transition dynamics. (Fleury's inferences to the contrary were based on a mistaken notion that the x-ray data showed no cell doubling at T_0.) Dorner *et al.* have shown that the soft mode is overdamped within ~200°K above T_0; if this condition also exists below T_0, it may have hindered Raman or ir (Petzelt, 1971; Petzelt and Dvorak, 1971) attempts to characterize the soft mode.

In closing this section, we stress again that the "antiferroelectric" phase transitions in $NH_4H_2PO_4$ (ADP) and $SrTiO_3$ are extremely similar to that of the $Gd_2(MoO_4)_3$ family. Note that antiferroelectricity and ferroelectricity are not mutually exclusive by our definitions: we would characterize $Gd_2(MoO_4)_3$ at ambient temperatures as exhibiting both properties. The family of ferroelectrics $BaMF_4$, where M is a divalent transition metal, is also similar to $Gd_2(MoO_4)_3$ in some respects. Ferroelectricity is produced by a displacement of Ba ions, according to a point-charge model of Keve *et al.* (1970); but the primary order parameter is probably the angle of rotation of MF_6 octahedra, as shown by the x-ray studies of the same authors. The dielectric constants and spontaneous polarizations of this class of crystals have been published by DiDomenico *et al.* (1969), but no phonon measurements of any kind have yet been reported. Raman studies in our laboratory are in progress. We have observed in work not yet published that $BaMnF_4$ has a cell-doubling (antiferrodistortive) phase transition at 255°K. We have measured the soft zone-boundary phonons in the low-temperature phase, where they become $q = 0$, and find that the soft mode is underdamped below 207°K, and overdamped between 207 and 225°K. This proof of cell doubling in $BaMF_4$ structures demonstrates the analogy with $Gd_2(MoO_4)_3$.

VIII. CHAIN-STRUCTURE V-VI-VII SEMICONDUCTORS

Chain-structure V-VI-VII semiconductors have been of considerable technological interest for the last several years. They are photoconductors with abnormally large temperature coefficients for their bandgaps; they are strongly piezoelectric; at least some are ferroelectric; and they have anomalous electrooptic and optomechanical properties—elongating or contracting under illumination. Thus far, SbSBr, SbSI, SbSeBr, SbSeI, SbTeI, BiSI, and BiSCl have all been studied as photoconductors, but only SbSI has received much attention from the standpoint of phase transitions. SbSI is the first known ferroelectric photoconductor.

A. SbSI

SbSI grows in needlelike crystals having space group D_{2h}^{16} (or *Pnam*) in the paraelectric phase, and C_{2v}^{9} or ($Pna2_1$) in the ferroelectric phase. The transition occurs at about 22°C and is first order (Arndt and Niggli, 1964; Kikuchi *et al.*, 1967; Takama and Mitsui, 1967). Fig. 39 illustrates the chainlike structure in SbSI and its isomorphs, and Fig. 40 shows the tilting distortion which occurs at $T_0 = 295°K$; the S- and Sb- ions are displaced slightly from the paraelectric position equidistant from the iodine ions. Figures 41 and 42 are plots of the spontaneous polarization and static dielectric constant versus temperature in SbSI (Fatuzzo *et al.*, 1962). It is expected from the Lyddane–Sachs–Teller relation that some polar TO phonon has frequency with temperature dependence $\omega_{TO}^2(T)\alpha\epsilon_0^{-1}(T)$. However, the initial two ir measurements on SbSI by Blinc *et al.* (1968) did not reveal such a mode. The primary contribution of the work by Blinc and co-workers was the group theoretical

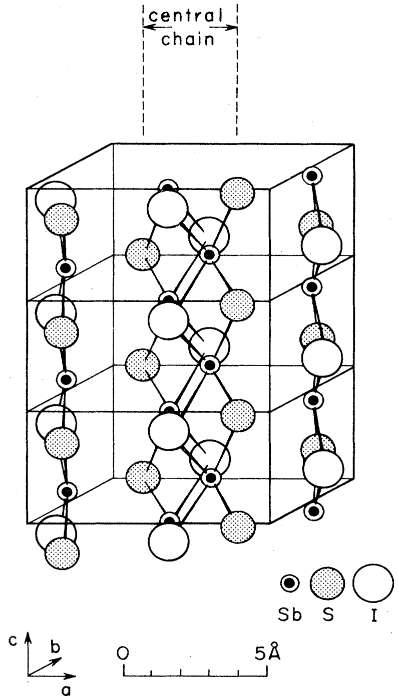

FIG. 39. SbSI structure (after Arndt and Niggli, 1964).

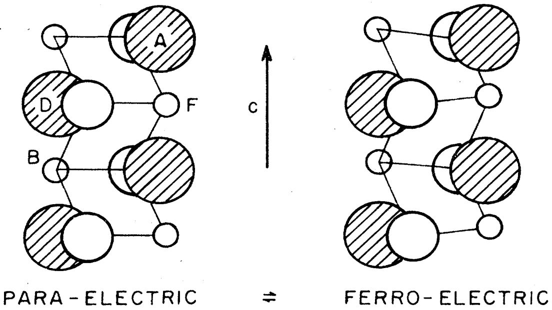

FIG. 40. SbSI structure and distortion below T_c (C. F. Drake and I. F. Scanlon, 1970).

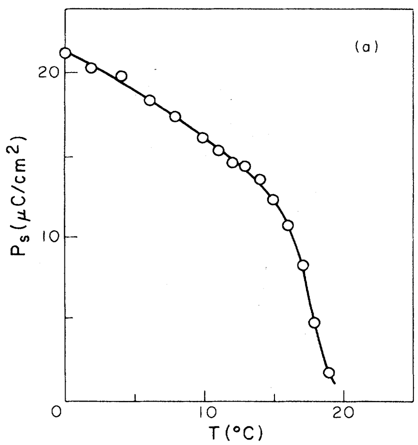

FIG. 41. Spontaneous polarization vs T in SbSI (Fatuzzo *et al.*, 1962).

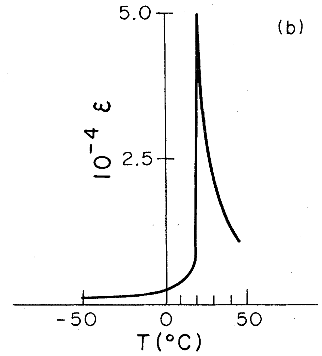

FIG. 42. Dielectric constant vs T in SbSI (Fatuzzo *et al.*, 1962).

description of SbSI phonon modes using a simplified unit cell. Taking advantage of the chainlike covalent structure in this lattice, they assumed interchain force constants to be very small and treated a simplified unit cell having half the atoms of the real primitive cell. The group theory was further simplified by assuming force constants to be approximately isotropic in the plane perpendicular to the chain. This lattice dynamical description is in good accord with experimental measurements of mode symmetries. It explicitly explains accidental degeneracies of even and odd parity modes in the paraelectric phase.

1. Raman and ir measurements

The breakthrough in understanding the dynamics of the ferroelectric phase transition of SbSI was afforded by the infrared studies of Petzelt (1969) in the paraelectric phase, and the Raman studies of Perry and Agrawal (1970) in the ferroelectric phase. Their results for $\omega_{\mathrm{TO}}(T)$ are shown in Fig. 43. Note that $\omega(T)$ does not extrapolate to zero at $T_0 = 22$°C, since the transition is first order.

The interaction of the soft mode with other optical phonon branches at temperatures far below T_0 has been described by Steigmeier *et al.* (1970) and by Balkanski *et al.* (1971). These mode couplings, while interesting in themselves, do not significantly affect the transition dynamics and will not be discussed further here.

2. Mode coupling and anamolous experiments

It is of interest that Steigmeier *et al.* report a temperature dependence of $\omega(T) = A(T_0 - T)^{1/3}$ for this crystal. This result is of some import. However, the determination of such an exponent for SbSI is slightly uncertain for several reasons. First, the transition is first order, with T_c obtained by extrapolating $P_s(T)$ to zero about 5°C above T_0 (Fatuzzo *et al.*, 1962); and it is T_c, not T_0, which should appear in frequency expressions $\omega(T) = A(T_c - T)^{\beta}$ for first-order transitions. Second, the transition temperature

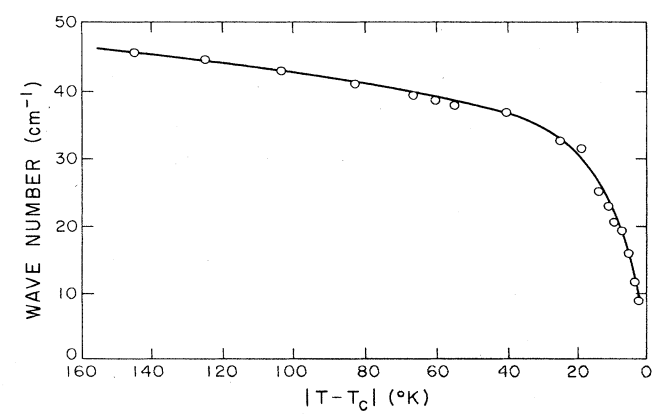

FIG. 43. Soft mode ω vs T in SbSI (Perry and Agrawal, 1970).

T_0 is itself sample dependent, varying from 20–25°C; third, there are *several* mode couplings between the soft mode and other optical phonons (Balkanski *et al.*, 1971). The net result is that it is almost impossible to measure the temperature dependence of the *uncoupled* soft mode over the several decades of $(T_c - T)/T_c$ required to determine an exponent β in the expression $\omega(T) = \omega_0(T_C - T)^{\beta}$. If we assume, however, that the value of $\beta = 1/3$ quoted by Harbeke *et al.* (1970) is correct, we can give the mean field theory of Banda *et al.* (1973), discussed in Sec. IV, as a very probable explanation. Thus, critical phenomena in SbSI have not been demonstrated, either by the occurrence of 1/3 exponents, or by the report of a central mode in this crystal by Steigmeier *et al.* Such a central mode is compatible with Cowley's mean field theory (1967) of weakly anharmonic crystals, as summarized in Sec. I.

B. SbSBr

SbSBr is also a ferroelectric. (Ferroelectric properties of other V-VI-VII's are discussed by Nitsche *et al.*, 1964.) Very recently Furman *et al.* (1973) reported soft modes in SbSBr and in $SbSBr_xI_{1-x}$ alloys. They find the same 1/3 exponent for the soft-mode temperature dependence as in SbSI, and determine a value of 39 ± 2°K for T_0.

C. BiSI

BiSI is ferroelectric with $T_c = 113$°K. An underdamped soft mode has been characterized by the ir studies Siapkas (1973).

