PHYSICAL REVIEW B VOLUME 1, NUMBER 12 15 JUNE 1970

Theory of a Structural Phase Transition in Perovskite-Type Crystals. II. Interaction with Elastic Strain

J. Feder

Institute of Physics, University of Oslo, Blindern, Norway

and

E. Pytte

IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

(Received 17 December 1969)

The interaction between soft-optical-mode coordinates and the elastic strain at structural phase transitions that have as soft modes linear combinations of the triply degenerate Γ_{25} optical mode at the R corner of the Brillouin zone are discussed with the help of a model Hamiltonian. The effect of the interaction on the soft-mode frequencies, the angle of rotation, and the strain distortions are calculated. The theory is compared with experimental results for $SrTiO_3$ and $LaAlO_3$, and good agreement is obtained with the available experimental data.

I. INTRODUCTION

A number of ABO_3 compounds with perovskite structure have structural phase transitions from the cubic high-temperature phase to a tetragonal or trigonal low-temperature phase which involve rotation of the BO_6 octahedra. Recently, a great deal of experimental[1-22] and theoretical[23-27] knowledge has been accumulated. $SrTiO_3$,[1-14] in particular, has been investigated by a wide range of experimental techniques, and will together with $LaAlO_3$,[6,15-20] be used in order to compare the theory with the experimental results.

The rotation of the oxygen octahedra may be either around a cube axis, as in $SrTiO_3$, to give a tetragonal distortion, or around a cube diagonal to give a trigonal distortion as in $LaAlO_3$. In both cases, the octahedra in neighboring unit cells rotate in opposite directions. Associated with these phase transitions is an optical-phonon instability, the soft mode being the triply degenerate Γ_{25} optical mode at the R corner of the Brillouin zone.

In a previous paper[25] (hereafter referred to as I) these phase transitions were discussed using a model Hamiltonian expressed in terms of localized normal mode coordinates describing the rotation of the oxygen octahedra. Although the model gave a good qualitative description of the phase transition, quantitative agreement with all the experimental results could not be obtained. In particular, for $SrTiO_3$, whereas the soft-mode frequencies and the temperature dependence of the rotation angle were well described by the model, the value obtained for the magnitude of the angle was too large, suggesting that additional interactions need to be taken into account. The importance of the coupling to the strains has been emphasized by Slonczewski and Thomas,[27] and in this paper we extend the calculations in I to include this interaction.

The derivation of a model Hamiltonian describing the interaction is presented in Sec. II. In Sec. III, we derive a coupled set of equations determining the soft-mode frequencies, the static values of the strains and the correlation functions using the equation of motion approach discussed in I. The required thermal averages are determined in a molcular field approximation. The derivation will be presented only for the case of tetragonal distortion. The corresponding set of equations for trigonal distortion is given in Sec. IV. In Sec. V, the theory is compared with experimental data, and the model parameters determined by a best-fit procedure.

II. MODEL HAMILTONIAN

In I, a Hamiltonian was constructed in terms of vectors $\vec{R}(l)$ describing the rotations of the oxygen octahedra and their canonically conjugate momenta $\vec{P}(l)$. This Hamiltonian had the form

$$H_R=\tfrac{1}{2}\sum_{ll'}\vec{P}(l)\cdot\vec{\theta}^{-1}(ll')\cdot\vec{P}(l')+\tfrac{1}{2}\sum_{ll'}\vec{R}(l)\,\vec{v}(ll')\cdot\vec{R}(l')+\tfrac{1}{2}\sum_{ll',\,\lambda\lambda'}\Gamma_{\lambda\lambda'}(ll')\times[R_\lambda(l)-R_\lambda(l')]^2[R_{\lambda'}(l)-R_{\lambda'}(l')]^2\quad,\quad(1)$$

where ll' refer to the different unit cells, and the index λ to the components along the cube axes.

A model Hamiltonian describing the interaction between the elastic strain and the normal mode coordinates $\vec{R}(l)$ may be obtained by expanding the potential energy of the distorted crystal in terms of the strain and the oxygen ions displacement fields. This Hamiltonian is of the form

$$H_{\text{int}}=\sum g_{ijk\alpha\beta}e_{ij}(lk)u_{\alpha}(lk)u_{\beta}(lk) \quad , \tag{2}$$

where $e_{ij}(lk)$ are localized strain tensor components and where $\vec{u}(lk)$ is the displacement of the kth oxygen ion in the lth unit cell from its equilibrium position $\vec{X}(lk)$ due to the rotational degrees of freedom. The oxygen site has tetragonal symmetry, and Eq. (2) has six independent coupling constants. The displacements of the individual oxygen ions may be expressed in terms of the operators $\vec{R}(l)$ by the transformation[25]

$$\vec{u}(lk)=\vec{\xi}_k\times[\vec{R}(l+k)-\vec{R}(l)](2m_0a^2)^{-1/2}. \tag{3}$$

