Anomalous Acoustic Dispersion in Centrosymmetric Crystals with Soft Optic Phonons*

J. D. Axe
Brookhaven National Laboratory, Upton, New York 11973
and
IBM Watson Research Center, Yorktown Heights, New York 10598

AND

J. Harada and G. Shirane
Brookhaven National Laboratory, Upton, New York 11973

(Received 14 August 1969)

A careful study of the dispersion of the transverse acoustic phonons and the low-frequency transverse optic phonons in $KTaO_3$ has been carried out by inelastic neutron scattering. In addition to the well-known temperature dependence of the optic-mode frequencies, both the acoustic-phonon frequencies and the neutron-scattering cross sections of the TO and TA phonons with $\mathbf{q}$ along [100] show a marked temperature dependence. This anomalous behavior is not, however, revealed in ultrasonic velocity measurements. By means of a long-wavelength expansion of the lattice-dynamical equations, we show that these phenomena are the result of quasiharmonic coupling of optic- and acoustic-like excitations. In centrosymmetric crystals, this interaction vanishes as the wave vector $\mathbf{q} \rightarrow 0$, in such a way as to leave the limiting acoustic velocity unaffected. The existence of this interaction suggests the possibility of a soft Brillouin-zone-center optic phonon precipitating an instability in a mode with mixed acoustic-optic character and nonzero wave vector, giving rise to an antiferroelectric (or microtwinned ferroelectric) phase.

I. INTRODUCTION

It is by now a well-established fact that the ferroelectric phase transformations which occur in several cubic perovskites result from an instability of a long-wavelength optical phonon.[1,2] More or less typical is the behavior of the lowest-frequency optic-phonon branch in $KTaO_3$, an incipient ferroelectric with an optic-phonon branch which tends toward, but never achieves, instability at the lowest temperatures.[3] This behavior is demonstrated directly in the data depicted in Fig. 1, which was obtained in the present study. More extensive data of this type, involving phonons with different wave vectors, $\mathbf{q}$, is summarized in Fig. 2. These results indicate that all of the transverse-optic (TO) modes with $\mathbf{q}=(\zeta,0,0)a^*$ show a marked temperature dependence, but the variation is most striking in the vicinity of the minimum at the Brillouin zone (BZ) center ($\mathbf{q}=0$). The increasing instability of this mode as the temperature is lowered accounts for the divergent low-frequency dielectric response characteristic of ferroelectric materials. Somewhat more unexpectedly, $\mathbf{q}=(\zeta,0,0)a^*$ transverse acoustic (TA) mode frequencies also show a remarkably strong temperature dependence, which is not only of much larger magnitude than typical, but of opposite sign. (Most materials become acoustically softer with increasing temperature.) This observation, first made by Shirane, Nathans, and Minkiewicz,[4] is all the more remarkable because of the fact that ultrasonic velocity measurements in $KTaO_3$ by Barrett[5] show that at very long wavelengths ($\mathbf{q} \rightarrow 0$) the $(\zeta,0,0)$ TA phonon frequencies have a rather low and "normal" (i.e., negative) temperature dependence. Barrett tentatively suggested that this apparent discrepancy between the two types of measurements might have resulted from the presence of small amounts of impurities deliberately incorporated into the sample investigated by neutron scattering. Yamada and Shirane[6] remarked upon the qualitatively similar behavior exhibited in $SrTiO_3$ and also noted that in this material the temperature dependence of the neutron-scattering cross sections for the soft $[\zeta 00]$ TO and the TA phonons could not be accounted for by the usual changes in the thermal occupation factors.

Several authors have discussed the acoustic-optic mode coupling mechanism by which soft optic modes cause elastic and piezoelectric anomalies in noncentrosymmetric crystals.[7–9] Lefkowitz and Hazony[10] have discussed the temperature dependence of the frequency of acoustic modes of cubic centrosymmetric lattices (such as $SrTiO_3$ and $KTaO_3$) on the basis of an oversimplified model which predicts elastic instabilities similar to those which can occur in noncentrosymmetric lattices. In fact, there are distinct differences between the acoustic-optic mode interaction in centrosymmetric and noncentrosymmetric structures. It is the purpose of the present paper to examine in detail the nature of optic-acoustic mode interaction in centrosymmetric

* Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] P. W. Anderson, in *Fizika Dielectrikov*, edited by G. I. Skanavi (Akademica Nauk SSSR Fizicheskii Institute, Moscow, 1960).
[2] W. Cochran, Advan. Phys. **9**, 387 (1960).
[3] S. H. Wemple, Phys. Rev. **137**, A1575 (1964).
[4] G. Shirane, R. Nathans, and V. J. Minkiewicz, Phys. Rev. **157**, 396 (1967).
[5] H. H. Barrett, Phys. Letters **26A**, 217 (1968).
[6] Y. Yamada and G. Shirane, J. Phys. Soc. Japan **26**, 396 (1969).
[7] W. Cochran, Advan. Phys. **10**, 401 (1961).
[8] V. Dvorak, Phys. Rev. **167**, 525 (1968).
[9] P. B. Miller and J. D. Axe, Phys. Rev. **163**, 924 (1967).
[10] I. Lefkowitz and Y. Hazony, Phys. Rev. **169**, 441 (1968).

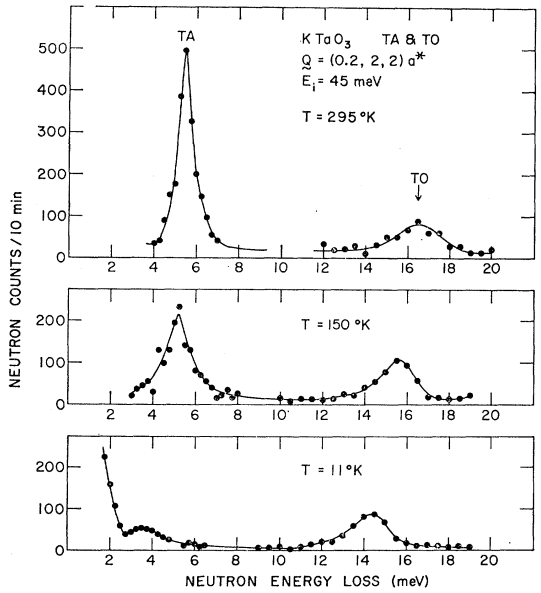

FIG. 1. Examples of inelastically scattered neutron groups in $KTaO_3$ illustrating the temperature-dependent frequencies and scattering cross sections for the TA and lowest-frequency TO modes with $q=(0.2,0,0)a^*$. Due to finite resolution elastic Bragg scattering is seen below about $\Delta E=3$ meV.

crystals, particularly in relation to the understanding of ferroelectric phase transformations.