IX. HYDROGEN-BONDED FERROELECTRICS

Hydrogen-bonded ferroelectrics have attracted an enormous amount of interest, both theoretical and experimental, over the last twenty years. From an experimental standpoint the reasons are practical: Such crystals are easy to grow from aqueous solution; they come as large single crystals of high optical quality; and they yield useful technological devices, such as high-speed electrooptic modulators. The theoretical interest is twofold: First, hydrogen-bonded ferroelectrics such as Rochelle Salt and KH_2PO_4 (KDP) have been known for a long time, so that theoretical work in the early days of ferroelectricity was effectively limited to such crystals; second, it is clear from the large effect deuteration has on the Curie temperature of KDP-structure crystals, that the occurrence of ferroelectricity is associated in large degree with proton tunneling and hydrogen bonding in these lattices. Since the proton displacements at T_0 in KDP are nearly perpendicular to the spontaneous polarization which develops at T_0, it is clear that some complicated coupling between the protons and the heavy ions must exist. The proton behavior in KDP-structure ferroelectrics has been treated via a pseudospin theory over the past several decades. This approach began with Slater (1941), Blinc (1960), DeGennes (1963), and Brout *et al.* (1966), and rests upon the physical idea that there are two equivalent positions on each O–H–O hydrogen bond; the left and right sides of the bond may be described by fictitious spin $+\frac{1}{2}$ and $-\frac{1}{2}$ states. This pseudospin formalism has been a prime source of theoretical interest in itself; it permits rather more elegant mathematics than do, say, free-energy treatments of ferroelectricity. Readers are referred to the work of Tokunaga (1966) and Tokunaga and Matusubara (1966) for a survey of the pseudospin approach to ferroelectricity. Kobayashi (1968) was the first theoretician to really come to grips with the problem of coupling the protons and heavy metal ions; his paper thus involves coupling the pseudospin formalism to the vibrational Hamiltonian.

One problem associated with the pseudospin formalism is that it has afforded almost no contact with experimental measurements or dynamical measurements of hydrogen-bonded ferroelectrics near the Curie temperatures, most of which are more easily explained by means of simpler "soft-mode" descriptions. Part of the problem, as emphasized recently by Reese, Cummins *et al.* (1973), is that explicit assumptions of well defined pseudospin waves are contained in the theories of Kobayashi *et al.* Such approximations are valid only at very low temperatures, whereas most experimental data are obtained near T_0, where the spin behavior is best characterized as diffusion, not as undamped spin waves.

It is not our intent here to review the theories relating to ferroelectricity in hydrogen-bonded systems. This has already been done in an excellent review by Cochran (1969). We attempt below only to summarize the experimental results, with appropriate emphasis upon recent analyses. Since the bulk of experimental studies on hydrogen-bonded ferroelectrics concerns KH_2PO_4 and its isomorphs, our discussion primarily involves KDP. Some less extensive work of high quality has also been published on triglycine sulfate (TGS) and is also included. Other work on systems such as thiourea, an organic ferroelectric, are mentioned briefly.

A. KH_2PO_4 and isomorphs

Above $T_0 = 122$°K, KH_2PO_4 crystallizes in the tetragonal point group $\bar{4}2m$. The protons are disordered, randomly occupying sites on either side of the O–H—O hydrogen bonds linking PO_4 tetrahedra. This structure and especially the proton positions are known from the neutron and x-ray studies of Bacon and Pease (1953, 1955) and Fraser and Pepinsky (1953).

Their work showed that the protons were randomly distributed on either side of the O–H—O bond and were *not* centered exactly between the oxygens (except in a statistical sense). This was the first direct information that the ferroelectric phase transition in KDP was of the order–disorder type. Such conclusions have been independently verified by NQR measurements in this class of crystal; Blinc (1971) has given a review of NMR work on the subject.

Whereas the protons (or deuterons) in ferroelectrics of the KDP class undergo an order–disorder transition at T_0, the metal ions undergo a displacive transition from one ordered arrangement to another. The ionic displacements at T_0 (i.e., the eigenvector of the soft mode) in KH_2PO_4 are shown in Fig. 44, based on a proposal of Cochran (1960, 1961). Detailed neutron studies by Paul *et al.* (1970) and Skalyo *et al.* (1970) have confirmed the essential details of Fig. 44.

1. Raman studies

A major breakthrough in understanding the dynamical behavior of KDP near T_0 came with the Raman study of

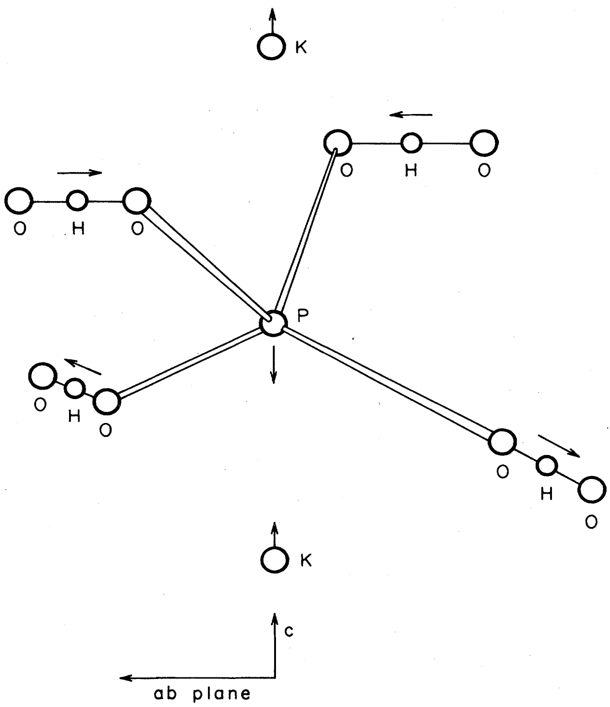

FIG. 44. Eigenvector, KDP (Cochran, 1961).

Kaminow and Damen (1968), who found an intense, overdamped, temperature-dependent response in the low-frequency B_2 symmetry spectra. Their spectra are shown in Fig. 45. Kaminow and Damen were able to fit their observed spectral line shapes to a damped harmonic oscillator model, i.e.,

$$S(\omega) = A\frac{KT}{\hbar\omega}\chi''(\omega),$$
$$S(\omega) = A\left(\frac{KT}{\hbar\omega}\right)\frac{\omega_0^2\Gamma\omega}{(\omega_0^2-\omega^2)^2+(\Gamma\omega)^2}, \tag{IX.1}$$

where $\chi(\omega) = \omega_0^2(\omega_0^2 - \omega^2 + i\Gamma\omega)^{-1}$.

The undamped frequency ω_0 was found by Kaminow and Damen to vary as

$$\omega_0 = A[(T - T)_0/T]^{1/2}, \tag{IX.2}$$

whereas Γ was essentially independent of T. Subsequently, Katiyar *et al.* (1971) and She *et al.* (1972) were able to show that the temperature dependence given in Eq. (IX.2) was not correct. The error arose in neglecting very strong mode coupling between the soft mode and the optic phonon of the same symmetry lying at 180 cm^{-1} in KH_2PO_4 (145 cm^{-1} in KH_2AsO_4; 96 cm^{-1} in CsH_2AsO_4). As in the case of $AlPO_4$, discussed in an earlier section, a coupled mode formalism was employed with Green function

$$G_{ij}^{-1} = \begin{bmatrix} \omega_1^2 - \omega^2 + i\Gamma_1\omega & \Delta^2 + i\Gamma_{12}\omega \\ \Delta^2 + i\Gamma_{12}\omega & \omega_2^2 - \omega^2 + i\Gamma_2\omega \end{bmatrix}. \tag{IX.3}$$

As Barker and Hopfield pointed out several years earlier, any ir or Raman spectrum of two coupled modes may be fitted *exactly* by such a mode coupling scheme with *either* a real off-diagonal matrix element Δ^2 *or* an imaginary (dashpot) coupling constant $i\Gamma_{12}\omega$. In general, therefore, there are an infinite number of *mathematically* correct descriptions of a coupled mode spectrum. However, the physically correct description can be chosen on the basis of heuristic criteria. For example, by fitting observed line shape data at many temperatures (or pressures, or electric fields, etc.) and requiring that all parameters ω_1, ω_2, Γ_1, Γ_2, Δ, and Γ_{12} have simple dependences upon these parameters—or be independent of them—we can choose the basis states which are most meaningful. When this was done for KH_2AsO_4 (Katiyar *et al.*, 1971a,b) the results shown in Table (IX.1) were obtained. It can be observed that the choice $\Gamma_{12} = 0$ gave little temperature dependence in any of the other parameters except ω_1, the undamped soft-mode frequency. Hence this solution with real coupling is very nearly correct. It is not exactly right, as the slight variation of ω_2 and Γ_2 with temperature shows. A small but nonzero Γ_{12} would correct this defect.

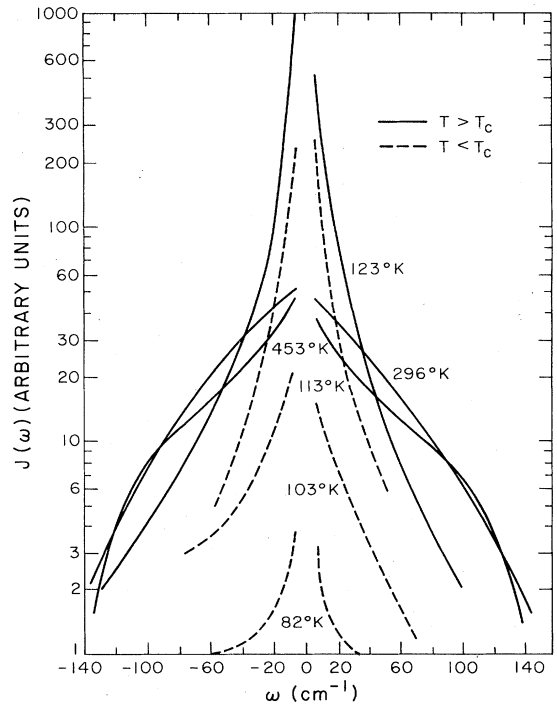

FIG. 45. Spectra, KDP (Kaminow and Damen, 1968). Such overdamped spectra were first analyzed in $BaTiO_3$ by DiDomenico, *et al.* (1967, 1968). Here $J(\omega)$ is the observed spectral intensity divided by the Bose factor.

In addition to the damped harmonic oscillator parameters ω and Γ, Table (IX.1) lists $\tau(T)$ for KH_2AsO_4. This relaxation time is defined as

$$\tau_a(T) = \Gamma_a(T)/\omega_a^2(T) \tag{IX.4}$$

and is a very convenient parameter to consider for KDP-structure systems. Overdamped harmonic oscillators yield a spectral distribution (proportional to the imaginary part of the susceptibility) very similar to that of a Debye relaxation spectrum. In the limit of very large damping, the two spectra become identical and the Debye relaxation time $\tau(T)$ is related to the damped harmonic oscillator parameters Γ and ω as in Eq. (IX.4). Katiyar *et al.* have characterized their spectra in terms of $\tau_a(T)$ because Γ_a and ω_a are correlated in the least-squares

TABLE IX.I. KDA parameters (cm^{-1}).[a]

	295°K	245°K	189°K	137°K
P_a	2440	2393	2385	2060
Γ_a	372	372	292	247
ω_a	161	158	134	112
P_b	380	403	431	391
Γ_b	11.8	14.5	14.7	12.9
ω_b	140	145	147	148
Γ_{ab}	0	0	0	0
Δ	112	116	112	107
τ_a(sec)	4.8 $\times 10^{-13}$	5.0 $\times 10^{-13}$	5.4 $\times 10^{-13}$	6.6 $\times 10^{-13}$

[a] Note that there is some evidence for a maximum in the phonon width Γ_b near the temperature at which ω_a crosses ω_b (~217°K).

fitting of observed line shapes, so that only the ratio $\tau_a(T)$ may be extracted from some of the spectra. Some authors have also felt that the parameter $\tau(T)$ may be the more fundamental quantity. As evidence for the latter point, both Ryan *et al.* (1972) and Reese *et al.* (1973) have observed that slightly better fits to the observed line shapes in KDP structures can be obtained when the soft-mode response is assumed to be of the Debye form, rather than that of a simply damped harmonic oscillator. This is also confirmed, so some degree, by the dielectric measurements of Hill and Ichiki (1962), who required a distribution of Debye relaxation times to explain their data. Very recently, however, Peercy (1973) obtained an underdamped soft mode in KDP by applying hydrostatic pressure. His work shows that the soft mode can be described only by a damped harmonic oscillator and not by a Debye relaxation spectrum.