Here

$$\vec{\xi}_1=a(1,0,0),\ \vec{\xi}_2=a(0,1,0),\ \vec{\xi}_3=a(0,0,1), \tag{4}$$

where a is the lattice constant of the cubic structure and m_0 is the mass of the oxygen ion. As long as we are only interested in the coupling to long-wavelength acoustic phonons, the k dependence of the strain components $e_{ij}(lk)$ may be neglected. Then the interaction Hamiltonian may be written

$$\begin{aligned}H_{\text{int}}=\sum_{ll'}&G_{\alpha\beta ij\lambda\lambda'}[e_{\alpha\beta}(l)+e_{\alpha\beta}(l')]\\&\times\gamma_{ij}(ll')[R_{\lambda}(l)R_{\lambda'}(l')+R_{\lambda}(l')R_{\lambda'}(l)] \quad .\end{aligned} \tag{5}$$

The coupling constants $G_{\alpha\beta ij\lambda\lambda'}$ are listed in the Appendix. Because $u_k(lk)=0$, Eq. (5) contains only four independent coupling constants.

The nonlocal form of this Hamiltonian reflects the fact that oxygen ions forming a given octahedron belong to more than one unit cell. When expressed in terms of its Fourier transform

$$\gamma_{ij}(ll')=\frac{1}{N}\sum_{\vec{q}}e^{i\vec{q}\cdot[\vec{X}(l)-\vec{X}(l')]}\gamma_{ij}(\vec{q}) \ , \tag{6}$$

the coupling function γ_{ij} has the simple form

$$\begin{aligned}\gamma_{ij}(\vec{q})&=\tfrac{1}{2}[1-\cos q_i a] \qquad \text{for } i=j \ ,\\&=\tfrac{1}{2}[1-\cos q_k a] \qquad \text{for } i\neq j\neq k \ ,\end{aligned} \tag{7}$$

where i, j, and k refer to the three-cube axes.

Because $\gamma_{ij}(\vec{q}=0)=0$, (8)

the interaction Hamiltonian vanishes when all the octahedra rotate in phase as required on physical grounds as this leaves all the oxygen ions undisplaced. We also note that

$$\gamma_{ij}(\vec{q}_R)=1 \quad , \tag{9}$$

for all i and j, where $\vec{q}_R$ is the wave vector at the R corner of the Brillouin zone.

Because the operators $\vec{R}(l)$ defined in I have the units $(\text{energy})^{1/2}\times\text{sec}$, and because $\gamma_{ij}(ll')$ have been chosen to be dimensionless, the coupling constants G_{ij} defined in the Appendix have the dimension of $1/\text{sec}^2$.

The Hamiltonian describing long-wavelength acoustic phonons may be expressed in terms of the localized strain tensor components. For cubic symmetry, we obtain

$$\begin{aligned}H_e=\tfrac{1}{2}\sum_l M\dot{u}(l)^2+\tfrac{1}{2}C_{11}\sum_l&[e_{11}(l)^2+e_{22}(l)^2\\&+e_{33}(l)^2]+C_{12}\sum_l[e_{11}(l)e_{22}(l)+e_{11}(l)\\&\times e_{33}(l)+e_{22}(l)e_{33}(l)]\\&+2C_{44}\sum_l[e_{12}(l)^2+e_{13}(l)^2+e_{23}(l)^2] \quad ,\end{aligned} \tag{10}$$

where $\vec{u}(l)$ is the displacement of the c. m. of the lth unit cell from its equilibrium position $\vec{X}(l)$ due to the acoustic-phonon modes, and M is the total mass of the unit cell. The constants C_{ij} have units of energy and are related to the usual elastic constants c_{ij} by

$$C_{ij}=a^3c_{ij} \quad . \tag{11}$$

The Hamiltonian given by Eqs. (1), (5), and (10) has the symmetry appropriate for the cubic perovskite structure. The distortion from cubic symmetry below the transition temperature is described by nonvanishing expectation values of the operators $R_{\lambda}(l)$ and the strains $e_{ij}(l)$. The strain tensor $e_{ij}(l)$ will, however, have nonvanishing expectation values also in the cubic phase above the transition temperature which then describes usual thermal expansion. We set

$$R_{\lambda}(l)=\langle R_{\lambda}(l)\rangle+r_{\lambda}(l) \quad , \tag{12}$$

where the brackets denote the thermal average and where $r_{\lambda}(l)$ describes the fluctuation about this average value. As the direction of the displacement alternates from one cell to the next, we write

$$\langle R_{\lambda}(l)\rangle=A_{\lambda}e^{i\vec{q}_R\cdot\vec{X}(l)} \quad , \tag{13}$$

where for tetragonal distortion

$$A_{\lambda}=A\delta_{\lambda 1} \quad . \tag{14}$$

For the strain tensor, we set

$$e_{ij}(l)=\langle e_{ij}(l)\rangle+u_{ij}(l) \quad . \tag{15}$$

The fluctuations about the average values of the strain may be expressed in terms of the normal mode coordinates of the acoustic phonons in the usual way,

$$u_{ij}(l)=\frac{i}{2\sqrt{N}}\sum_{\mu\vec{q}} e^{i\vec{q}\cdot\vec{X}(l)} \times\left[q_i e_j(\mu\vec{q})+q_j e_i(\mu\vec{q})\right] Q(\mu\vec{q}) \quad , \tag{16}$$

where $Q(\mu\vec{q})$ is the normal mode coordinate for the μth acoustic branch of frequency $\omega(\mu\vec{q})$, wave vector $\vec{q}$, and polarization vector $\vec{e}(\mu\vec{q})$.

