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Elastic and Dielectric Anomalies and the Lattice-Dynamical Theory of Ferroelectric Phase Transitions*

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The lattice-dynamical theory of ferroelectric phase transitions relates the dielectric anomaly with an anomalous "softening" of a TO mode as $q\to 0$. It is shown that the elastic anomalies, which are commonly observed at ferroelectric phase transitions, are predicted by the lattice-dynamical theory of ferroelectricity, within a diatomic approximation. The softening of the TO mode is associated with variations in $d(\omega_{\mathrm{TA}})/dq$ which are reflected in the behavior of the transverse and shear elastic constants. The discussions are extended to more complicated systems and are illustrated by an examination of the available neutron scattering data on the temperature dependence of the dispersion curves of the TO and TA modes of $SrTiO_3$ and $KTaO_3$.

THE dielectric anomalies of the ferroelectric phase transitions are commonly associated with anomalies in the elastic properties.[1,2] The two anomalies may be shown to be intimately connected with the lattice dynamical instability in potassium ferrocyanide $[K_4Fe(CN)_6\cdot 3H_2O]$.[3] Imry, Pelah, and Wiener have proposed a dynamical model which associates the dielectric and elastic anomalies of KH_2PO_4(KDP) with the cooperative motion of the protons in the lattice.[4] The lattice-dynamical theory, as proposed by Cochran[5] and Anderson,[6] associates the ferroelectric transition with a low-lying TO mode for which $\omega_{\mathrm{TO}}\to 0$ at $q\to 0$ when $T\to T_c$. The purpose of this paper is to show the interdependence of the elastic and dielectric anomalies within a diatomic approximation of the lattice-dynamical theory of ferroelectricity. Cochran has discussed this interdependence for the special case of a zinc-blende structure.[7]

The 6×6 matrix that describes the lattice dynamics of an alkali halide in a symmetry direction factors into three sets of 2×2 matrices, and leads to the characteristic equations[8]

$$\begin{vmatrix} A_{11}(q)-m_1\omega^2 & A_{12}(q) \\ A_{12}^*(q) & A_{22}(q)-m_2\omega^2 \end{vmatrix}=0. \qquad (1)$$

This expression is general; where more than nearest-neighbor interactions are included, all the A coefficients are q-dependent. The solution of Eq. (1) for a given q gives two frequencies. For positive solutions of ω^2, A_{11} and A_{22} must be positive. The solutions may be expressed:

$$\omega_o^2(q)=B(q)+[B^2(q)-C(q)]^{1/2}, \qquad \text{(optic)} \quad (2a)$$

$$\omega_a^2(q)=B(q)-[B^2(q)-C(q)]^{1/2}, \qquad \text{(acoustic)} \quad (2b)$$

where

$$B(q)=\frac{1}{2}\left(\frac{A_{11}(q)}{m_1}+\frac{A_{22}(q)}{m_2}\right)=\tfrac{1}{2}\mathrm{Tr}\,D, \qquad (3a)$$

$$C(q)=\frac{A_{11}(q)}{m_1}\frac{A_{22}(q)}{m_2}-\frac{A_{12}(q)}{m_1}\frac{A_{12}^*(q)}{m_2}=|D|. \qquad (3b)$$

The determinant D is obtained by dividing the first row of A by m_1 and the second row by m_2.

The relation between the elastic constant E and the dispersion curve for the acoustic branch is given by[9]

$$\omega_a^2(q\to 0)=(2\pi/s)^2(E/\rho)q^2, \qquad (4)$$

where s is the length of the unit cell and the density is $\rho=(m_1+m_2)/s$. Taylor expansion of Eq. (2b) gives

$$\omega_a^2(q\to 0)=B(q)-B(q)\{1-\tfrac{1}{2}[C(q)/B^2(q)]+\cdots\}$$
$$=\tfrac{1}{2}[C(q)/B(q)]. \qquad (2c)$$

Combination of Eqs. (4) and (2c) gives

$$E=\tfrac{1}{2}\rho(s/2\pi)^2[C(q)/B(q)q^2]. \qquad (5)$$

At $q=0$, the determinant A becomes[7]

$$|A(0)|=\begin{vmatrix} A_{11}(0) & -A_{11}(0) \\ -A_{11}(0) & A_{11}(0) \end{vmatrix}. \qquad (6)$$

Assuming that all the elements of A are continuous in q and dividing each by $B(q)$ one obtains

$$C(q)=[m_1m_2/(m_1+m_2)^2]B^2(q)P(q), \qquad (7)$$

where $P(q)$ is a polynomial whose first term is a_2q^2.

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TABLE I. Temperature dependence of ω_{TO} and ω_{TA}.