The specific model for KH_2AsO_4 and CsH_2AsO_4 discussed above does reveal one interesting anomaly: the soft-mode frequency $\omega_0(T)$ does not extrapolate to zero at $T = T_0$. This is shown dramatically in Fig. 46 for KH_2AsO_4 and CsH_2AsO_4 (Cowley *et al.*, 1971; Katiyar *et al.*, 1971b). Such a temperature dependence would not be unusual for a first-order phase transition, but the ferroelectric transitions in this class of materials are very nearly second order, as determined by the dielectric measurements of Kaminow (1965). Put in other words, this means that the Lyddane–Sachs–Teller relationship (1941) below is not satisfied

$$\epsilon_0(T)/\epsilon_\infty = \omega_{\mathrm{LO}}^2/\omega_{\mathrm{TO}}^2(T). \qquad \text{(IX.5)}$$

The physical reason for the failure of this relationship has been pointed out by Cowley *et al.* (1971). Whereas the soft mode is able to equilibrate with fluctuations in acoustic phonon density (i.e., the "bath") on the time scale probed by the dielectric measurements (~10^{-10}sec), equilibrium is not obtained on the time scale probed by Raman measurements (< 10^{-11}sec). This distinction is essentially that encountered in acoustic phonon theory, where differences occur between the collision-free regime (zeroeth sound) and the collision-dominated regime. These ideas are discussed further in Sec. XII, using Nb_3Sn as an example.

Coombs and Cowley (1972) have shown that the effect of including certain anharmonic decays of soft optic modes via acoustic phonon channels is to modify the response function G_{ij} normally given for a single mode by

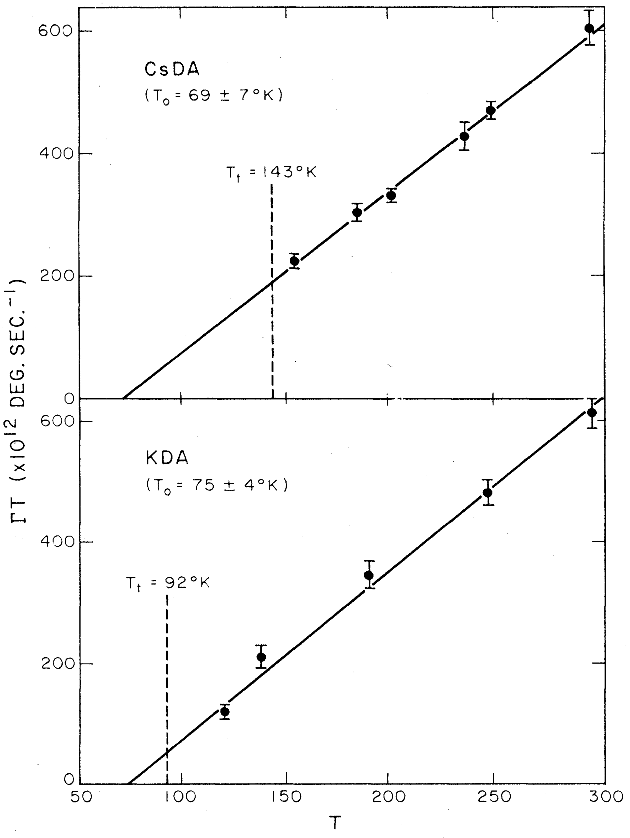

FIG. 46. ω^2 vs T in KDA and CsDA (Cowley *et al.*, 1971).

$$G^{-1}(\omega) = (\omega_0^2 - \omega^2 + i\Gamma\omega) \approx \chi^{-1}(\omega) \qquad \text{(IX.6)}$$

to the form

$$G^{-1}(\omega) = \{\omega_0^2 - \omega^2 + i\Gamma\omega + [\alpha T/(1 + i\omega \mathrm{T}_0)]\}. \qquad \text{(IX.7)}$$

In this expression T_0 is expected to approximate an acoustic phonon lifetime, ~10^{-11}sec. Thus, measurements at frequencies less than ~10^{11} Hz will probe a different response than measurements above ~10^{11} Hz. In fact, the latter will manifest a Curie temperature T_c (deduced by extrapolating $\omega(T)$ to zero frequency) which differs from the actual phase transition T_0 by $\Delta T = \alpha/K$, even for a second-order transition. That is, for high frequencies

$$\omega_0^2 = K(T - T_0) \qquad \text{(IX.8)}$$

will be satisfied, but for low frequencies

$$\omega_0^2 + \alpha T = K(T - T_0) \qquad \text{(IX.9)}$$

or

$$\omega_0^2 \cong K(T - T_c) \qquad \text{(IX.10)}$$

will result, where $T_c \cong T_0 - (\alpha/K)T_0$. Although not discussed in the paper by Cowley *et al.* (1971), the anomalous self-energy term α in Eq. (IX.7) cannot be evaluated experimentally if a representation of the response function in Eq. (IX.3) is chosen with $\Delta \neq 0$. If Δ is set $= 0$ in

Eq. (IX.3) and the values of $\omega_1(T)$ determined for the soft mode in CsDA or KDA, the self-energy term α is found to be nonzero (J. F. Ryan, Ph.D. thesis, Univ. Edinburgh, 1972) as suggested earlier by Cowley *et. al.* (1971).

Another significant feature of the modified response function given in Eq. (IX.7) is that it predicts a peak at $\omega \approx 0$, a central mode which grows in intensity as $T \rightarrow T_0$. This central mode has nothing to do with critical phenomena, since it arises within the context of mean-field theory. It is based on earlier theories of Cowley (1967, 1970) and Mountain (1966) and may be compared with a similar theory of Shirane and Axe, discussed in Sec. XII. The physical content of the two theories is the same, although the algebra differs somewhat in the expressions for frequency-dependent damping.

While the work of Cowley *et al.* described above has been valuable in elucidating the dynamics of KDP structures above T_C, even greater breakthroughs have been made in deciphering the spectra below T_C. In addition to the quasielastic scattering manifest above T_C (the overdamped soft mode), KDP structures exhibit an underdamped temperature-dependent feature below T_C. This mode, of A_1 symmetry, lies at about 150 cm^{-1} at low temperatures. Its unusual temperature dependency was reported independently by Wilson (1971) and by Shigenari and Takagi (1971). The latter authors suggest, correctly, that this mode and the quasielastic scattering below T_C were *both* soft modes. This view was strengthened by the analysis of Lavrencic *et al.* (1972), who pointed out that this underdamped spectral feature has frequency proportional to the spontaneous polarization and is absent in deuterated KDP. They assigned this mode, and the quasielastic scattering, as part of the same soft-mode response. The origin of the quasielastic component below T_C is not exactly the same as that of the central mode discussed above. In the theory of Blinc and Zeks (1973) it arises from the following considerations: In the pseudospin theory, as developed by Brout *et al.* (1966), there is no damping of the pseudospin tunneling mode. Lavrencic *et al.* (1971) have incorporated damping in a phenomenological way by writing Blochlike equations for the spins. This was also done by Silverman (1970), but only for the paraelectric phase. With this formalization, two characteristic relaxation times appear analogous to the T_1 and T_2 times for real spin systems. The width of the underdamped peak and that of the quasielastic scattering are determined by the two times, T_1 and T_2. The difference between this theory, with its two characteristic times, and that of Cowley *et al.* (which has as two characteristic times in Eq. (IX.7) the values $1/\Gamma$ and T_0), is not completely transparent. However, in Cowley's theory, one time T_0 is that required for a mode to come into thermal equilibrium, i.e., is temperature independent and not a relaxation time; whereas in Blinc's theory, both T_1 and T_2 are real relaxation times and explicitly temperature dependent near T_C. The ferroelectric spectrum of KDP, as calculated by Lavrencic *et al.* (1972), is in excellent agreement with the experimental data of Shigenari and Takagi (1971) and Wilson (1971).

2. *NMR of* KH_2PO_4 *structures*

Nuclei such as deuterons, Cs^{133}, or As^{75}, which have nonzero spin, can be used to probe the static and dynamic behavior of ferroelectrics of the KDP class. NMR, NQR, and double resonance techniques have been employed to this end, and a comprehensive review has been given by Blinc (1971).

NQR frequencies are proportional to the rms quadrupole moment for a particular ion; in general this will consist of a static part due to site symmetry, plus a fluctuating part due to phonon-induced ionic displacements. For certain ions, such as tetrahedrally coordinated as in arsenate isomorphs of KDP, the static part is zero, and we can treat the entire NQR frequency as due to phonon amplitudes.

As an example of the utility of such investigations, we consider in some detail below the analysis of NQR data on As^{75} in CsH_2AsO_4 given by Blinc *et al.* (1970). We shall not interpret the data exactly as Blinc *et al.* have, and in fact a reconciliation of their data with dielectric and Raman measurements is given at the end of this section, following Scott and Worlock (1973). However, the value of such NQR data is independent and complementary to other analytical techniques is nevertheless demonstrated.

Blinc *et al.* relate the electric field gradient tensor V_{ij} at the ^{75}As site in CsH_2AsO_4 to the soft-mode rms amplitude. They show that the NQR frequency

$$e^2qQ/h \equiv eV_{zz}Q/h \tag{IX.11}$$

is determined by an electric field gradient V_{zz} at the arsenic site induced by soft-mode fluctuations. An effective Hamiltonian

$$\mathcal{H}_0 = \mathcal{H}_M + \langle \mathcal{H}_Q \rangle_t \tag{IX.12}$$

is employed, where the brackets denote a time average over the As ion position; $\mathcal{H}_M$ is the external field Zeeman term; and

$$\mathcal{H}_Q = e^2 V_{zz} Q/4I(2I-1) \times [3I_z^2 - I(I+1) + \tfrac{1}{2}\eta(I_+^2 + I_-^2)] \tag{IX.13}$$

is the coupling of the ^{75}As quadrupole with the electric field gradient. It is assumed that the major contribution to V_{zz} in Eqs. (IX.13) and (IX.12) is due to the rms value of the phonon-induced fluctuation in V_{zz}. Therefore V_{zz} is expanded in terms of the phonon coordinates. Since only one mode, the soft mode, has a large dipole moment, the expansion is restricted to that normal mode:

$$V_{zz}(\xi) = A + B\xi + C\xi^2 + \cdots \tag{IX.14}$$

The time average of Eq. (IX.14) yields

$$\langle V_{zz} \rangle_t = C\langle \xi^2 \rangle \tag{XI.15}$$

since A is zero for the tetrahedrally coordinated As in the paraelectric phase, and since $B\langle \xi \rangle$ averages to exactly zero as ξ oscillates sinusoidally.