When Eq. (15) is substituted in the elastic Hamiltonian equation (10), it separates into static terms, terms which are linear in the fluctuation $u_{ij}(l)$ and terms which are quadratic in the fluctuations. For tetragonal distortion, in which case

$$\begin{aligned} \langle e_{ij}(l)\rangle &= 0 \ , \qquad\qquad i\neq j \\ \langle e_{11}(l)\rangle &= e_1 \quad , \\ \langle e_{22}(l)\rangle &= \langle e_{33}(l)\rangle = e_2 \quad , \end{aligned} \tag{17}$$

the static part of the Hamiltonian takes the form

$$H_e^{(s)}=C_{11}(e_1^2+\tfrac{1}{2}e_1^2)+C_{12}(e_2^2+2e_1e_2) \quad . \tag{18}$$

The linear term may be written

$$H_e^{(l)}=\left[(C_{11}+C_{12})e_2+C_{12}e_1\right]\sum_l\left[u_{22}(l)+u_{33}(l)\right] +(C_{11}e_1+2C_{12}e_2)\sum_l u_{11}(l) \quad . \tag{19}$$

The term quadratic in the fluctuations is most conveniently expressed in terms of the acoustic normal mode coordinates,

$$H_e^{(f)}=(1/2M)\sum P(\mu,-\vec{q}) +\tfrac{1}{2}M\sum \omega_0^2(\mu\vec{q})\,Q(\mu\vec{q})Q(\mu,-\vec{q}) \quad , \tag{20}$$

where $P(\mu\vec{q})$ is the canonical conjugate momentum to $Q(\mu\vec{q})$,

$$\left[Q(\mu\vec{q}),\ P(\mu'\vec{q}\,')\right]=i\delta_{\mu\mu'}\delta_{\vec{q}\vec{q}'} \quad . \tag{21}$$

Similarly, the strain variables in H_{int} may be expressed in terms of the static strains and the acoustic normal mode coordinates $Q(\mu\vec{q})$ by means of Eqs. (15) and (16).

III. EQUATIONS OF MOTION SELF-CONSISTENCY CONDITIONS

The equations of motion for the operators $r_\lambda(l)$ are calculated as in I. Relationships between A, e_1, e_2, and the correlation functions involving pairs of operators r_λ are obtained by requiring that the static parts of the equations of motion be equal to zero. From the r_λ equations we obtain, in the notation of I.

$$A\left[\omega_0^2(\vec{q}_R)+\Gamma_1(2A^2+3\Delta_1{}^{(1)})+2\,\Gamma_2\Delta_2{}^{(1)}+2\Gamma_1\Delta_1{}^{(2)} +(\Gamma_1+2\Gamma_2)\,\Delta_1^{(3)}+2G_{11}e_1+4G_{12}e_2\right]=0 \quad . \tag{22}$$

The equations of motion are linearized by replacing pairs of operators r_λ by their thermal average and by neglecting quadratic terms of the type $r_\lambda Q(\mu)$. Further we neglect in this paper the resonant coupling between the eigenfrequencies ϵ_λ associated with the normal mode coordinate r_λ and the acoustic-phonon frequencies ω_μ. The effect of the resonant interaction[28] as well as the quadratic terms $r_\lambda Q(\mu)$ are discussed elsewhere.[26] For the optical-phonon frequencies ϵ_λ, we then obtain

$$\epsilon_1^2(\vec{q}_R)=\omega_0^2(\vec{q}_R)+3\Gamma_1(2A^2+\Delta_1{}^{(1)})+2\Gamma_2\Delta_2{}^{(1)} +2\Gamma_1\Delta_1{}^{(2)}+(\Gamma_1+2\Gamma_2)\,\Delta_1{}^{(3)}+2G_{11}e_1+4G_{12}e_2 \ , \tag{23}$$

$$\epsilon_{2,3}^2(\vec{q}_R)=\omega_0^2(\vec{q}_R)+\Gamma_2(2A^2+\Delta_1^{(1)})+(3\Gamma_1+\Gamma_2)\Delta_2^{(1)} +2\Gamma_1\Delta_2^{(2)}+(\Gamma_1+2\Gamma_2)\Delta_2{}^{(3)}+2G_{11}e_2+2G_{12}(e_1+e_2) \ , \tag{24}$$

where for simplicity we have given the form of $\epsilon_\lambda^2(\vec{q})$ only for $\vec{q}=\vec{q}_R$. When $G_{ij}=0$, Eqs. (22)–(24) reduce to those given in I where also the various constants and the correlation functions $\Delta_\lambda^{(\alpha)}$ are defined.