In the Appendix we develop a long-wavelength expansion of the dynamical equations of a complex (i.e., non-Bravais) lattice. This formalism admits, in Sec. II, to further obvious simplifications useful in discussing the interaction of a nearly unstable optic phonon branch with other branches. By this means we show in particular that in centrosymmetric crystals there exists quasiharmonic coupling of optic- and acoustic-like excitations which does not, however, affect the limiting acoustic velocities, nor does it affect the macroscopic elastic properties. In Sec. III we present the results of an inelastic neutron-scattering study of some of the anomalous low-frequency transverse phonons in $KTaO_3$ and demonstrate that the acoustic-optic mode coupling mechanism outlined above provides a quantitative description of these observations. Finally, in Sec. IV we suggest that the existence of mode interaction of this type must, in certain cases, influence the course of displacive phase transformations. In such cases, although the driving force for the transformation is the collapse of a $\mathbf{q}=0$ optic-phonon mode, the lattice first becomes unstable against a coupled excitation with a nonzero wave vector.

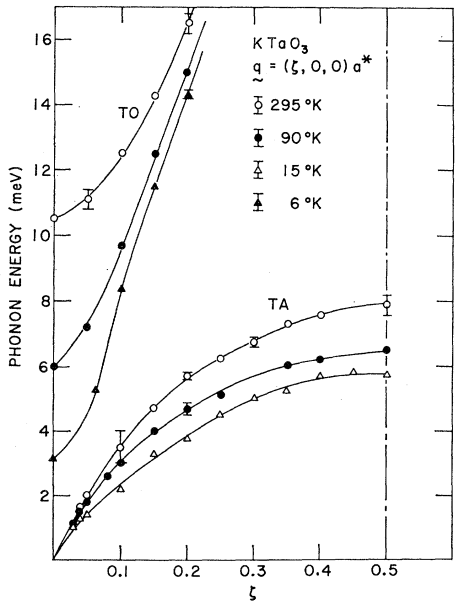

FIG. 2. Summary of the temperature-dependence dispersion curves for $(\zeta,0,0)$ TA and soft TO phonons in $KTaO_3$.

II. ACOUSTIC-OPTIC MODE INTERACTION IN CENTROSYMMETRIC LATTICES

In order to discuss the microscopic theory of elastic behavior, Born and Huang[11] introduced the method of long waves which consists of an expansion and solution of the lattice-dynamical equations in successive powers of the magnitude, q, of the wave vector of the phonons. Because it was primarily directed at terms which affected the acoustic velocities in the limit $\mathbf{q}\rightarrow 0$, Born's development is not sufficiently general for the present purpose. In the Appendix we have extended this method in order to derive the expressions relevant to our discussion. After expansion of the dynamical equations in a power series in q, the equations are subjected to a transformation which diagonalizes the $q=0$ contributions, leaving nondiagonal parts which are small for small q and which exhibit an explicit q dependence. In this formalism the equations governing the mode eigenfrequencies $\omega(j\mathbf{q})$ [Eq. (A11)] are

$$|[\omega^2(j\mathbf{q})-\omega_0^2(j\hat{q})]\delta_{jj'}-q^2F_{jj'}{}^{(2)}(\hat{q}) +q^4F_{jj'}{}^{(4)}(\hat{q})+\cdots|=0, \quad (1)$$

where $\omega_0(j\hat{q})$ is the eigenfrequency of the $q=0$ mode belonging to the jth phonon branch. [Because of the well-known singular behavior of Coulombic lattice sums, the $\omega_0(j\hat{q})$ may depend upon the direction $\hat{q}$ of the wave vector even as $\mathbf{q}\rightarrow 0$, as long as electromagnetic retardation is neglected.] The expansion is even in q for centrosymmetric lattices and the matrix elements $F_{jj'}{}^{(n)}(\hat{q})$ which are responsible for dispersion of the phonon branches are seen from Eq. (A10) to be projections of the harmonic dynamical matrix onto the space of the $\mathbf{q}=0$ eigenvectors. We emphasize that the effects being discussed are essentially *harmonic* in origin, and that anharmonicity is invoked only implicitly to

[11] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1962), Chap. V.

provide temperature dependent mode frequencies (the so-called "quasiharmonic approximation").

The transformation performed consists of an expansion of the eigenstates at nonzero $\mathbf{q}$ in terms of the complete set of $\mathbf{q}=0$ eigenstates

$$w_{k\alpha}(j\mathbf{q})=\sum_{j'} S_{jj'}w_{k\alpha}{}^{0}(j'),$$

and results in the appearance of the off-diagonal elements of the matrices $\mathbf{F}^{(n)}(\hat{q})$ which have the effect of coupling together these $\mathbf{q}=0$ basis states. "Mode coupling" is a convenient descriptive term to describe this situation an we shall adopt it. It is important to realize, however, that although the actual physical situation we are describing is one of renormalizing or "recoupling" of temperature-dependent harmonic modes, the description of what, in fact, constitute the uncoupled basis modes is arbitrary. The $q=0$ modes are chosen as the basis set because the resulting formalism is extremely convenient, and because of the singular nature of the $q=0$ acoustic eigenmodes.