The expectation value of $\langle \xi^2 \rangle$ may be evaluated from the equipartition theorem as

$$\tfrac{1}{2}k\langle \xi^2 \rangle = \tfrac{1}{2}KT, \tag{IX.16}$$

where k is the force constant:

$$k = m\omega_0^2 \tag{IX.17}$$

for the soft mode. If we assume the validity of the Lyddane–Sachs–Teller relation for the soft mode as measured with a low-frequency probe, i.e., $\omega_0^2(T) = A[\epsilon_0(T)]^{-1}$, we can then rewrite Eq. (IX.16) as

$$\langle \xi^2 \rangle = (\text{const.})T\epsilon_0(T), \tag{IX.18}$$

where ϵ_0 is the static dielectric constant for fields along the ferroelectric z axis.

From this line of analysis, Blinc *et al.* concluded that the NQR frequency $eV_{zz}Q/\hbar$, given from Eqs. (IX.13), (IX.15), and (IX.18), should vary as

$$eV_{zz}Q/h = DT/(T - T_0), \tag{IX.19}$$

where D is a constant; i.e. that it should diverge at T_0. Their actual data, plotted in Fig. 47 do not indicate a divergence at T_0, but upon extrapolation indicate a divergence at a much lower temperature. As pointed out by Scott and Worlock, this conclusion is unwarranted and arises from the failure of Blinc *et al.* to perform certain integrations over the Brillouin zone.

The proper average of $\langle \xi^2 \rangle$ entering Eq. (IX.15) includes phonons of all wave vectors. It is not necessary that the *phase* of the electric field gradient fluctuations be the same at each As site.[6] Thus Eqs. (IX.18) and (IX.19) do not follow, since they apply only to $q = 0$ phonons. Using a simple model for the CsH_2AsO_4 soft-mode dispersion, we calculate the NQR frequency including the effects of $q \neq 0$ phonons.[6] This point was made independently by F. Borsa and A. Rigamonti, Phys. Lett. **40a**, 399 (1972).

We know that for $q \approx 0$, the undamped soft-mode frequency is given approximately by

$$\omega_0^2(T) \approx A^2[(T/T_c) - 1]. \tag{IX.20}$$

From the neutron scattering intensities of Skalyo *et al.* (1970) on KDP structures, we know that $\omega_0^2(T,q)$ is given to a rough approximation by

$$\omega_0^2(T,q) = A^2[(T/T_c) - 1] + B^2q^2, \tag{IX.21}$$

where A and B are constants independent of T and q. With this model we obtain

$$\begin{aligned} \frac{eV_{zz}Q}{h} &= KT\frac{\int q^2\,dq/\omega^2(q)}{\int q^2\,dq} \\ \frac{eV_{zz}Q}{h} &= aT\left(1 - x\tan^{-1}\frac{1}{x}\right) \end{aligned} \tag{IX.22}$$

with a = constant and $x = A[(T/T_c) - 1]^{1/2}$. Figure 47 compares the calculation of Eq. (IX.22) with the observed values. A fairly good agreement is present, considering the gross simplicity of the assumed dispersion. Most important is the fact that no divergence of NQR frequency is predicted by Eq. (IX.22); the integration over q removes that.

In order to explain the experimental lack of divergence, Blinc *et al.* had proposed that somehow the proton motion and heavy ion motion become uncoupled near T_0, and that one of these two modes—the soft mode—obeys a Curie–Weiss dependence

$$\omega^2 = A(T - T_c), \tag{IX.23}$$

with T_c much less than the actual transition temperature T_0. In our analysis, there are *many* modes which would reach zero frequency at some temperature below T_0; they are simply the $q \neq 0$ optical phonons on the soft-mode branch.

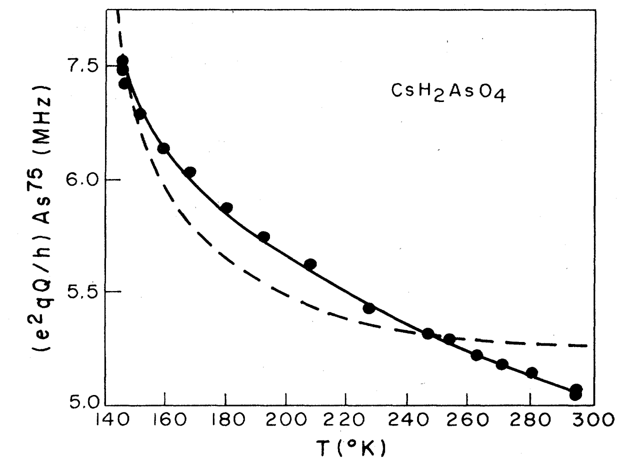

FIG. 47. NQR quadrupole coupling constant vs T in CsDA- (theory and experiment) (Scott and Worlock, 1973).

Thus, our analysis requires no proton–phonon decoupling. This is compatible with the most recent results of Blinc *et al.* (1972), who find that the NQR frequency dependences of D and heavy ions in deuterated KDP structures are the same near T_0.

3. Acoustic phonons

Elastic coefficients and acoustic phonons in KDP structures have been studied extensively. KH_2PO_4 is piezoelastic in the paraelectric phase, and thus a direct (piezoelectric) coupling between the soft optic mode and certain acoustic modes is permitted. This has been discussed in some detail by Brody and Cummins (1969). Their experimental results for $C_{66}^E(T)$ are shown in Fig. 48. It can be seen that this elastic constant decreases continuously to very nearly zero as T_0 is approached from above or below, and that the temperature dependence of C_{66}^E is quite different on the high- low-temperature sides of T_0. Elliott *et al.* (1972) have fitted these temperature dependences very accurately using a mean field theory; the different behavior above and below T_0 therefore has nothing to do with critical effects, although such asymmetric curves as in Fig. 48 are reminiscent of the behavior of density, etc., versus T for fluids in the critical fluctuation regime.

In addition to the characteristics of the soft mode, including its interaction with acoustic phonons and its effect upon NQR response, the behavior of phonons not directly relating to the spontaneous polarization in KDP has also been investigated. We shall not review here the sundry studies of the various high-frequency optical modes, although their energies and intensities yield information on hydrogen bonding and other ion displacements at various temperatures. It does seem worth mentioning, however, that a broad, featureless background exists from zero to ~100 cm^{-1} in the E-symmetry $(\alpha_{xz}\alpha_{yz})$ spectra of all KDP isomorphs in their paraelectric $\bar{4}2m$ phases. This feature was first reported by Lavrencic *et al.*

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[6] This point was made independently by F. Borsa and A. Rigamonti, Phys. Lett. **40a**, 399 (1972).

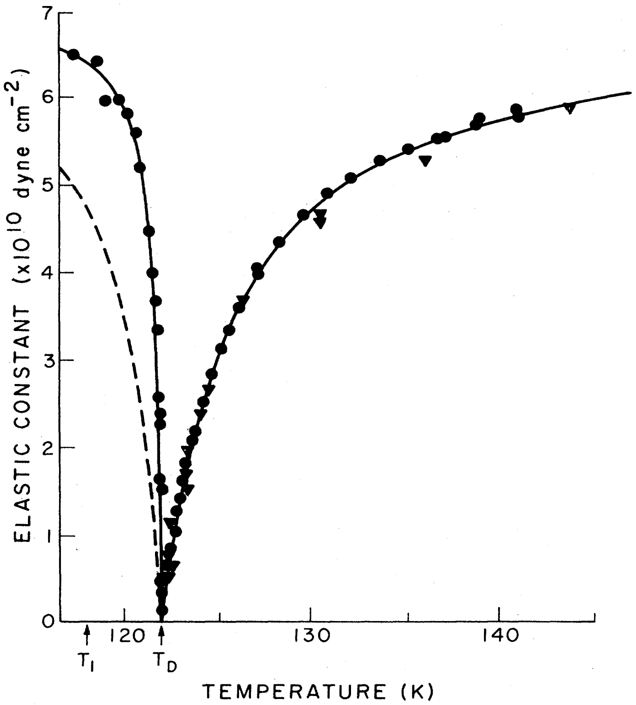

FIG. 48. A comparison between experiment and theory (Elliott, Smith and Young, 1972) for C_{66} in KDP. The adiabatic theory (solid curve) and isothermal theory (dashed curve) are compared with experimental data (circles) from Garland and Novotny (1969) and (triangles) from Brody and Cummins (1968). T_I is the transition temperature for a clamped crystal; T_D, the domain-formation temperature.

(1970), and independently by Hammer (1971), and by Wilson (1971). One curious aspect of this otherwise featureless background is that it interacts strongly with the lowest frequency E-symmetry transverse optical phonon at about 95 cm^{-1}, yielding an interference shape characteristic of Breit–Wigner interactions between discrete states and continua. A similar effect was reported for the A_1 symmetry spectra in the ferroelectric phase by Shigenari and Takagi (1971). These line shape anomalies in KDP have been analyzed by Scott and Wilson (1972), who suggested that the origin of the E-symmetry feature is simply that of scattering from the one-phonon density of states, where disorder above T_0 allows $q \neq 0$ modes to become Raman-active. The rapid decrease to zero of the intensity of this background within 5°K below T_0, as long-range order of protons develops, lends support to this interpretation, as does the fact that the E-symmetry background cannot be fitted as a single "mode", either of damped harmonic oscillator or Debye form. Thus, the E spectra yield information concerning order evolution through the temperature dependence of their intensities (compare with the discussion of NH_4Br in Sec. XI), but are not "soft modes" with temperature-dependent frequencies.

The same descriptions apply to the broad features of B_2 and E symmetry in $NH_4H_2PO_4$ (ADP). ADP has been studied via Raman spectroscopy by many different groups. No soft mode is observed. As discussed by Cochran (1961), the soft mode in paraelectric ADP would be at the Brillouin zone boundary. It becomes $q = 0$ and Raman active in the low-temperature antiferroelectric phase, but unfortunately ADP invariably shatters as it is lowered through the transition temperature, thus precluding efforts to study its dynamics below T_0.

B. Triglycine sulfate and thiourea

Several other hydrogen-bonded ferroelectrics are of significant interest. Triglycine sulfate TGS is very useful as a pyroelectric detector and is probably the ferroelectric of greatest technological importance. Its spontaneous polarization was measured as a function of temperature by Hoshino *et al.* (1957) and is shown in Fig. 49. The static dielectric constant confirms the implication of Fig. 49 that the transition is second order; Fig. 50 shows the results of Triebwasser (1958) for $\epsilon_0(T)$ above and below T_0. Note that Curie–Weiss behavior is exhibited in each phase. An infrared study by Barker and Tinkham (1963) revealed no undamped soft mode in TGS. and suggested that it, like KDP, might instead be characterized by a nonresonant response, e.g. of the Debye form. Further ir and Raman studies have yielded little qualitatively new information concerning the transition dynamics in TGS or the isomorphic selenate.