The equations of motion for $Q(\mu\vec{q})$ are derived from the Hamiltonian with the help of the commutation relation Eq. (21). Requiring the static parts to vanish, we obtain

$$C_{11}e_1+2\,C_{12}e_2+\tfrac{1}{2}G_{11}(2A^2+\Delta_1^{(4)})+G_{12}\,\Delta_2^{(5)} +G_{13}(\Delta_2^{(4)}-\Delta_2{}^{(5)})=0 \ , \tag{25}$$

$$C_{11}e_2+C_{12}(e_1+e_2)+\tfrac{1}{2}G_{12}(2A^2+\Delta_1^{(4)}+\Delta_2^{(4)}) +\tfrac{1}{4}G_{11}(\Delta_2^{(4)}+\Delta_2^{(5)})-\tfrac{1}{2}G_{13}(\Delta_2^{(4)}-\Delta_2^{(5)})=0 \quad , \tag{26}$$

where we have introduced

$$\Delta_1^{(4)}=I_{12}=I_{13}\ ,\ \ \Delta_2^{(4)}=I_{21}=I_{31}\ ,\ \ \Delta_2^{(5)}=I_{23}=I_{32}\ , \tag{27}$$

with $$I_{\lambda\lambda'}=\frac{2}{N}\sum_{\vec{q}}\gamma_{\lambda'\lambda'}(\vec{q})\,\Delta_{\lambda\lambda}(\vec{q}) \quad , \tag{28}$$

where $$\Delta_{\lambda\lambda}(\vec{q})=\langle r_\lambda(\vec{q})\,r_\lambda(-\vec{q})\rangle \quad , \tag{29}$$

as defined in I.

In the present approximation in which the equations of motion are linearized and the resonant coupling between the acoustic and optical phonons are neglected, the acoustic-phonon frequencies are not affected by the interaction.

Equations (22)–(26) may be derived alternatively by a free energy approach analogous to that used in I.[29,30]

As in I, the thermal averages will be determined in a molecular field approximation in which the wave-vector-dependent interaction tensors are approximated by their average values over the Brillouin zone. Upon averaging, all the correlation functions vanish except $\Delta_1^{(1)}=\Delta_1^{(4)}\equiv\Delta_1$, $\Delta_2^{(1)}=\Delta_2^{(4)}=\Delta_2^{(5)}\equiv\Delta_2$, and the molecular field equations take the form

$$C_{11}e_1+2C_{12}e_2+\tfrac{1}{2}G_{11}(2A^2+\Delta_1)+G_{12}\Delta_2=0, \qquad (30)$$

$$C_{11}e_1+C_{12}(e_1+e_2)+\tfrac{1}{2}G_{12}(2A^2+\Delta_1+\Delta_2)+\tfrac{1}{2}G_{11}\Delta_2=0 \quad , \qquad (31)$$

$$A[\omega_0^2(\vec{q}_R)+\Gamma_1(2A^2+3\Delta_1)+2\Gamma_2\Delta_2 + 2(G_{11}e_1+2G_{12}e_2)]=0 \quad , \qquad (32)$$

$$\Delta_1=\langle r_1(l)\,r_1(l)\rangle=\frac{1}{\omega_1}\coth\frac{\beta\omega_1}{2} \quad , \qquad (33)$$

$$\Delta_2=\langle r_2(l)\,r_2(l)\rangle=\langle r_3(l)\,r_3(l)\rangle =\frac{1}{\omega_2}\coth\frac{\beta\omega_2}{2} \quad , \qquad (34)$$

$$\omega_1^2=2\,\Omega_0^2+3\Gamma_1(2A^2+\Delta_1)+2\Gamma_2\Delta_2 + 2(G_{11}e_1+2G_{12}e_2) \quad , \qquad (35)$$

$$\omega_2^2=2\Omega_0^2+\Gamma_2(2A^2+\Delta_1)+(3\Gamma_1+\Gamma_2)\Delta_2 + 2[G_{11}e_2+G_{12}(e_1+e_2)] \quad . \qquad (36)$$

The molecular field energies ω_λ are used only to determine the thermally averaged quantities A, e_1, e_2, Δ_1, and Δ_2. The true excitations of the system are given by Eqs. (23) and (24).

In the molecular field equations and in the expressions for eigenfrequencies at $\vec{q}=\vec{q}_R$ only the three cubic coupling constants G_{11}, G_{12}, and G_{44} enter.

From Eqs. (30) and (31), the strains may be expressed in terms of the order parameter A and the correlation functions Δ_1 and Δ_2. We obtain

$$e_1=-\frac{1}{6}\left(\frac{2C_1}{G_{11}-G_{12}}+\frac{C_2}{G_{11}+2G_{12}}\right)(2A^2+\Delta_1) -\frac{1}{6}\left(\frac{-2C_1}{G_{11}-G_{12}}+\frac{2C_2}{G_{11}+2G_{12}}\right)\Delta_2 \quad , \qquad (37)$$

$$e_2=-\frac{1}{6}\left(\frac{-C_1}{G_{11}-G_{12}}+\frac{C_2}{G_{11}+2G_{12}}\right)(2A^2+\Delta_1) -\frac{1}{6}\left(\frac{C_1}{G_{11}-G_{12}}+\frac{2C_2}{G_{11}+2G_{12}}\right)\Delta_2 \quad , \qquad (38)$$

where we have introduced the constants

$$C_1=\frac{(G_{11}-G_{12})^2}{C_{11}-C_{12}} \quad , \quad C_2=\frac{(G_{11}+2G_{12})^2}{(C_{11}+2C_{12})} \quad . \qquad (39)$$