$\mathrm{SrTiO_3}$		296°K	90°K	28°K	$\omega(296°\mathrm{K})/\omega(90°\mathrm{K})$
ω_{TO} [a]	$q=(0.2, 0, 0)$	4.1	3.5		1.17
ω_{TA} [b]	$q=(0.2, 0, 0)$	1.92	1.63		1.18
$\mathrm{KTaO_3}$					$\omega(296°\mathrm{K})/\omega(28°\mathrm{K})$
ω_{TO} [c]	$q=(0.25, 0, 0)$	13.5		10.7	1.26
ω_{TA} [d]	$q=(0.38, 0, 0)$	5.5		3.75	1.46

[a] Reference 10, Fig. 7, energy in 10^{12} Hz.

[b] Reference 10, Fig. 6, energy in 10^{12} Hz.

[c] Reference 11, Fig. 1, energy in meV.

[d] Reference 11, Fig. 4, energy in meV. [Conversion factors: $(\mathrm{meV\,cm})^{-1}=8.07$; $(\mathrm{Hz/meV})=0.242\times10^{-12}$.]

Substituting Eqs. (2a) and (7) into Eq. (5) gives

$$E=\tfrac{1}{4}\rho(s/2\pi)^2[m_1m_2/(m_1+m_2)^2]a_2\omega_o^2(0). \qquad (8)$$

The proportionality between the elastic constant E and ω_o^2 implies that a dielectric anomaly, where $\omega_{\mathrm{TO}}\rightarrow0$ at $q\rightarrow0$, should be associated with an elastic anomaly. Equation (2a) describes the dispersion curve of the optic branch whose polarization vector describes the relative motion of the positive ions in the unit cell against the motion of negative ions and may, therefore, be denoted as the "ferroelectric mode." Substitution of Eq. (3) into Eq. (4) gives

$$\omega_a^2(q\rightarrow0)=\tfrac{1}{4}[m_1m_2/(m_1+m_2)^2]a_2q^2\omega_o^2(0). \qquad (9)$$

It is clear from Eq. (9) that if $\omega_{\mathrm{TO}}\rightarrow0$ at $q\rightarrow0$ ($q\neq0$), then ω_{TA} must change anomalously for the same q.

ω_a^2, a_2, and ω_o^2 depend differently on the long- and short-range interactions in the solid. One may construct a situation in which the temperature dependence of a_2 and ω_o^2 cancel and leave ω_a^2 unchanged. Such a situation will require cancellation of the temperature dependence of many unrelated parameters and cannot be considered a general case.

The elastic constants are determined by the square of the slopes of the acoustic branches at $q\rightarrow0$ [Eq. (4)]. Pure shear elastic constants are determined by the appropriate TA branches, while the transverse elastic constants are determined by combinations of TA and LA modes. The anomalous behavior of the shear elastic constant at the phase transition will, therefore, depend on the temperature dependence of the frequency of the ferroelectric mode at $q\rightarrow0$.

This diatomic treatment may be extended to more complicated cases like $\mathrm{BaTiO_3}$, where the crystalline structure below T_c suggests that the ferroelectric mode is the transverse optic mode in which all the positive ions (Ba and Ti) are vibrating in phase against all the negative ions (oxygen).

Direct measurements of the temperature dependence of the frequencies of both the TO and TA modes have been performed by Cowley[10] on $\mathrm{SrTiO_3}$ and by Shirane, Nathans, and Minkievicz[11] for $\mathrm{KTaO_3}$ using inelastic neutron scattering techniques. Careful examination of their data shows that, for similar values of q, the frequencies of both the TO and TA modes indeed show a similar dependence on temperature. The experimental results are summarized in Table I.

This treatment may be extended to more complicated solids if one considers the relative displacements of the center of mass of the positive and negative charges, respectively. The amplitude of this vibration will be predominantly determined by the optical vibration in which all the positive ions are vibrating in phase against all the negative ions, and Eq. (1) should hold. Since in the more complicated solids there may be several different ions of the same charge, other optical vibrations will also make small contributions. If the ferroelectric mode is one in which all the positive ions vibrate against all the negative ions, the dielectric anomaly should be accompanied by an elastic anomaly involving shear. Since the elastic constant E may vanish as a result of $a_2\rightarrow0$ [Eq. (8)] with no change in ω_o^2, the inverse is not always true.

When $d(\omega_{\mathrm{TA}})/dq$ changes at $q\rightarrow0$ and a dielectric anomaly occurs, this may be considered as strong evidence that a lattice-dynamical instability occurs and that $\omega_{\mathrm{TO}}\rightarrow0$. The only alternative explanation requires the accidental occurrence of an elastic anomaly at the same temperature as the ordering of a system of permanent dipole moments. Such an explanation is unlikely since the elastic anomalies have been observed for a wide range of ferroelectric materials. If the coincidence between the two anomalies is not accidental, then when a dielectric anomaly occurs and an elastic (shear or transverse) anomaly is also observed, the mechanism of the transition must involve the lattice dynamics of the structure and $\omega_{\mathrm{TO}}\rightarrow0$ at $q\rightarrow0$. Many ferroelectric transitions that have been previously classified as order-disorder transitions can now be identified as lattice-dynamical transitions. Some important examples are potassium dihydrogen phosphate,[1] potassium ferrocyanide,[3] guinadine sulphate hexahydrate,[1] and Rochelle Salt.[1]

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