The information concerning triglycine sulfate is not limited to dielectric measurements. Probes of acoustic phonon behavior have been made by O'Brien and Litovitz (1964) using conventional ultrasonic techniques, and by Gammon and Cummins (1966) using Brillouin spectroscopy. Each group was able to confirm indirectly the Curie–Weiss behavior of the inverse relaxation time. In the expression

$$\tau = A(T_c - T)^{-1} \qquad \text{(IX.24)}$$

$A(\omega)$ was deduced as 2.25×10^{-10} deg sec in the ultasonic regime and $(2.9 \pm 0.3) \times 10^{-11}$ deg sec in the hypersonic regime. (Recall that in relating relaxation times of the Debye-type to damped harmonic oscillators, $\tau = \Gamma/\omega_0^2$.) The physical origin of the dispersion $\tau(\omega)$ thereby measured was not discussed, but we have seen in the preceding

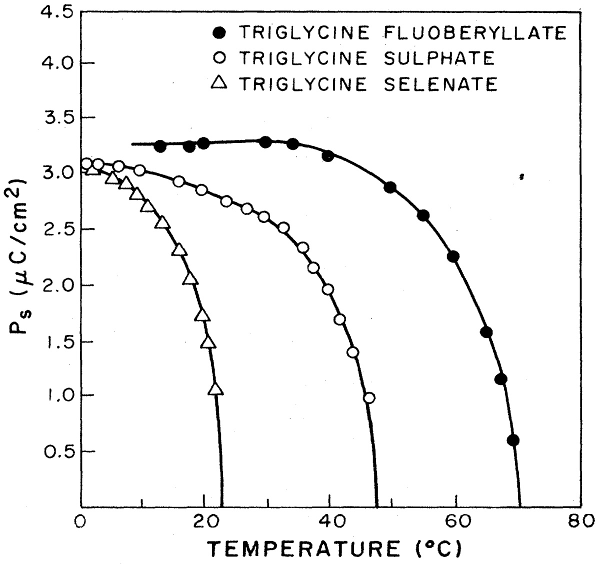

FIG. 49. Spontaneous polarization $P(T)$ in triglycine sulfate (Hoshino *et al.*, 1957).

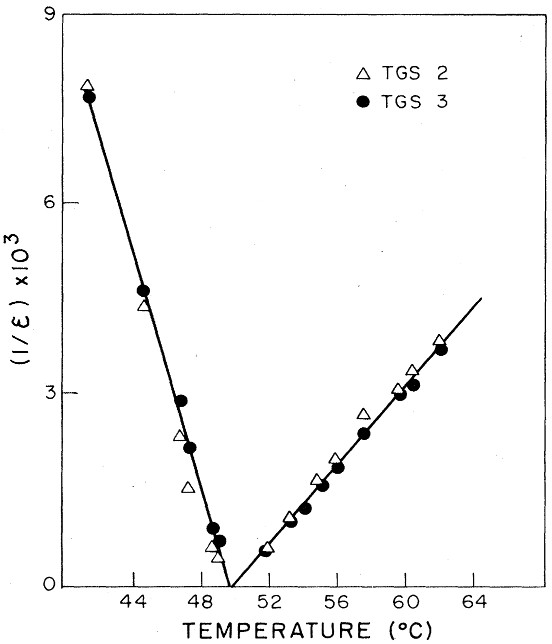

FIG. 50 Dielectric constant vs T in TGS (Triebwasser, 1958).

section how Cowley's theory includes explicitly a frequency-dependent relaxation time.

Thiourea is an unusual ferroelectric in that it is an organic compound. Its ferroelectric properties have been known for more than a decade (Solomon, 1956; Goldsmith and White, 1959), but little spectroscopy has been performed on it. Recently, Raman spectroscopy on thiourea by Schrader's group in Dortmund (Schrader *et al.*, 1971) revealed a wing on the Rayleigh line for the trace (α_{yy}) scattering polarizability somewhat suggestive of KDP spectra, but this feature was not emphasized in their studies, and we cannot conjecture about its temperature dependence in the absence of detailed data.

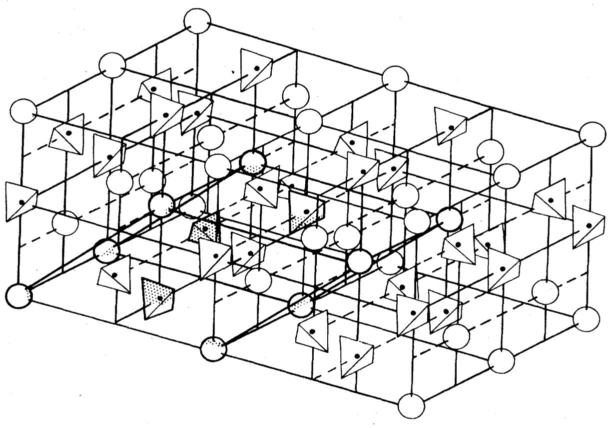

FIG. 51 DyVO₄ structure (Cooke *et al.*, 1971).

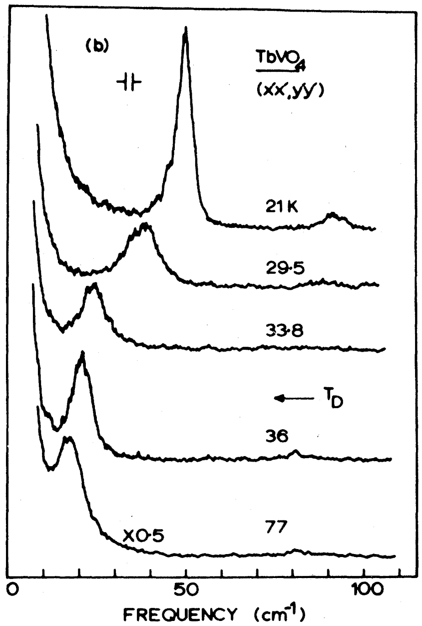

FIG. 52. Soft electronic mode spectra, TbVO₄ (R. T. Harley, W. Hayes, and S. R. P. Smith, 1971).

X. JAHN–TELLER SYSTEMS

A. DyVO₄, TbVO₄

Although Jahn–Teller systems have an old and highly developed literature of their own, we must make contact with such materials if we wish to summarize the complete range of structural distortions in crystals. In the conventional Jahn–Teller description, a lattice containing an ion with a degenerate electronic state spontaneously distorts in a way such that the total internal energy is lowered. This lattice distortion removes the degeneracy (at least partially) of the electronic levels. In most systems studied, the transition is from cubic to uniaxial (tetragonal or rhombohedral). However, in the systems DyVO₄, and TbVO₄, the Jahn–Teller distortions (at 14°K, 12°K, and 34°K respectively) involve a simpler distortion from tetragonal (D_{4h}^{19} zircon structure) to orthorhombic (D_{2h}^{28} for DyVO₄ or DyAsO₄; D_{2h}^{24} for TbVO₄). In these transitions the twofold degeneracies of the tetragonal structures are removed; only nondegenerate levels occur below T_0. A complete survey of these systems has been given by Elliott *et al.* (1971), and by Sandercock *et al.* (1972). It is important to emphasize that the transition temperatures given here are *not* the Neél temperatures, which are lower. There are additional structural distortions occurring at T_N; for example, at $T_N = 3.05$°K, DyVO₄ undergoes a lattice strain of 0.17% (Cooke *et al.*, 1971; Sayetat *et al.*, 1971); these distortions at T_N will not be discussed further here.

The structure of these RMO₄ compounds is shown in Fig. 51. Figure 52 shows the temperature dependence of the lowest energy electronic level in DyVO₄ and DyAsO₄ as measured by Raman spectroscopy. This electronic state is the soft mode for the transitions in question.

The lattice distortions may be interpreted in terms of $q = 0$ optical phonons, as discussed by Englman and Halperin (1970, 1971); or they may be described in terms of direct interaction between magnetic ions and macroscopic elastic strain, i.e., acoustic phonon–electron interaction (Kanamori, 1960). The distinction has been pointed out by Pytte (1971b). We shall not elaborate further on these two mechanisms here, but a related free-energy description is given in Sec. XII, following Shirane and Axe (1971), in the discussion of Nb_3Sn and V_3Si.

$KCoF_3$ and $RbCoF_3$

$KCoF_3$, $RbCoF_3$, and $TlCoF_3$ order antiferromagnetically at $T_N = 114°K$, $101°K$, and $94°K$, respectively. At the Neél temperature there is a contraction of the lattice along the direction c of spin alignment (Allain *et al.* 1971). The resulting tetragonal distortion is manifest in the x-ray measurement of c/a, and the behavior of certain of the elastic constants near T_N. The Raman spectrum below T_N (Nouet *et al.* 1973) is compatible with a simple c-axis contraction; all ions apparently remain at inversion sites, and all phonons retain odd parity and Raman inactivity. Despite the fact that the Γ_{25} mode at the [111] zone boundary is somewhat unstable (Buyers *et al.*, 1968), and that it couples strongly with the magnon near T_N (Holden *et al.*, 1971; Buyers *et al.*, 1971), this optical phonon does not collapse at T_N. Thus, the ionic displacements in $KCoF_3$ below T_N are not those of fluorine octahedron rotation about [100] axes (as in $KMnF_3$ and other perovskites exhibiting cell-doubling transitions).

No detailed analyses of structural distortions at T_N in perovskites have been published. However, in his 1960 paper, Kanamori explicitly suggested that the distortions in CoO and $KCoF_3$ were analogous and could both be described by a Jahn–Teller formalism. The application of Jahn–Teller theories to systems having Co^{2+} ions (which have orbital angular momenta unquenched by the crystal field) is fairly complicated and has not been done for $KCoF_3$. However, Kanamori's conjecture concerning CoO and $KCoF_3$ seems well founded: the $(a - c)/a$ distortion is of the same sign (positive) in each and of about the same magnitude (roughly 1% at $T = 0°K$.)

Thus, in the case of $KCoF_3$ and $RbCoF_3$, Kanamori's theory of magnetic ions interacting directly with elastic strains (acoustic phonons) seems most applicable. In the case of rare-earth vanadates, it is not so clear, and Elliott *et al.* have concluded that acoustic phonon interactions are of very different magnitude for $DyVO_4$ and $TbVO_4$.

In the case of both $KCoF_3$ and $RbCoF_3$ the soft mode is simply the magnon. The sublattice magnetization is the macroscopic order parameter for both magnetic and structural transition. It is of interest that the magnon frequency is *not* proportional to the sublattice magnetization (Nouet *et al.*, 1973). This shows that the linear response theory (which assumes infinite-range magnetic forces) is not satisfied.

Thus, in both rare-earth vanadates and in Co^{2+} fluoroperovskites the soft modes and order parameters for the structural distortions are electronic. For a cogent description of such effects in UO_2, readers are referred to the earlier work of Allen (1968).

XI. ORDER–DISORDER TRANSITIONS

A. $NaNO_2$

Thus far we have considered only crystals in which ionic positions change from one ordered array below T_0 to a second, different ordered array above T_0. Even in the KDP class of ferroelectrics, the heavy metal ions (K and P, or Rb and As, etc.) undergo such an order–order transition at the same temperature T_0 at which the protons become disordered. In the present section we will consider $NaNO_2$, the most thoroughly understood ferroelectric which is disordered in the paraelectric phase, and the ammonium halides, which exhibit nonferroelectric order–disorder transitions in which the protons play a key role, as in KH_2PO_4.