With the help of Eqs. (37) and (38) the strains may be eliminated from the remaining equations. For $T< T_a (A\neq 0)$, Eq. (32) may be written

$$(2\Gamma_1-\tfrac{4}{3}C_1-\tfrac{2}{3}C_2)A^2+\omega_0^2(\vec{q}_R)+(3\Gamma_1-\tfrac{2}{3}C_1-\tfrac{1}{3}C_2)\Delta_1 +(2\Gamma_2+\tfrac{2}{3}C_1-\tfrac{2}{3}C_2)\Delta_2=0 \quad . \qquad (40)$$

The molecular field energies for $T< T_a$ take the form

$$\omega_1^2=[2\Omega_0^2-\omega_0^2(\vec{q}_R)]+4\Gamma_1A^2 \quad , \qquad (41)$$

$$\omega_{2,3}^2=[2\Omega_0^2-\omega_0^2(\vec{q}_R)]+2(\Gamma_2-\Gamma_1+C_1)A^2 +(\Gamma_2-3\Gamma_1+C_1)(\Delta_1-\Delta_2) \quad , \qquad (42)$$

when we make use of Eqs. (37), (38), and (40). From Eqs. (37) and (38), the c/a ratio in the tetragonal phase is given by

$$\frac{c}{a}-1=e_1-e_2=-\frac{C_1}{2(G_{11}-G_{12})}(2A^2+\Delta_1-\Delta_2). \qquad (43)$$

The transition temperature is determined from Eq. (40) by noting that $A\to 0$ and $\Delta_{1,2}\to\Delta$ as $T\to T_a$. We obtain

$$\Delta(T_a)=-\omega_0^2(\vec{q}_R)/(3\Gamma_1+2\Gamma_2-C_2). \qquad (44)$$

For $T>T_a$, $\omega_1=\omega_{2,3}\equiv\omega$. Using Eq. (44), the molecular field equations may be written

$$\omega^2=[2\Omega_0^2-\omega_0^2(\vec{q}_R)]+(3\Gamma_1+2\Gamma_2-C_2)[\Delta(T)-\Delta(T_a)] \quad , \qquad (45)$$

$$\Delta=\frac{1}{\omega}\coth\frac{\beta\omega}{2} \quad . \qquad (46)$$

The contribution to the thermal expansion for $T>T_a$ is given by

$$e=e_1=e_2=-\frac{C_2}{2(G_{11}+2G_{12})}\Delta \quad . \qquad (47)$$

Similarly, the soft-optical-mode frequencies may be written

$$\epsilon_1^2(\vec{q}_R)=4\,\Gamma_1A^2 \quad , \qquad (48)$$

$$\epsilon_{2,3}^2(\vec{q}_R)=2(\Gamma_2-\Gamma_1+C_1)A^2+(\Gamma_2-3\Gamma_1+C_1)(\Delta_1-\Delta_2) \quad \text{for } T< T_a, \qquad (49)$$

and $\epsilon^2(\vec{q}_R)=(3\Gamma_1+2\Gamma_2-C_2)[\Delta-\Delta(T_a)]$ for $T>T_a$. (50)

From the requirement that $\epsilon_\lambda^2>0$, we obtain stability conditions for the tetragonal and cubic phases.

We note, that the self-consistency equations (33), (34), (40)–(42), and (44)–(46) depend on the constants C_{ij} and G_{ij} only in the combinations C_1 and C_2. These equations may be solved by iteration for any given set of the six-model parameters Ω_0^2, $\omega_0^2(\vec{q}_R)$, Γ_1, Γ_2, C_1, and C_2 to determine A, e_1, e_2, Δ_1, and Δ_2. These molcular field values are then used to calculate the soft-mode frequencies from Eqs. (48)–(50). When in addition the elastic constants are known, the strains are obtained from Eqs. (37) and (38).

For $T\sim T_a$, it follows from the molecular field equations that

$$\Delta_{1,2}(T) - \Delta(T_a) \propto |T - T_a| , \qquad A^2 \propto |T - T_a| , \tag{51}$$

and the soft-mode frequencies vanish at T_a, as

$$\epsilon_\lambda^2(\vec{q}_R) \propto (|T - T_a|)^{1/2} . \tag{52}$$

We obtain the same temperature dependence of the soft modes and of the order parameter near T_a as in I. The phase transition remains of second order also, when the interactions with the strains are taken into account, and the qualitative conclusions in I remain unchanged. As in I, the singlet soft-mode frequency in the low-temperature phase has the same temperature dependence as the order parameter A or the rotation angle φ; whereas, the frequency of the doubly degenerate mode has a more complicated temperature dependence. We also note that the change in the c/a ratio is not proportional to ϕ^2.