For a general direction of $\mathbf{q}$ all branches are coupled. When $\mathbf{q}$ is along a high symmetry direction in the BZ certain of the elements $F_{jj'}{}^{(n)}(\hat{q})$ may be shown to vanish for all n; i.e., some branches become noninteracting. In fact only modes which transform according to the same irreducible representations of the group of the wave vector $\mathbf{q}$ under consideration will interact with one another.

If the off-diagonal elements are small (small q), Eq. (1) may be solved by standard perturbation techniques, a useful procedure for examining some of the characteristics of the solutions. Further specializing to the eigenfrequencies of the three acoustic branches, for which $\omega_0{}^2(j_a,\hat{q})=0$,

$$\omega^2(j_a,\mathbf{q})=[F_{j_aj_a}{}^{(2)}(\hat{q})]q^2 + \left[F_{j_aj_a}{}^{(4)}(\hat{q})-\sum_{j'}\frac{F_{j_aj'}{}^{(2)}(\hat{q})^2}{\omega_0{}^2(j')}\right]q^4+\cdots. \quad (2)$$

Suppose we are considering the high-temperature paraelectric phase of a typical displacive ferroelectric, with one branch exhibiting typical unstable soft-mode behavior, which for the sake of definiteness we might assume to be of the form $\omega_0{}^2(j')=\alpha(T-T_c)$. Equation (2) shows that we should expect a corresponding temperature-dependent *softening* of the acoustic branch. But one notices further that this anomalous contribution to the acoustic-mode frequency is of lowest order q^4 and is thus without effect upon the limiting acoustic velocity $(\partial\omega_{j_a}/\partial q)_{q=0}=|F_{j_aj_a}{}^{(2)}|^{1/2}$. The macroscopic elastic behavior is therefore not affected, a point we have previously anticipated. [In noncentrosymmetric lattices, the expansion of the dynamical matrix contains, in general, off-diagonal terms *linear* in q, leading to quadratic contributions to $\omega^2(j_a\mathbf{q})$ proportional to $-\sum_{j'}|F_{j'j_a}{}^{(1)}|^2/\omega_0{}^2(j')$. These are the internal-strain contributions to the elastic constants mentioned previously, which in conjunction with soft-optic modes, do give rise to anomalous elastic behavior in noncentrosymmetric lattices.[9]]

The mixed acoustic-optic character of the phonons directly affects the polarization vectors of the modes, and when the coupling is strongly temperature dependent as in ferroelectrics, this effect is necessarily reflected in temperature-dependent changes in the cross section for inelastic neutron scattering. In the harmonic approximation the integrated inelastic neutron-scattering cross section for a phonon of wave vector $\mathbf{q}$ is given by

$$\frac{d\sigma}{d\Omega}\propto\frac{k_f}{k_i}\frac{n(j\mathbf{q})+1}{\omega(j\mathbf{q})}|F_{in}(j\mathbf{Q})|^2. \quad (3)$$

Here k_i and k_f are the momenta of the incident and scattered neutrons and $(\mathbf{k}_i-\mathbf{k}_f)=\mathbf{Q}$ is the momentum transferred to the crystal. $n(j\mathbf{q})$ is the phonon occupation number for a phonon of frequency $\omega(j\mathbf{q})$. $\mathbf{Q}$ is related to the wave vector of the phonon by $\mathbf{Q}=\mathbf{q}+\mathbf{G}$, where $\mathbf{G}$ is a reciprocal lattice vector. The inelastic structure factor for the $(j\mathbf{q})$th normal mode may be written as

$$F_{\text{inel}}(j\mathbf{Q})=\sum_{k}^{\text{unit cell}} m_k{}^{-1/2}[\mathbf{Q}\cdot\mathbf{w}_k(j\mathbf{q})]b_k e^{-W_k}e^{i\mathbf{G}\cdot\mathbf{R}_k}. \quad (4)$$

Here b_k and e^{-W_k} are, respectively, the neutron-scattering length and the Debye-Waller factor for the kth nucleus. Due to the coupling effects we have been considering, aside from temperature dependent changes in $\omega(j\mathbf{q})$, W_k and n, there occur changes in the polarization vectors $\mathbf{w}_k(j\mathbf{q})$. Using Eq. (A8), we may express the structure factor at a general $(j\mathbf{q})$ in terms of the structure factors of the $q=0$ modes, as observed at the nearest reciprocal lattice point $\mathbf{G}$;

$$F_{\text{inel}}(j\mathbf{Q})=\sum_{j'} S_{jj'}F_{in}(j'\mathbf{G}), \quad (5)$$

where we have additionally assumed that $\mathbf{Q}\cdot\mathbf{w}_k(j\mathbf{q})\approx\mathbf{G}\cdot\mathbf{w}_k(j\mathbf{q})$, and $W_k(\mathbf{Q})\approx W_k(\mathbf{G})$, since $\mathbf{q}$ is small compared with $\mathbf{G}$.

The perovskite lattice is sufficiently complex (15 branches for a general direction of $\mathbf{q}$) that some simplification of Eq. (1) is desirable. By limiting $\mathbf{q}$ to the high symmetry directions ([100], [110], [111]) the 15×15 secular determinant factors into three 5×5 determinants, representing one set of coupled longitudinal modes and two sets of transverse ones.[12] In the case of the transverse excitations further simplification is afforded by an approximation which immediately suggests itself. Near the BZ center, particularly at temperatures near T_c[13] the TA and soft TO branches

[12] A general description of the symmetry properties of the normal modes for a perovskite lattice can be found in the work of R. A. Cowley, Phys. Rev. **134**, A981 (1964).

[13] R. C. Miller and W. G. Spitzer, Phys. Rev. **129**, 94 (1963).