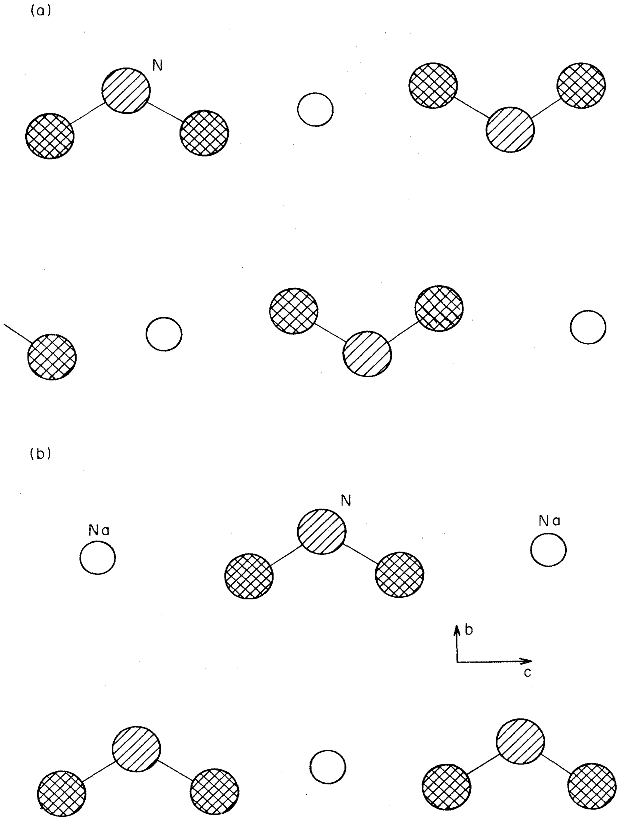

FIG. 53. Atomic positions in $NaNO_2$ in (a) the paraelectric disordered phase, and (b) the ferroelectric ordered phase. The oxygen ions are cross shaded.

The static structure and dynamic response of $NaNO_2$ above and below the Curie temperature have been analyzed in an important study at Chalk River (Sakurai *et al.*, 1970). The occurrence of ferroelectricity in this crystal was reported many years earlier (Sawada *et al.*, 1958).

The ionic positions of $NaNO_2$ in the ferroelectric phase are shown in Fig. 53a. Figure 53b shows the positions of $NaNO_2$ ions in the disordered paraelectric phase. Since the difference between the positions of the oxygen atoms in the two phases is not infinitesimal, this transition is necessarily first order.

Let us now consider the response associated with this ionic displacement. The potential in which the NO_2 ions move may be described as a double well, as diagrammed in Fig. 54. The left side of the well corresponds to oxygens to the left of N ions. At low temperatures most of the NO_2 ions lie on the same side of the double well. The atoms vibrate with small amplitude and high frequency in this essentially quadratic well; only very infrequently do they tunnel to the other side of the double well. The system may be considered to have not

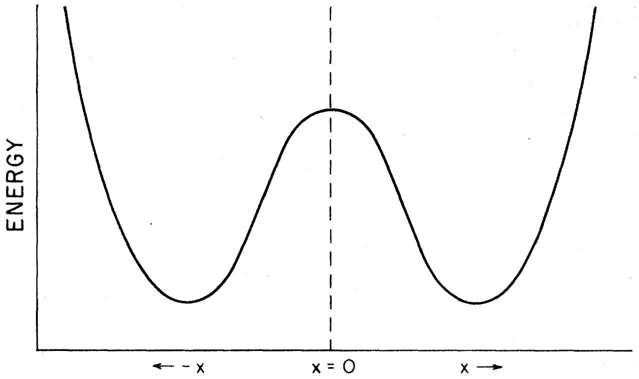

FIG. 54. Simple double-well potential schematically descriptive of the two stable NO_2 orientations in ferroelectric $NaNO_2$.

one, but *two*, characteristic frequencies: one given by the quasiharmonic frequency ω_0 within either side of the double well; and a second given by the reciprocal of the average tunneling time from well to well. Thus, two peaks may be expected in the imaginary part of the susceptibility for this system—one at ω_0, and one at much lower frequencies. These peaks have the same symmetry and indeed the same eigenvector. The reason only one peak in the response function for each normal mode is predicted by group-theoretical calculations, is that *infinitesimal* amplitudes are assumed for each normal coordinate; in order–disorder systems such as $NaNO_2$, very large, finite displacements must be considered. When we include the effects of phonon damping in this description, we arrive at a hypothetical response function (χ'', or scattering cross section) shown schematically in Fig. 55: a Lorentzian centered at ω_0 and an overdamped mode centered at zero frequency. Both the high-frequency response and the very low-frequency response contribute to the dielectric function. The vee-shaped NO_2 ions possess an electric dipole which creates a spontaneous polarization in the low-temperature phase of $NaNO_2$, and the inelastic neutron scattering results of Sakurai *et al.* (1970) for the NO_2 flopping mode are in good accord with the schematic diagram shown in Fig. 55. Eigenvector determination showed that the ionic displacements at ω_0 and at $\omega \approx 0$ were equivalent. Equally important, a complete measurement of dispersion curves for all the group-theoretically predicted modes (except the high-energy NO_2 internal modes) showed clearly that the very low-frequency mode was "extra" in the group theoretical sense, i.e. arises from finite amplitude displacements of the NO_2 ions. (We note that the soft mode in KH_2PO_4 has not yet been shown to be "extra." There is some difficulty in counting the modes of B_2 symmetry in paraelectric KDP to see whether six or seven are present; this is due to the complexity of the spectrum, mode interactions, and possible second-order peaks.)

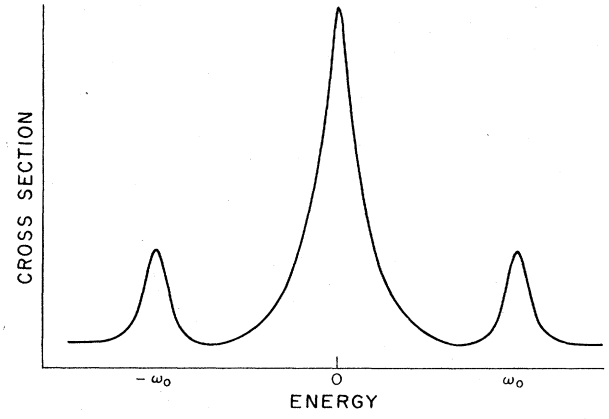

FIG. 55. Three-component spectrum predicted for a single normal coordinate response in an anharmonic double-well potential.

It was not possible to the Chalk River experiments to determine a characteristic frequency for the overdamped low-frequency mode. That is, the low-frequency response was not fitted to either a damped harmonic oscillator expression or to a Debye relaxation function. All that could be said was that the characteristic response frequency was very low (less than 1.7×10^9 Hz.) This value is in rough agreement with that obtained in the dielectric study of Hatta *et al.* (1966), who found the low-frequency response to be characterized by a Debye relaxation time of

$$\tau(T) = (1.6 \times 10^{-8})/(T - 160°\mathrm{C}) \text{ sec.} \qquad (\mathrm{XI.1})$$

Thus, at 22°C, $\tau(T) \approx 10^{-10}$ sec., and $1/2\pi\tau = 1.6 \times 10^9$ Hz, which agrees with the neutron scattering estimate very well. (By comparison, the Debye relaxation time extracted for CsH_2AsO_4 and KH_2AsO_4 by Katiyar *et al.* (1971) was $\sim 5 \times 10^{-13}$ sec.—two orders of magnitude shorter.) The use of conventional ir or Raman spectoscopy to study systems with $\tau > 10^{-12}$ sec. is not promising; for such systems most of the response occurs at frequencies less than 1 or 2 cm^{-1}.

The work of Hatta *et al.* (1966) does show one important thing: that the response is characterized by a single "mode," i.e., one relaxation time. Thus we may refer to a "soft" mode in $NaNO_2$, although it is not one of the group-theoretically predicted optical phonons. Even this semantic privilege is not allowed in the ammonium halides, as we shall see below, since the very low-frequency response is not characterized by a single relaxation time.

Before leaving $NaNO_2$, we should comment that two additional phase transitions have been analyzed by x-ray diffraction studies (Hoshino and Motegi, 1967). Only the paraelectric–ferroelectric transition from orthorhombic space groups D_{2h}^{25} to C_{2v}^{20} (or *Im2m*) have been analyzed dynamically. The antiferroelectric and "ferrielectric" phases reported by Hoshino and Motegi should provide interesting dynamics for future study.

B. NH_4Cl

The ammonium halides have order–disorder transitions which are analogous to that in $NaNO_2$; the ammonium ions undergo a rotational disorder in which the proton positions become randomized. The transitions have been carefully studied via ultrasonic techniques (Garland and Renard, 1966), Rayleigh and Brillouin scattering (Lazay *et al.*, 1969), and Raman spectroscopy (Wang and Fleury, 1969).

From the linewidth of acoustic phonons in NH_4Cl at 24°C, Lazay *et al.* determined a relaxation time of

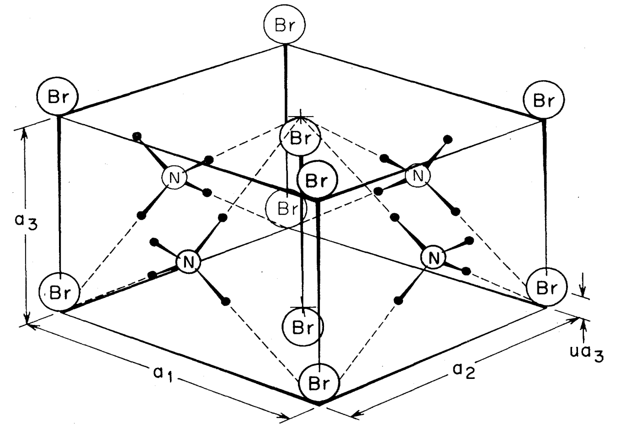

FIG. 56. NH_4Br structure (Wagner and Hornig, 1950).

$\tau = 8.6 \times 10^{-11}$ sec. As in the case of $NaNO_2$, this time is too long to produce measurable quasielastic Raman spectra. The value of τ was independently determined by proton NMR (Purcell, 1951); good numerical agreement is obtained for the two methods, and the time is interpreted as in NH_4^+ tetrahedra reorientation time.

The structure of both NH_4Br and NH_4Cl just above their order–disorder temperatures (234.5 and 242.8°K, respectively) is CsCl-like: T_d^1 (or $P\bar{4}3m$) space group, with the NH_4^+ ions in Cs positions having random rotational alignment of their protons; this is generally called Phase II. Phase I is a disordered NaCl structure with space group $0_h^1(Pm3m)$. Below the ordering temperature, NH_4Cl becomes tetragonal, with the NH_4^+ tetrahedra aligned parallel; the structure is $D_{4h}^{10}(P4/mcm)$ and is also observed at low temperatures (<110°K) or high pressures (>2 kbar) in NH_4Br. In NH_4Br, however, a fourth phase occurs, in which the NH_4^+ tetrahedra order antiparallel, thus doubling the unit cell. This $D_{4h}^7(P/nmm)$ arrangement is shown in Fig. 56, after Wagner & Hornig (1950).

All of the phase transitions discussed above involve NH_4^+ tetrahedra reorientations with times long compared to those measured by Raman, ir, or inelastic neutron spectroscopy. Thus direct information concerning the transition dynamics is difficult to obtain. We have already seen that a response centered at $\omega = 0$ was detected in the inelastic neutron scattering on $NaNO_2$, and that this response was further characterized by dielectric measurements as having Debye relaxation properties with a single decay time. Since the disorder in NH_4Cl or NH_4Br does not involve a dipole moment, analogous dielectric measurements are not possible; however the Rayleigh scattering measurements of Lazay *et al.* (1969) give similar information to that supplied by neutron scattering on $NaNO_2$.