IV. TRIGONAL DISTORTION

In the case of trigonal distortion, we obtain from simple symmetry considerations

$$\begin{aligned} A_\lambda^2 &= \tfrac{1}{3}A^2 && \text{for all } \lambda , \\ \langle e_{ij}(l)\rangle &= e_1 && \text{for } i=j , \\ &= e_2 && \text{for } i \neq j , \\ \langle r_\lambda(l) r_{\lambda'}(l)\rangle &= \Delta_1 && \text{for } \lambda = \lambda' , \\ &= \Delta_2 && \text{for } \lambda \neq \lambda' . \end{aligned} \tag{53}$$

The equations appropriate for trigonal distortion may be obtained formally from Eqs. (33), (34), (37)–(42), and (44)–(50) derived for the tetragonal case by a simple replacement of model parameters, strain, and correlation functions according to the prescription given in Table I.

The deviation from cubic symmetry, the rhombicity, is measured by the angle α included by the rhombohedral axes. In terms of the strains,

$$\cos\alpha = 2\langle e_2\rangle . \tag{54}$$

V. COMPARISON WITH EXPERIMENTS

For $SrTiO_3$, the variation of the rotation angle with temperature,[4,6] the soft-mode frequencies,[5,7,8] the elastic constants,[10] the thermal expansion, and the c/a ratio[9] have all been measured. In addition, measurements have been made of the pressure dependence of transition temperature[11] and the shift in the sound velocity, at T_a,[10,12–14] which yield information concerning the coupling constants G_{ij}. The theory presented in I contained four model parameters which were well overdetermined by the experimental data. The coupling to the strain introduces two more parameters G_{11} and G_{12}, or C_1 and C_2, assuming the elastic constants to be known. In addition to the data discussed in I, the measured pressure dependence of the transition temperature and the c/a ratio have been used to determine the model parameters – these therefore remain well overdetermined.

TABLE I. The quantities in the first line are replaced by those in the second line in Eqs. (33), (34), (37)–(42), and (44)–(50) in order to obtain the equations for trigonal distortion.

Tetragonal
$\Gamma_1, \Gamma_2, \Delta_1, \Delta_2, C_{11} - C_{12}, G_{11} - G_{12}, e_1, e_2$
Trigonal
$\frac{1}{3}(\Gamma_1 + 2\Gamma_2), \Gamma_1, \Delta_1 + 2\Delta_2, \Delta_1 - \Delta_2, 2C_{44}, 2G_{44}, e_1 + 2e_2, e_1 - e_2$

From the observed pressure dependence of the transition temperature, we obtain[31]

$$G_{12} = -0.63\, G_{11} \quad \text{or} \quad C_2 = 1.0\; 10^{-2}\, C_1 .$$

In Figs. 1–4, the experimental results are presented together with the theoretical curves. The set of five model parameters that minimized the difference between the mean square deviation of experimental points and the theoretical curves is given in Table II.

Agreement with the experimental results is generally very good. Only for the soft-mode frequency for $T > T_a$, shown in Fig. 3, is the difference between the theoretical and experimental curves significantly bigger than the experimental uncertainties. For $T = 2T_a$, the theoretical value is too large by about 20%.

The thermal averages A_λ and Δ_λ have been calculated only in a molecular field approximation. It is possible that an improved calculation may

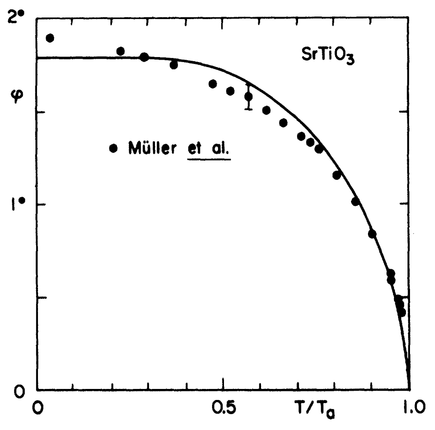

FIG. 1. Angle of rotation of the oxygen octahedron in $SrTiO_3$. Experimental points obtained by EPR. The solid line is the theoretical curve.

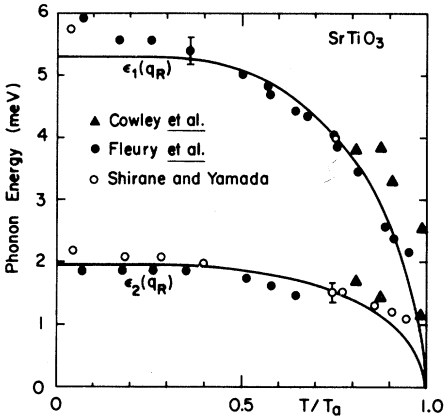

FIG. 2. Γ_{25} optical-phonon frequencies in $SrTiO_3$ as function of reduced temperature in the tetragonal phase. ● Experimental points obtained by Raman scattering. ○ and ▲ experimental points obtained by neutron scattering. The solid lines are the theoretical curves.

remove this discrepancy.[32] It is, of course, also possible that additional anharmonic interactions may be important.

From the stability condition $\epsilon_2^2(\vec{q}_R) > 0$, we find that the tetragonal phase is stable also when the interaction with the strain is neglected. However, because $\Gamma_1 \sim \Gamma_2$, $SrTiO_3$ is then very close to the stability limit separating tetragonal and trigonal distortions.

For the harmonic mode frequency we obtain $\omega_0(\vec{q}_R) = i8.2$ meV. This may be compared to the result of model V in the model calculation of Cowley[3] for which $\omega_0(\vec{q}_R) = i17.4$ meV. This frequency is, however, very dependent on the details of the model as discussed by Cowley.