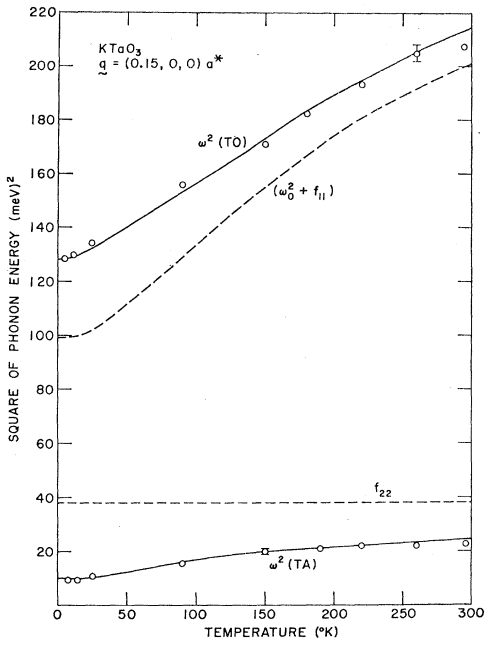

FIG. 3. A comparison of the observed and calculated eigenfrequencies of the (0.15,0,0) TA and soft TO phonons. [Note that the ordinate is ω^2, i.e., the eigenvalues of the dynamical matrix, Eq. (6).] The dotted lines represent the diagonal elements of Eq. (6), and indicate the extent to which the TA mode is depressed and the TO mode raised by the off-diagonal term. The only temperature-dependent parameter necessary to give this agreement is the $q=0$ TO eigenfrequency, $\omega_0(T)$.

are at much lower frequencies than the remaining "hard" TO modes which may therefore be neglected. Thus along the high-symmetry $\mathbf{q}$ directions, we may approximately limit our attention to two coupled modes, and the secular determinant assumes the simple form

$$\begin{vmatrix} \omega_0^2+f_{11}(\mathbf{q})-\omega^2(\mathbf{q}) & f_{12}(\mathbf{q}) \\ f_{12}(\mathbf{q}) & f_{22}(\mathbf{q})-\omega^2(\mathbf{q}) \end{vmatrix}=0, \qquad (6)$$

where $f_{ij}\equiv F_{ij}^{(2)}q^2+F_{ij}^{(4)}q^4+\cdots$, $\omega_0^2(\mathrm{TO})=\omega_0^2$, and $\omega_0^2(\mathrm{TA})=0$. It is generally accepted that the strongly temperature-dependent soft-optic mode characteristic of displacive ferroelectrics results from rather normal temperature variation of long- and short-range harmonic forces which happen to nearly cancel for the soft mode. Thus the existence of a soft mode in no way implies exceptional temperature dependences for any of the interatomic force constants. Since this is the case it is reasonable, in the first approximation, to consider the quantities appearing in Eq. (6) to be temperature independent, with the sole exception of the $\mathbf{q}=0$ soft-mode frequency ω_0, for which measured temperature-dependent values may be substituted.

III. EXPERIMENTAL

Inelastic neutron-scattering experiments were performed on a triple axis crystal spectrometer at the Brookhaven High Flux Beam Reactor, using "constant-Q" scanning and incident neutron energies ranging from 13 to 45 meV. The $KTaO_3$ sample was grown by Linz by a top seeded solution technique and was approximately 9×14×17 mm, with mosaic spread of less than 3 min. There were no deliberately added impurities. The sample temperature was controlled to ±0.1°K at the lowest temperatures and within ±0.5°K above liquid N_2 temperatures.

A survey of the temperature dependence of the lowest transverse-phonon branches for which $\mathbf{q}=(\zeta,0,0)a^*$ is shown in Fig. 2. The room-temperature data are in good agreement with that of Shirane, Nathans, and Minkiewicz.[4] The frequencies of the TA mode at the BZ boundary at various temperatures are in generally good agreement with (uniformly 0.2 to 0.3 meV higher than) those deduced from second order Raman scattering by Nilsen and Skinner,[14] confirming the correctness of their assignment.

Because of the long-wavelength nature of the expansion developed in the Appendix, the majority of the temperature-dependent data was restricted to small q values, $0\leqslant q\leqslant 0.2a^*$. Plotted in Fig. 3, in a way convenient for subsequent analysis, are the observed frequency changes in both TA and soft TO branches

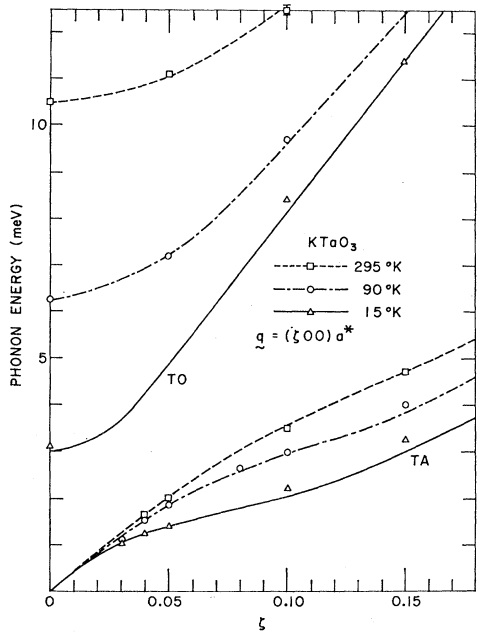

FIG. 4. A comparison of the wave-vector dependence of observed and calculated $(\zeta,0,0)$ TA and soft TO phonon eigenfrequencies. Notice that particularly at low temperatures, there is remarkably large dispersion even at these q values, which are smaller than typically studied by inelastic neutron scattering. The limiting slope at $q=0$ is temperature-independent and in agreement with ultrasonic velocity measurements. The size of the markers representing the points is roughly indicative of the experimental uncertainty.

[14] W. G. Nilsen and J. G. Skinner, J. Chem. Phys. 47, 1413 (1967).