In Fig. 57 we show the Rayleigh ($\omega \approx 0$) intensity of NH_4Cl at temperatures near T_0, the ordering temperature. The sharp increase in intensity is due to fluctuations in NH_4^+ order. The polarized (i.e., trace polarizability) spectral intensity was found to obey the temperature dependences

$$I = I_0|T - T_0|^{1.0}, \; T < T_0, \qquad \text{(XI.2)}$$

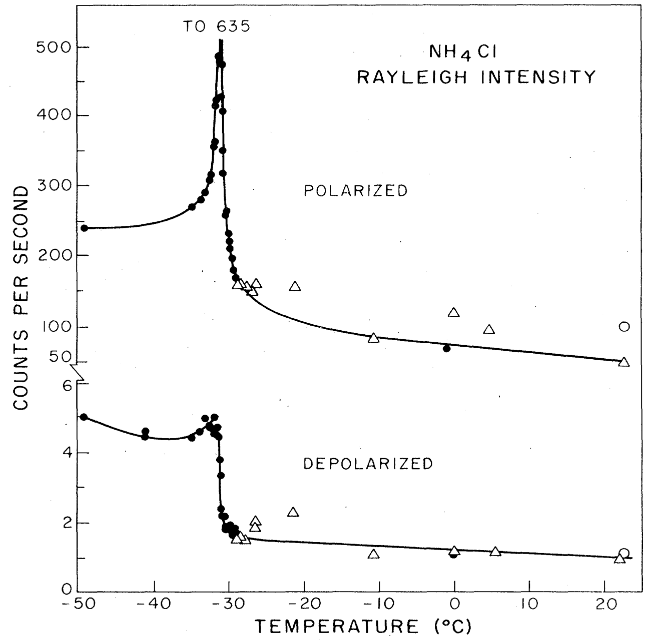

FIG. 57. Cross section vs T for Rayleigh scattering in NH_4Cl (Lazay *et al.*, 1969).

and

$$I = I_0|T - T_0|^{0.63}, \; T > T_0. \qquad \text{(XI.3)}$$

In concluding the discussion of NH_4Cl, we must stress that the interpretation of the Rayleigh intensity data of Lazay *et al.* is still open to question. It is not obvious that they represent a "critical" phenomenon in which very large fluctuations render mean field theories incorrect. It is equally possible that, by analogy with $NaNO_2$, the response centered at $\omega = 0$ is due to slow, large-amplitude, tunneling-like displacements of protons—which can still be described within the context of mean field theories. However, in the latter case, an exponent $2\beta = 1$ should be observed both above and below T_0, in contrast with experiment. Bartis (1973) has interpreted the anomalous exponents in NH_4Cl in terms of point defects and edge dislocations. As Benedek (1969) has discussed in detail, measurement of the temperature dependence of the Rayleigh width in NH_4Cl would clarify the picture, since true critical phenomena would require a decrease in width concurrent with the increase in intensity.

C. NH_4Br

While the dependence of optical phonon frequencies upon temperature is not of great interest in NH_4Cl or NH_4Br, the intensities and widths of various optical modes may relate directly to the evolution of order near the order–disorder transition, T_0. This was first suggested by Garland and Schumaker (1967), who found that an optical phonon broadened and decreased in intensity in their ir spectra as T was increased toward T_0 in the ordered phase. Detailed Raman measurements of the analogous mode (at ~1420 cm^{-1}) in NH_4Br have been given by Wang and Fleury (1969), who also interpret the mode broadening as gradual evolution of disorder in the ordered phase. Presumably, short-range ordering of NH_4^+ orientations persists well above T_0, but the very long-range order (~5000 Å or larger), upon which Raman spectroscopy selection rules are dependent, decays monotonically to zero as T_0 is approached from below. The widths of the 1444 and 1420 cm^{-1} lines in NH_4Cl and NH_4Br are measures of the region of momentum space contributing to the Raman spectra at each temperature. (If the optical phonon branch in question were dispersionless, no broadening would occur.)

Just as the intensities and widths of the high-energy lines discussed above relate to the occurrence of disorder in the ordered phases of NH_4Cl and NH_4Br, information can also be extracted from the low-energy, lattice-mode region of the spectrum. In NH_4Br Wang and Fleury report a mode (at 56 cm^{-1}) whose intensity dependence is *opposite* that discussed in the preceding paragraph: As the disordering temperature is approached from below, this mode *increases* rapidly in intensity. It is interpreted as a large-q (zone boundary) phonon made Raman-active by residual disorder in the ordered phase. Its intensity dependence below T_0 therefore substantiates the interpretation of disorder below T_0 implied by the 1420 cm^{-1} mode.

Wang and Fleury also discuss the surprisingly symmetric, Loretzian shape of this mode in the disordered phase. They suggest that the 56 cm^{-1} line in the disordered phase arises from phonons at critical point $X = (\pi/a, 0, 0)$. Such phonons would, however, be Raman allowed in the ordered, antiparallel phase below T_0. The predicted intensity dependence is therefore decreasing below T_0 and rapidly decreasing above T_0. Hence, we do not agree with the assignment of the 56 cm^{-1} mode as occurring at $X = (\pi/a, 0, 0)$ in the disordered phase. The mode which satisfies the predictions of an X-point phonons is that at 67 cm^{-1} in NH_4Br, not that at 56 cm^{-1}. This reviewer believes that the acoustic phonon frequency increases monotonically along $(q, 0, 0)$ to 67 cm^{-1} at the boundary in NH_4Br. This 67 cm^{-1} zone-boundary phonon is Raman-allowed in the ordered phase having two formula groups per unit cell; the $(q = \pi/a, 0, 0)$ point becomes a reciprocal lattice point in this phase. Above T_0, all phonons near $(\pi/a, 0, 0) = x$ contribute to the Raman intensity; but these all have energies slightly less than 67 cm^{-1}. The density of states for this branch is maximum for q slightly less than π/a, and yields a peak at ~56 cm^{-1} for the fully disordered system.

To summarize: We predict that the [100] zone boundary transverse acoustic phonon frequency in disordered NH_4Br lies at 67 cm^{-1}, not the 56 cm^{-1} level assigned by Wang and Fleury, whose intensity data seem inconsistent with their assignment.

An attempt to make qualitative the relationship between the intensity data of Fleury and Wang for the 56 cm^{-1} line and the specific heat data of Sorai *et al.* (1965) has been reported by Wang (1971), who showed that

$$I(T) = AC(T), \tag{XI.4}$$

where $I(T)$ is the intensity of the 56 cm^{-1} line, and $C(T)$ is the temperature-dependent part of the specific heat, i.e., a large, approximately constant value has been subtracted from the total specific heat, such that $C(T)$ asymptotically approaches zero for temperatures far below T_0.

This work by Wang shows that the 56 cm^{-1} line intensity is a good measure of the NH_4 disorder. It does *not*, however, substantiate in any way the assignment of the 56 cm^{-1} line as an $x = (\pi/a, 0, 0)$ phonon; to the contrary, it supports the assignment given here that $TA^x = 67$ cm^{-1}.

We will await the results of inelastic neutron scattering on ND_4Cl and ND_4Br with keen interest. (Deuterated crystals must be employed for coherent neutron spectroscopy.)

Independent of this specific interpretation, the work of Wang and Fleury, and of Rimai *et al.* (1969) on Raman intensities of disordered systems shows that microscopic, dynamical information can be obtained even for crystals in which the soft mode lies at very low frequencies—frequencies far below the range of grating spectrometers.

XII. A-15 STRUCTURE HIGH-TEMPERATURE SUPERCONDUCTORS

A. Theory of Blount and Anderson

The A-15 or β-tungsten structure crystals exemplified by Nb_3Sn and V_3Si are of enormous importance as high-temperature superconductors. They also exhibit structural phase transitions at temperatures slightly above their superconducting temperatures. Because ir and Raman studies on metals are quite difficult, and because single crystals of these compounds of size sufficient for inelastic neutron scattering were not available, the only experimental data for many years relating to the displacive phase transitions in Nb_3Sn or V_3Si were the acoustic phonon studies of Testardi *et al.* (1965, 1966, 1967). The existence of a structural transition in these materials was demonstrated earlier by Batterman and Barrett (1964, 1966), and Anderson and Blount (1965) had proposed a soft-mode interpretation of the phase transition. Unfortunately, no information existed concerning optical phonon frequencies or temperature dependences; and the space group could not be determined unambiguously by x-ray methods. Consequently, the soft-mode descriptions which evolved following Anderson and Blount were somewhat speculative: Birman (1966, 1967) and Klein and Birman (1970) simply had little experimental data around which to structure their lattice dynamical theories.

B. Theory of Labbé and Friedel

In 1966, Labbé and Friedel (1966,a,b) proposed a qualitatively different explanation of the transition dynamics. Their theory involved no soft optical phonon, but instead a strong interaction between acoustic phonons and electrons. This point of view has recently extended by Pytte (1970), who exploited the analogy with Jahn–Teller systems; and a modification of Labbé and Friedel's basic ideas has been given recently by Sham (1971). Fortunately, in the intervening eight years since Anderson and Blount's theory appeared, the amount of experimental data has vastly improved. Shirane and Axe (1971a) were able to determine the low-temperature space group of Nb_3Sn via *elastic* neutron scattering. And the same authors (1971b) extended Testardi's soft acoustic phonon studies to large wave vector, by means of *inelastic* neutron scattering on Nb_3Sn. In addition, a central mode centered at $\omega = 0$ in the inelastic neutron spectrum was reported and interpreted by a theory analogous to Cowley's 1967 work.

Historically, Batterman and Barrett showed that V_3Si and Nb_3Sn underwent a transition from cubic O_h^3 space group ($Pm3m$) to an unidentified tetragonal structure, and the ultrasonic measurements of Testardi *et al.* showed that this distortion was accompanied by a softening of the transverse acoustic phonon (shear wave) along [110] directions. Anderson and Blount (1965) pointed out that according to Landau's theory the acoustic phonon frequency could not be the order parameter for the phase transition; the acoustic phonon must be driven soft by something else—and the "something else" must be the order parameter. They suggested two possibilities: one, an electron–acoustic phonon interaction "perhaps having to do with pairing," i.e. Cooper-pair formation; and two, optical phonon instability (soft-mode) and phonon–phonon coupling. They greatly prefered the latter hypothesis and described this possibility as a "ferroelectric metal," a term suggested by Matthias as perhaps characterizing the $M_x WO_3$ tungsten bronzes.

Subsequently, Perel *et al.* (1968) described the four possible tetragonal distortions in Nb_3Sn or V_3Si compatible with second-order transitions from the cubic O_h^3 space group. They are diagrammed in Fig. 58 and correspond to static displacements of the Nb sublattice having eigenvector of the Γ_{25}^-, Γ_{15}^-, $\Gamma^{+}{}_{15}$ and Γ_{12}^+ optical modes at $q = 0$.