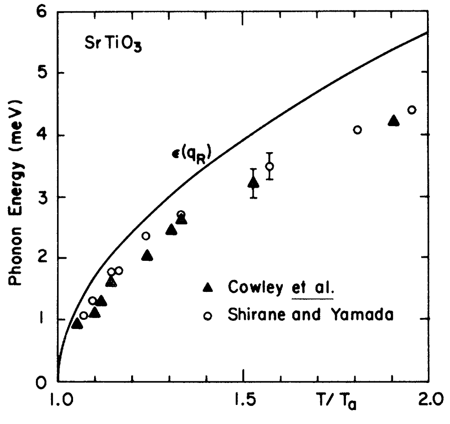

FIG. 3. Γ_{25} optical-phonon frequencies in $SrTiO_3$ in the high-temperature phase as function of reduced temperature. ○ and ▲ experimental points obtained by neutron diffraction. The solid line is the theoretical curve.

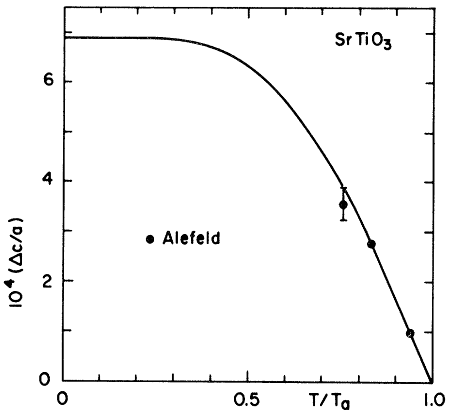

FIG. 4. $\Delta c/a$ ratio in the tetragonal phase of $SrTiO_3$ as function of reduced temperature. ● experimental points obtained by neutron backscattering.

The molecular field energy at $T = T_a$, $\omega = 22$ meV, gives a measure of the width of the energy bands $\epsilon_\lambda(\vec{q})$.[33]

For the coupling constants G_{11} and G_{12} we obtain the values

$$G_{11} = -2.9 \times 10^{27}\ \mathrm{sec}^{-2} \quad ,$$

$$G_{12} = 1.8 \times 10^{27}\ \mathrm{sec}^{-2} \quad .$$

The sign of G_{11} is determined by the fact that $c/a > 1$.

Due to resonant interaction between the acoustic- and soft-optical-phonon frequencies, there is a shift in the sound velocity in going through the transition at T_a.[13,26,27] In addition, there is a singular contribution to the sound velocity and the ultrasonic attenuation due to critical fluctuations.[26]

Using the values of G_{11} and G_{12}, the soft-mode frequency ϵ_1 and the distortion angle obtained by the best-fit procedure, we predict a shift in the velocity of a longitudinal sound wave propagating along the c axis and along an a axis of 2.7% and 1.1%, respectively. This should be compared with reported shifts of 4%[12] and 2.7%[14] obtained from Brillouin scattering experiments for propagation along a crystal axis. Within experimental error, the measured shifts are consistent with

TABLE II. Model parameters giving best fit to experimental results. (Appropriate factors of $\hbar$ 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
Γ_1	(meV^3)	246	99
Γ_2	(meV^3)	255	285
C_1	(meV^3)	50	139

the value predicted for propagation along the tetragonal axis.

From the shift in the transverse sound velocity,[13,14] we obtain

$$|G_{44}| = 1.7\ 10^{27}\,\mathrm{sec}^{-2}\ .$$

The coupling constant G_{44} does not enter the expressions for the soft-mode frequencies, the rotation angle or the strains in the case of tetragonal distortion, and is listed here only for completeness.

The strain for $T > T_a$ may be calculated from Eq. (47). We find, that the interaction of the strain with the particular soft-mode coordinates considered here contributes only a few percent to the over-all thermal expansion.

For LaAlO$_3$, the variation of the order parameter with temperature has been measured by EPR,[6] the soft-mode frequency above T_a by neutron diffraction,[19] and the soft-mode frequencies in the trigonal phase by Raman scattering experiments.[20] The elastic constants have, however, not been measured. We shall assume, that the contribution of the interaction we consider to the over-all thermal expansion is small also for LaAlO$_3$, and set $C_2 = 0$. The experimental results together with the theoretical curves giving the best fit are presented in Figs. 5–7. The corresponding model parameters are given in Table II. Within the experimental errors, the data may be well fitted by the model. However, for LaAlO$_3$ we have in effect one more free parameter than for SrTiO$_3$ due to the limited amount of experimental information available. The values for the model parameters are therefore quite tentative.

Because $\Gamma_1 \sim \frac{1}{3}\Gamma_2$ for LaAlO$_3$ one is beyond the stability limit of the trigonal phase if the interaction with the strains is neglected.