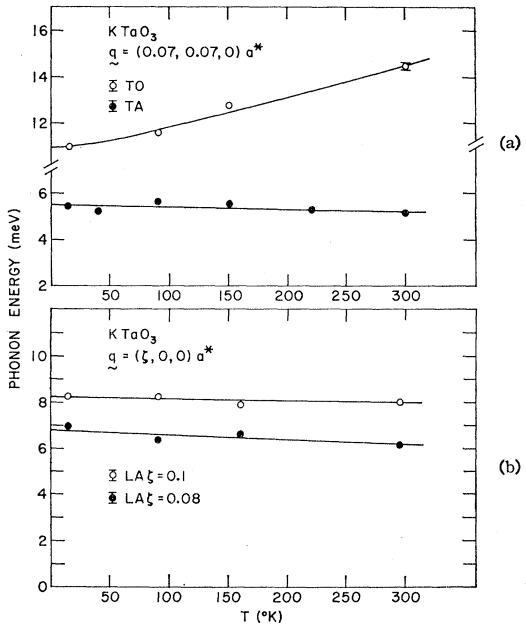

FIG. 5. (a) The temperature dependence of the TA and soft TO modes with $q=(0.7,0.7,0)a^*$ and displacements along $[\bar{1}10]$, and illustrating by comparison with Fig. 2 the anisotropy of the TA-TO coupling in $KTaO_3$. (b) The temperature dependence of $(\zeta,0,0)$ LA phonons is small and "normal" $(d\omega/dT<0)$, in contrast to the behavior of $(\zeta,0,0)$ TA modes.

for fixed $\mathbf{q}=(0.15,0,0)a^*$. Also shown for comparison are the results of a least-square fit of Eq. (1) to the observations, using the measured temperature dependence of $\omega_0^2(\mathrm{TO})$ and treating the three independent elements f_{ij} as adjustable but temperature-independent parameters. The good agreement demonstrates the approximate validity of two of the simplifying assumptions: temperature-independent dispersive terms $f_{ij}(q)$ and negligible influence from higher-frequency branches. The magnitude of the diagonal terms in Eq. (6) are also indicated in Fig. 3 to show the extent to which the TA mode is depressed and the TO mode raised in frequency by the off-diagonal term f_{12}. Comparably good agreement was obtained with similar data for phonons with $\mathbf{q}=(0.1,0,0)a^*$. For $\mathbf{q}=(0.2,0,0)a^*$ somewhat poorer but still reasonably good agreement was found. This indicates, perhaps, the limit at which the effect of higher-frequency modes can safely be ignored.

The best fitting values of the f_{ij} at three q values (0.1, 0.15, and $0.2a^*$) were used to determine the lowest terms in the power expansion in q. Writing $\mathbf{q}=(\zeta,0,0)a^*$ we obtain

$$f_{11}=4.67(\pm0.3)\times10^3\zeta^2-2.4(\pm0.7)\times10^4\zeta^4\ (\mathrm{meV})^2,$$
$$f_{22}=1.83(\pm0.8)\times10^3\zeta^2-0.8(\pm0.6)\times10^4\zeta^4\ (\mathrm{meV})^2, \quad (7)$$
$$f_{12}=2.80(\pm0.15)\times10^3\zeta^2-2.4(\pm0.4)\times10^4\zeta^4\ (\mathrm{meV})^2.$$

The quartic terms are negligible for ζ values smaller than about 0.05, and even higher order terms and/or inclusion of higher-frequency branches seem necessary for $\zeta>0.2$. From the leading term in f_{22} we predict a limiting (temperature-independent) transverse-acoustic-phonon velocity of $4.16(\pm0.1)\times10^5$ cm/sec, to be compared with the value $3.909(\pm0.01)\times10^5$ cm/sec at 300°K measured by Barrett.[5] The close agreement removes the apparent discrepancy between ultrasonic and previous neutron measurements.

In order to more fully investigate the $\mathbf{q}$ dependence of the mode coupling, further measurements of the behavior of $(\zeta,0,0)$ TA phonons at smaller ζ values were made using low energy (13 meV) incident neutrons to increase the resolution and minimize contamination from nearby Bragg scattering. Even at such small q values there is appreciable dispersion in the acoustic branch as evidenced by the failure of the measured points to extrapolate to $\omega=0$ as $q\rightarrow0$ (see Fig. 4). However, calculations based upon Eqs. (1) and (7) reproduce this unusually strong temperature-dependent dispersion with considerable accuracy in this small q region.

The dependence of the mode interaction on the *direction* of $\mathbf{q}$ was investigated briefly by observing the the temperature dependence of transverse (T_1) phonons with $\mathbf{q}=(\zeta,\zeta,0)a^*$ and displacements along $[1\bar{1}0]$. As shown in Fig. 5(a), the behavior of both the TA and TO modes differ markedly from that of their $(\zeta,0,0)$ counterparts. The frequencies of the TO modes increase much more rapidly with $\mathbf{q}$ along $[\zeta,\zeta,0]$ at low temperatures and there is a much smaller fractional frequency change with temperature. In contrast to the large positive $(\partial\omega/\partial T)$ found for $(\zeta,0,0)$ TA phonons, the $(\zeta,\zeta,0)$ TA phonon frequencies have a weakly negative normal temperature dependence. Thus along

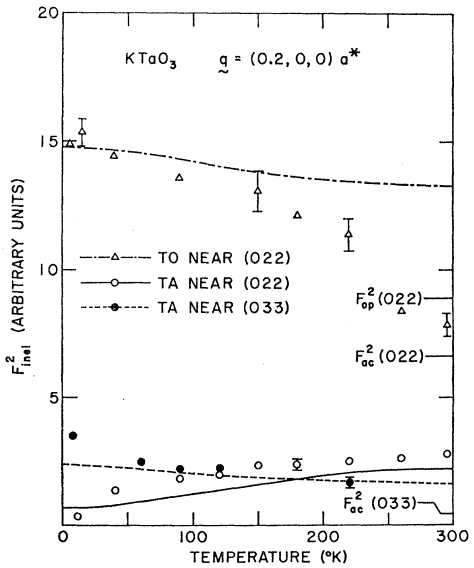

FIG. 6. A comparison of the observed changes in the inelastic structure factors, $F_{\mathrm{in}}(\mathbf{Q})$, with those calculated on the basis of TO-TA mode interaction. If the mode eigenvectors were independent of q (and thus equal to the $q=0$ eigenvectors), the structure factors for the respective modes should be given by $F_{ac}(022)$, $F_{op}(022)$, and $F_{ac}(033)$.