The theoretical work of Birman (1965) and Klein and Birman (1970) was more restrictive in its conclusions: Only the Γ_{25}^- and Γ_{15}^- distortions were possible. These predictions were based on a screening argument. As the temperature lowers and the Fermi level falls into a region of very large electron density-of-states, the Coulombic forces are screened out and two $q=0$ optic modes become unstable. The Γ_{25}^- and Γ_{15}^- distortions Klein and Birman predict as possible may be compared with the two space groups $D_{2d}^5(P\bar{4}m2)$ and $C_{4v}^7(P4mc)$, earlier predicted as possible by Birman (1965). Unfortunately, the actual Nb_3Sn space group, as determined by Shirane and Axe (1971a), is $D_{4h}^9(P4_2/mmc)$. Thus, it is the $\Gamma_{12}^+(q = 0)$ mode displacements which actually occur, as diagrammed in Figure 58 from Perel *et al.* Although the predictions of Klein and Birman are completely wrong, their method of calculation affords some insight into the character of electron–phonon interactions in these materials.

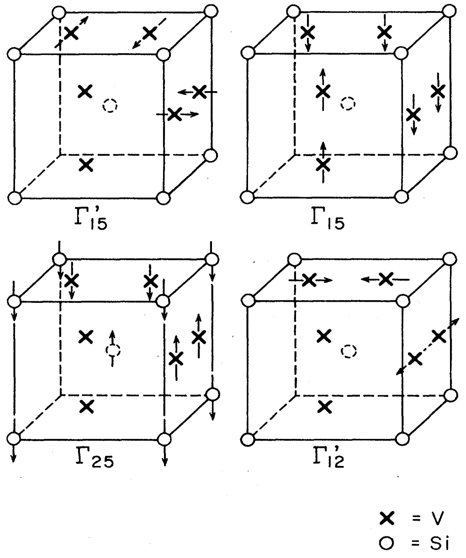

FIG. 58. Possible eigenvectors for phase transitions in V_3Si or Nb_3Sn (Perel *et al.*, 1968).

C. Neutron studies in Nb_3Sn

Shirane and Axe explain clearly the equivalence of ionic displacements in Nb_3Sn with the Γ_{12}^+ phonon which softens. They describe the acoustic phonon instability *and* the ionic displacements via a free-energy expression of form[7]

$$F_0 = (\tfrac{1}{2}\omega_0^2 Q_0^2 + \tfrac{1}{4}V_4 Q_0^4 + \cdots) + \tfrac{1}{2}Cu^2 + \tfrac{1}{2}du^2 Q_0^2 \cdots \tag{XII.1}$$

This equation contains a coupling term between elastic strain u and optical phonon displacement Q_0. The [110] shear strain has symmetry Γ_{12}^+. If the optical phonon had symmetry Γ_{15}^+, Γ_{15}^-, or Γ_{25}^-, then the term $u^2 Q_0^2$ is the lowest order coupling permitted by symmetry (i.e., the free energy must be a scalar). From this equation it would follow by minimizing free energy with respect to u, that

$$0 = \alpha F/\alpha u = Cu + dQ_0^2 u \tag{XII.2}$$

or

$$|u| = (d/c)Q_0^2. \tag{XII.3}$$

And in the case in which the soft-mode amplitude varied as

$$Q_0^2(T) = A|T - T_0|^{-1}, \tag{XII.4}$$

we would find an *induced* elastic anomaly

$$|u| = B|T - T_0|^{-1} \tag{XII.5}$$

just as we observed in $Gd_2(MoO_4)_3$ and $Tb_2(MoO_4)_3$. This is in fact the content of Anderson and Blount's hypothesis.

However, in the actual case of Nb_3Sn, as explained by Shirane and Axe, the ionic displacements Q_0 have the *same* Γ_{12}^+ symmetry as does the acoustic [110] shear wave u. Thus, a lower-order coupling is possible, viz.

$$F' = \tfrac{1}{2}\omega_1 Q_1^2 + \tfrac{1}{2}cu^2 + gQ_1 u + \cdots \tag{XII.6}$$

since $(\Gamma_{12}^+) \times (\Gamma_{12}^+)$ is a scalar. Minimizing this free energy F' with respect to u yields

$$u = (g/c)Q_1. \tag{XII.7}$$

Equation (XII.7), like Equation (XII.3), predicts that if an optic phonon softens in frequency and increases in amplitude, then an acoustic anomaly (elastic strain) will also occur. But Equation (XII.7) predicts that a sublattice displacement will occur which is *proportional* to the strain u even if no softening of $\omega_1(T)$ occurs.

If we substitute $u = (g/c)Q_1$ from Equation (XII.7) back into Equation (XII.6), we obtain

$$F' = \tfrac{1}{2}\omega_1^2 Q_1^2 + \tfrac{1}{2}(g^2 Q_1^2/c). \qquad \text{(XII.8)}$$

Minimizing F' with respect to Q_1 yields

$$c = -g^2/\omega_1^2 \qquad \text{(XII.9)}$$

Thus the total effective stiffness constant c' is normalized as

$$c' = c(T) - g^2/\omega_1^2(T) \qquad \text{(XII.10)}$$

which yields $c' = c(T)$ for $\omega_1 \to \infty$.

This implies that the shear instability ($c'(T_0) = 0$) may occur *either* by $\omega_1(T) \to 0$, or by $c(T) \to 0$. These are the theories of Anderson and Blount (1965), and Labbé and Friedel (1966), respectively. Thus the experimental data are still compatible with either theory.

Labbé and Friedel's work suggests that the partially filled, narrow d bands in these intermetallic compounds plays a key role in softening $c(T)$ in these materials via direct acoustic phonon–electron coupling. Indeed, to support this, no low-frequency soft optic mode has yet been observed in neutron scattering. However, it is still possible that both softening of $\omega_1(T)$ and $c(T)$ in Equation (XII.10) contribute to the actual phase transition in Nb_3Sn and V_3Si.

D. Central modes in Nb_3Sn

Finally, we should mention that in the inelastic neutron scattering experiments on Nb_3Sn, Shirane and Axe (1971) found an anomalous central component which was very narrow and increased in intensity as the transition temperature was approached. Their treatment of this mode is analogous to that in $SrTiO_3$, and relies on Cowley's theory, suitably extended to four-phonon interactions to include centric crystals. The basic idea is that at frequencies much larger than the average inverse lifetime of the acoustic phonon "bath," the propagation of phonons is in the collision-free (zero sound) regime. In the opposite, collision-dominated (first-sound) regime, the phonon damping must be renormalized [see Cowley (1967); Woodruff and Ehenreich (1961); Kwok *et al.* (1965); and Miller (1965)]. In contrast to $SrTiO_3$, where optic mode decay into acoustic phonons yields the central peak, in Nb_3Sn only acoustic phonons are involved.

Shirane and Axe have approximated the damping $\Gamma(\omega)$ as

$$\Gamma(\omega) = \Gamma_0 + \zeta^2(\alpha - i\omega)^{-1}, \qquad \text{(XII.11)}$$

which, when inserted into the usual expression for scattering cross section

$$S(\omega) = (kT/\hbar\omega)\,\mathrm{Im}(\omega_0^2 - \omega^2 + i\omega\Gamma)^{-1} \qquad \text{(XII.12)}$$

yields

$$S(\omega) = \left(\frac{kT}{\hbar}\right)\Gamma_0 + \frac{\delta^2\alpha}{\omega^2+\alpha^2}\left[\left(\omega_\infty^2 - \frac{\delta^2\alpha^2}{\omega^2+\alpha^2} - \omega^2\right)^2 + \omega^2\left(\Gamma_0 + \frac{\delta^2\alpha}{\omega^2+\alpha^2}\right)^2\right]^{-1}, \qquad \text{(XII.13)}$$

where $\omega_\infty^2 = \omega_0^2 + \delta^2$.

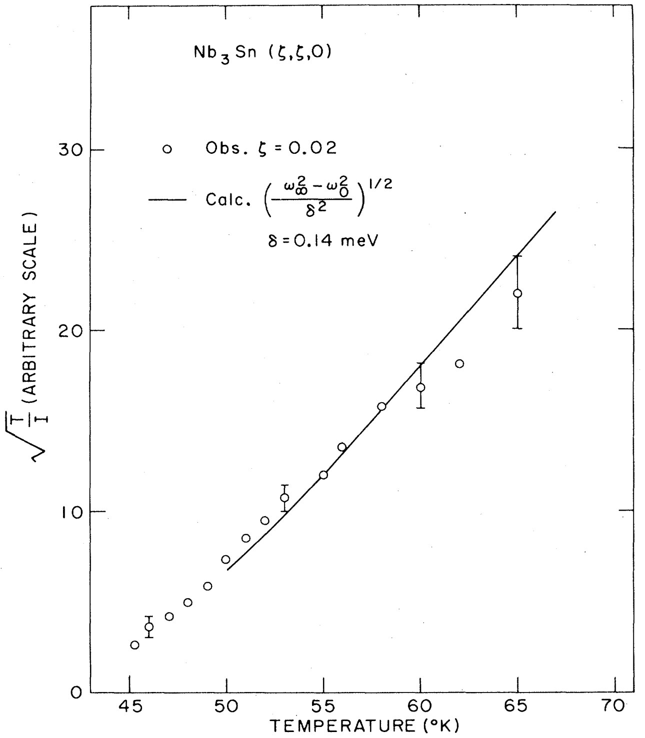

FIG. 59. Cross section vs T for central mode in Nb_3Sn (Shirane and Axe, 1971a).

Application of Eq. (XII.13) to the central part ($\omega = 0$) of the spectrum yields

$$I(T) = AT\delta^2/\omega_\infty^2(\omega_\infty^2 - \delta^2), \qquad \text{(XII.14)}$$

where ω_∞ is the frequency of the acoustic phonons for $T \gg 50°K$. The experimental results are in good agreement with Eq. (XII.14); Figure 59 shows the linear T dependence. Here δ is deduced to be $1.1 \pm 0.3\ \mathrm{cm}^{-1}$.

We must emphasize three points in closing this discussion: First, the central modes discussed by the authors cited above are distinctly analogous to those described by Mountain (1966) in fluids, where a central peak in the response arises due to density fluctuations; second, in order to demonstrate critical behavior in solids associated with diverging central mode intensities, it is still necessary to show the narrowing of the central mode linewidth, as first pointed out by Benedek (1969); third, in general, it is difficult to distinguish experimentally between central modes due to disorder, as in $NaNO_2$, and those due to self-energy anomalies, as in $SrTiO_3$–one must show that a large body of data (Curie constants, x-ray data, and measured exponents for central intensity and soft mode frequency) are all self-consistent.

XIII. SUMMARY

In closing, it appears to this reviewer that the experimental studies of soft modes have taken us from a macroscopic description of structural phase transitions in which thermodynamic characterizations were important, and order parameters, if specified at all, were bulk properties such as spontaneous polarization—to a microscopic picture in which the order parameter is a specific ionic displacement, often a rotation. This new microscopic framework has finally permitted contact with subtle aspects of statistical mechanics, particularly in the deviation from mean-field theory and in the occurrence of central modes in the response functions of the crystals studied.

Future work on soft modes will probably emphasize complex systems in which macroscopic phenomena are coupled. For example, $BaMnF_4$ is simultaneously ferroelectric, antiferroelectric, and antiferromagnetic. Nickel–iodine–boracite is simultaneously ferroelectric and ferromagnetic. Microscopic dynamical analyses of these systems warrant detailed theoretical and experimental study.

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