$[\zeta,\zeta,0]$ the effect of TO-TA mode coupling is so small as to be more than offset by the slight temperature dependence of f_{22}, which was completely negligible in discussing the behavior of $[\zeta,0,0]$ TA phonons.

The lowest LO mode at $q=0$ is neither particularly soft (24.8 meV at room temperature) nor does it display any exceptional temperature dependence.[15] We would therefore expect LO-LA mode interaction to be weak and nearly temperature-independent. Figure 5(b) shows, in agreement with these predictions, that the temperature dependence of a $(\zeta,0,0)$ LA phonon is again rather weak and "normal." No attempt was made to study the mode interaction in more general $\mathbf{q}$ directions.

Finally, we have observed changes in the inelastic scattering cross sections for $(\zeta,0,0)$ TO and TA phonons similar to those found in $SrTiO_3$.[6] Correction of the observed intensity data for temperature induced changes in the mode frequencies and thermal occupation factors $n(j\mathbf{q})$ reveals the presence of temperature-dependent structure factors, as demonstrated in Fig. 6. Note that the square of the structure factors for the same (0.2,0,0) TA phonon taken about different reciprocal lattice points show completely different behavior with temperature. These observations can be explained in a nearly quantitative manner as resulting from the same temperature-dependent TO-TA coupling mechanism that causes the frequency shifts we have just analyzed. From the least-square solution of Eq. (6) as a function of temperature it is straightforward to obtain temperature-dependent coefficients $S_{ij}(\mathbf{q})$ describing the mode eigenvectors in terms of the $q=0$ eigenvectors. What is additionally necessary [see Eq. (5)] is a knowledge of these $q=0$ eigenvectors in order to calculate the structure factor for the $q=0$ phonons at various reciprocal lattice points. The $q=0$ acoustic eigenvector is just an appropriately normalized uniform translation of the lattice [Eq. (A13)] and presents no difficulty. A study of the structure factor of the soft $q=0$ TO mode at many reciprocal lattice points has recently been used by the present authors to deduce the form of the soft mode eigenvector in $KTaO_3$ and other perovskites.[16] This information is all that is necessary to calculate the expected behavior of the inelastic structure factors.

A comparison of the calculated and measured values is shown in Fig. 6. A single multiplicative factor has been used to scale the observed data, which are relative measurements, in order to maximize the agreement with the calculations. We have assumed $e^{-W_k}=1$ for all atoms, which introduces little error in the present case. The calculations predict rather accurately the qualitative behavior of the TA structure factors, particularly the reversal of magnitude with changing temperature. A definite discrepancy appears to exist in the magnitude of the (022) TA structure factor and similarly develops in F_{op} at higher temperatures. In line with our previous discussion it is possible that this latter effect is due to the influence of higher-frequency modes. In view of the well-known difficulties involved in obtaining really accurate eigenfunctions by perturbation theory, the results shown in Fig. 6 are quite satisfactory. Note how greatly the actual structure factors differ from F_{inel} (022) and F_{inel} (033) which would apply if the eigenvector were those appropriate to $q=0$.

IV. DISCUSSION

The existing dynamical theory of displacive ferroelectrics describes a lattice distortion resulting from a $q=0$ phonon instability. Although this concept has proved enormously useful in discussing many ferroelectric phase transformations, there are questions which arise in connection with transformations in real systems which have not been fully answered. For example, the condensation of a $q=0$ mode gives rise to a new structure with a spatially uniform polarization. Yet in the absence of external fields real ferroelectrics invariably condense into domains with differently oriented polarization vectors, which must contain non-$q=0$ spatial components. It is perhaps worth pointing out that acoustic-optic mode interaction of the type under discussion provides one possible mechanism for incorporating such displacements into the general soft-mode scheme.

As a result of the interaction between acoustic and soft optic branches, the former are driven down developing a downward bulge of the sort indicated by the calculations shown in Fig. 4. An interesting question now arises. Is it not possible, in some cases, that before the $q=0$ soft optic mode frequency goes to zero, causing the appearance of a ferroelectric phase with uniform polarization, that the lattice might first become unstable with respect to an acoustic phonon with nonzero wave vector? If this were possible (we shall see that it is), such an unstable mode would give rise to a phase which differed from the parent phase by spontaneous displacements which would be sinusoidally modulated with a period and direction dictated by $\mathbf{q}_{\text{crit}}$ the wave vector of the unstable phonon mode. Furthermore, because of the coupled nature of the excitation, the displacements would necessarily give rise to a (sinusoidally modulated) spontaneous polarization. This simple description is adequate only at temperatures infinitesimally lower than the (presumed second-order) transformation temperature to this new staggered phase. Subsequent evolution of the condensed phase, complicated by further instabilities of modes with wave vectors adjacent to $\mathbf{q}_{\text{crit}}$ would require careful analysis, but can easily be conceived as giving rise to what might be alternately described as an antiferroelectric phase or as ferroelectric domains, depending upon the magnitude of the wave vectors involved.

[15] G. D. Boyd and R. C. Miller, quoted by A. S. Barker in *Ferroelectricity*, edited by E. F. Weller (Elsevier Publishing Co., New York, 1962), p. 237.

[16] J. Harada, J. D. Axe, and G. Shirane (to be published).

The condition that the two coupled modes described by Eq. (6) be stable with respect to their mutual interaction is simply

$$|f(q)| = \begin{vmatrix} \omega_0^2 + f_{11} & f_{12} \\ f_{12} & f_{22} \end{vmatrix} > 0.$$

The condition determining which mode wave vector, $\mathbf{q}_{\rm crit}$, first becomes unstable is given by requiring simultaneously that $|f(q)|=0$ and $\partial/\partial q|f(q)|=0$. Disregarding spurious solutions at large q, it is found that such an instability occurs only if

$$\begin{aligned} \beta &= \{F_{11}^{(2)}F_{22}^{(2)} - (F_{12}^{(2)})^2 + \omega_0^2 F^{(4)}\} < 0, \\ \gamma &= \{F_{11}^{(2)}F_{22}^{(4)} + F_{22}^{(2)}F_{11}^{(4)} - 2F_{12}^{(2)}F_{12}^{(4)}\} > 0. \end{aligned} \tag{8}$$

$\mathbf{q}_{\rm crit}$ and $\omega_0(\text{crit})$, the frequency of the $q=0$ soft mode at the transition temperature (and thus indirectly the transition temperature itself), are given by

$$\begin{aligned} q_{\rm crit}^2 &= -\tfrac{1}{2}\beta/\gamma, \\ \omega_0^2(\text{crit}) &= -(\beta/2F_{22}^{(2)})q_{\rm crit}^2. \end{aligned} \tag{9}$$

Assuming that the inequalities of Eq. (8) are satisfied, it appears that it is the β parameter which is decisive in determining the quantitative features of the proposed transformation. If $|\beta|$ is small the instability occurs at small q and at a temperature just above the ferroelectric transition temperature ($\omega_0^2=0$). For larger values of $|\beta|$ the instability involves shorter wavelength phonons and transformation temperatures further removed from the incipient $q=0$ instability. It is difficult to predict the behavior of the pertinent parameters for any given material, but it is reasonable to suppose that materials exist or will be found satisfying Eq. (9) for a considerable range of values of $\mathbf{q}_{\rm crit}$.

It must be pointed out that in materials which exhibit a real instability, e.g., $BaTiO_3$, the TO branch is often highly damped and the quasiharmonic approximation may not be adequate for a truly quantitative description of the transformation itself. For other materials not satisfying the instability criteria [e.g., $KTaO_3$, for which we find $\beta/(a^*)^2=(0.7\pm0.9)\times10^6$ (meV)^2, and $\gamma/(a^*)^4=52\times10^6$ (meV)^2] it would appear that a dynamical theory of domain formation is to be constructed from different considerations involving normal modes of finite samples, the role of surface charges and related unpleasant effects.

ACKNOWLEDGMENTS

We would like to express our thanks to Dr. M. DiDomenico and Dr. A. Linz for generously loaning us the excellent $KTaO_3$ sample used in this study.

APPENDIX: LONG-WAVE LATTICE DYNAMICS

In the harmonic approximation the vibrational normal modes of a lattice are determined by the dynamical matrix $C_{\alpha\beta}(kk',\mathbf{q})$

$$C_{\alpha\beta}(kk';\mathbf{q}) = (m_k m_{k'})^{-1/2} \sum_{l'} \Phi_{\alpha\beta}(lk;l'k') e^{-i\mathbf{q}\cdot[\mathbf{x}(lk)-\mathbf{x}(l'k')]}, \tag{A1}$$

where $\Phi_{\alpha\beta}(lk;l'k')$ is the harmonic force constant coupling atoms at the sites $\mathbf{x}(lk)$ and $\mathbf{x}(l'k')$. Expressing the wave vector $\mathbf{q}$ in terms of a unit vector $\hat{q}$ ($\mathbf{q}=q\cdot\hat{q}$), for a fixed direction of $\mathbf{q}$ the dynamical matrix can be expanded in a power series

$$C_{\alpha\beta}(kk';\mathbf{q}) = C_{\alpha\beta}^{(0)}(kk';\hat{q}) + iqC_{\alpha\beta}^{(1)}(kk';\hat{q}) + \tfrac{1}{2}q^2 C_{\alpha\beta}^{(2)}(kk';\hat{q}) + \cdots. \tag{A2}$$

By definition $C_{\alpha\beta}(kk';-\mathbf{q}) = C^*(kk';\mathbf{q})$ and therefore

$$C_{\alpha\beta}^{(n)}(kk';\hat{q}) = C_{\alpha\beta}^{(n)*}(kk';\hat{q}). \tag{A3}$$

If the lattice is centrosymmetric

$$C_{\alpha\beta}(kk';\mathbf{q}) = C_{\alpha\beta}^*(kk';\mathbf{q}),$$

i.e., the dynamical matrix is real, from which it follows that

$$C_{\alpha\beta}^{(n)}(kk';\hat{q}) = 0 \quad (n \text{ odd}). \tag{A4}$$

Since we are here exclusively concerned with centrosymmetric crystals, all odd order terms will henceforth be omitted.

Defining the displacements associated with the normal mode of wavevector $\mathbf{q}$ in the jth branch as

$$u_{kl\alpha}(j\mathbf{q}) = (m_k)^{-1/2} w_{k\alpha}(j\mathbf{q}) e^{i[\mathbf{q}\cdot\mathbf{x}(lk)-\omega(jq)t]}. \tag{A5}$$

The equation of motion of $w_{k\alpha}(j\mathbf{q})$ is given by

$$\omega^2(jq) w_{k\alpha}(j\mathbf{q}) = \sum_{k'\beta} C_{\alpha\beta}(kk';\mathbf{q}) w_{k'\beta}(j\mathbf{q}), \tag{A6}$$

and the eigenvectors of (A6) satisfy orthogonality and completeness relations

$$\begin{aligned} \sum_{k\alpha} w_{k\alpha}(j\mathbf{q}) w_{k\alpha}(j'\mathbf{q}) &= \delta_{jj'}, \\ \sum_{j} w_{k\alpha}(j\mathbf{q}) w_{k'\beta}(j\mathbf{q}) &= \delta_{\alpha\beta}\delta_{kk'}. \end{aligned} \tag{A7}$$

Since the eigenvectors at $q=0$, $w_{k\alpha}(j, q=0) \equiv w_{k\alpha}{}^0(j)$ are a complete set, the eigenvectors at finite q may be expanded in terms of them:

$$w_{k\alpha}(j\mathbf{q}) = \sum_{j'} S_{jj'} w_{k\alpha}{}^0(j'), \tag{A8}$$

where the transformation matrix $\mathbf{S}$ depends of course upon $\mathbf{q}$. Upon substituting Eq. (8) into Eq. (6), multiplying by $w_{k\alpha}{}^0(j)$, and summing the result upon $(k\alpha)$, one finds that

$$\omega^2(jq) S_{jj} = \sum_{j'} \{F_{jj'}{}^{(0)}(\hat{q}) + q^2 F_{jj'}{}^{(2)}(\hat{q}) + q^4 F_{jj'}{}^{(4)} + \cdots\} S_{jj'}, \tag{A9}$$

where

$$F_{jj'}{}^{(n)}(\hat{q}) = (n!)^{-1} \sum_{k\alpha;\, k'\beta} w_{k\alpha}{}^{0}(j) C_{\alpha\beta}{}^{(n)}(kk';\, \mathbf{q}) \times w_{k'\beta}{}^{0}(j'). \quad \text{(A10)}$$

Equation (9) is the familiar eigenvalue problem with solutions given by

$$|[\omega_0{}^2(j) - \omega^2(j\mathbf{q})]\delta_{jj'} + [q^2 F_{jj'}{}^{(2)}(\hat{q}) + q^4 F_{jj'}{}^{(4)}(\hat{q}) + \cdots]| = 0, \quad \text{(A11)}$$

where use has been made of the fact that

$$F_{jj'}{}^{0}(\hat{q}) = \omega^2(j,\, q=0)\delta_{jj'} \equiv \omega_0{}^2(j)\delta_{jj'}. \quad \text{(A12)}$$

The acoustic eigenvectors at $q=0$ consist of the uniform translations

$$w_{k\alpha}{}^{0}(j_a) = m_k{}^{1/2} v_\alpha(j_a), \quad \text{(A13)}$$

where $\mathbf{v}(j_a)$ is an arbitrary vector. There are thus three linearly independent eigenvectors $\mathbf{w}_k{}^{0}(j_a)$ with eigenfrequencies $\omega_0{}^2(j_a)=0$. The $\mathbf{w}_k{}^{0}(j_a)$ can be completely defined by requiring in addition to $\mathbf{w}^0(j_a)\cdot\mathbf{w}^0(j_a') = \delta_{j_a, j_a'}$ [Eq. (A7)], that $F_{j_a, j_a'}{}^{(2)}=0$ if $j_a \neq j_a'$. If there are other degeneracies in the optic branches at $q=0$ any arbitrariness in the eigenvectors $\mathbf{w}^0(j_0)$ can also be removed by requiring within the degenerate set that $F_{j_0, j_0'}{}^{(2)}=0$ for $j_0 \neq j_0'$.

PHYSICAL REVIEW B VOLUME 1, NUMBER 3 1 FEBRUARY 1970

Effect of the Spin-Phonon Interaction on the Thermal Conductivity

D. WALTON
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830*
and
Department of Physics, McMaster University, Hamilton, Ontario, Canada
(Received 11 June 1969)

The effect of dilute concentration of the Kramers ion, Yb^{+++}, and the non-Kramers ion, Ni^{++}, on the thermal conductivity of CaF_2 has been measured as a function of magnetic field at various temperatures in the range 0.3–1.3°K. The results have been compared with a theory due to Elliott and Parkinson based on the Jacobsen and Stevens dispersion relations. It has been found that it is possible to account for the effect of temperature on the change in conductivity with magnetic field in both cases, for fields such that $g\beta H/kT < 6$. If the temperature dependence is factored out of the expression for the change in conductivity, the remaining terms predict that at low fields it should increase as $H^{7/2}$ for the Kramers ions, and as $H^{5/2}$ for the non-Kramers ions, unless a zero-field splitting is present which dominates, and then the change in conductivity should increase as H^3 increases. The Yb-doped crystal yielded an $H^{7/2}$, and the Ni-doped yielded an H^3 dependence in agreement with the theory.

INTRODUCTION

THE first data on the thermal conductivity of a system for which the spin-phonon interaction is important were obtained by Morton *et al.*[1] for holmium ethylsulphate. The characteristic behavior of these systems lies in the variation of the conductivity K with magnetic field at fixed temperature. Typically, K is expected to first decrease with field, then reach a minimum, and recover finally to a value equal to the zero-field value if the magnetic ion obeys Kramers's rule, or an amount greater than this for the non-Kramers ions.

Qualitatively, this behavior is readily understood in terms of a strong interaction between the spins and a band of phonons whose frequencies are close to the Larmor frequency of the spin system (see Fig. 1); at low temperatures, the phonon carrier distribution is a function which has a maximum. The interaction suppresses the contribution of those carriers close to the Larmor frequency (see Fig. 2). As the field is increased, more important carriers are affected until the peak in the distribution is reached, after this the interaction occurs at less important frequencies until at very high fields the interaction is with phonons whose contribution is negligible.

Because the spin-phonon interaction affects the conductivity by suppressing a relatively narrow band of phonon frequencies, the variation of thermal conductivity with magnetic field forms a convenient phonon spectrometer,[2,3] which has been used[4] to study the resonant scattering by the Li ion in KCl. For this reason, it is important to understand in some detail how the spin-phonon interaction modifies the conductivity.

For those ions which do not obey Kramers's rule, an interaction is possible at zero magnetic field, which is removed at very high fields and, as McClintock *et al.*[5]

* Research supported by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[1] I. P. Morton and H. M. Rosenberg, Phys. Rev. Letters **8**, 200 (1968).

[2] R. Berman, J. C. F. Brock, and D. J. Huntley, Phys. Letters **3**, 310 (1963).

[3] D. Walton, Phys. Rev. **151**, A267 (1966).

[4] D. Walton, Phys. Rev. Letters **19**, 305 (1967).

[5] P. V. E. McClintock, I. P. Morton, and H. M. Rosenberg, in *Proceedings of the International Conference on Magnetism, Nottingham, England, 1964* (The Institute of Physics and the Physical Society, London, England, 1965), p. 455.