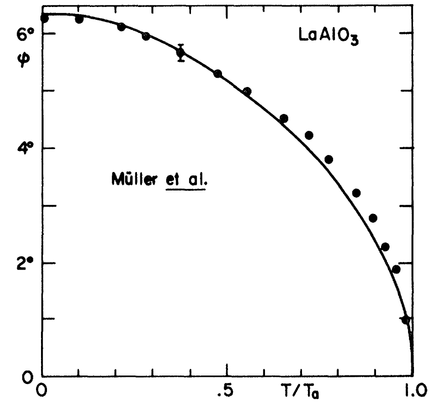

FIG. 5. Angle of rotation of the oxygen octahedron in LaAlO$_3$. ● Experimental points obtained by EPR. The solid line is the theoretical curve.

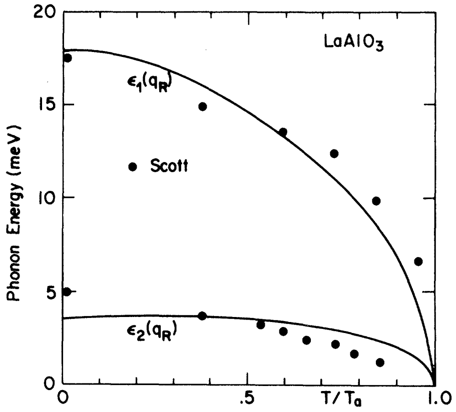

FIG. 6. Γ_{25} optical-phonon frequencies in LaAlO$_3$ in the trigonal phase. ● Experimental points obtained by Raman scattering. The solid lines are the theoretical curves.

Figure 8 shows the predicted temperature dependence of the rhombicity together with experimental values measured by Gränicher and Müller.[16]

VI. CONCLUSION

We have extended the theory in I to include the interaction between soft-mode coordinates and the strains. Whereas, in I we were not able to obtain a good fit for both the soft-mode frequencies and the magnitude of the rotation angle, good agreement is now obtained with all the available experimental results. For SrTiO$_3$, the model parameters are well overdetermined. For LaAlO$_3$, additional experiments to determine the elastic constants and the coupling constants G_{ij} are required in order to determine the model parameters and to check the predictions of the model.

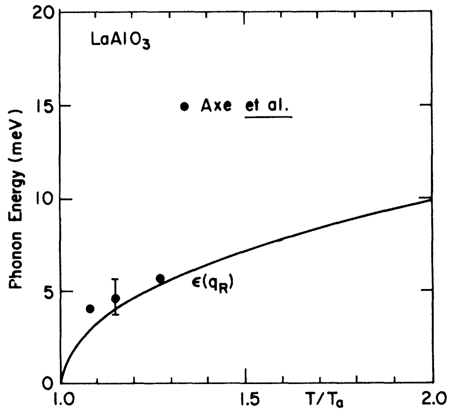

FIG. 7. Γ_{25} optical-phonon frequency in LaAlO$_3$ in the high-temperature phase. ● Experimental results obtained by neutron diffraction. The solid line is the theoretical curve.

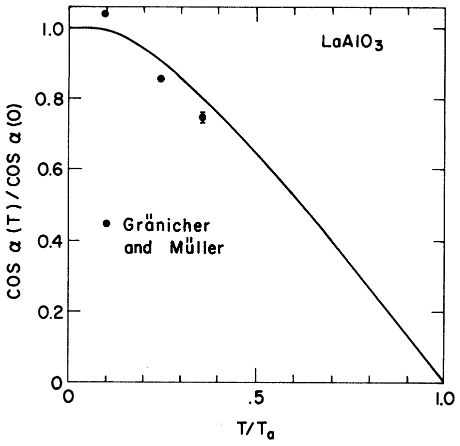

FIG. 8. Predicted temperature dependence of cosα. The experimental points have been scaled for best fit.

ACKNOWLEDGMENTS

Discussions with H. Thomas, K. A. Müller, and J. C. Slonczewski are gratefully acknowledged. We are indebted to R. Zurek and D. C. O'Shea for making their theses available to us; and to J. F. Scott and B. Alefeld for sending us their papers prior to publication.

APPENDIX

The interaction Hamiltonian Eq. (5) contains four independent coupling constants. These are

$$\tfrac{1}{4}G_{11}=G_{112211}=G_{113311}=G_{221122}=G_{223322}=G_{331133}=G_{332233}\ ,$$

$$\tfrac{1}{2}G_{13}=G_{111122}=G_{111133}=G_{222211}=G_{222233}=G_{333311}=G_{333322}\ ,$$

$$\tfrac{1}{2}(G_{12}-G_{13})=G_{112233}=G_{113322}=G_{221133}=G_{223311}=G_{331122}=G_{332211}\ ,$$

and $G_{44}=G_{121212}=G_{131313}=G_{232323}$.

All other coupling constants $G_{\alpha\beta ij\lambda\lambda'}$ are equal to zero.

---

[*] Present address: IBM Watson Research Center, Yorktown Heights, N.Y. 10598.

[1] H. Gränicher, Helv. Phys. Acta 29 , 211 (1956).

[2] K. A. Müller, Helv. Phys. Acta 31, 173 (1958).

[3] R. A. Cowley, Phys. Rev. 134, A981 (1964).

[4] H. Unoki and T. Sakudo, J. Phys. Soc. Japan 23, 546 (1967).

[5] P. A. Fleury, J. F. Scott, and J. M. Worlock, Phys. Rev. Letters 21, 16 (1968).

[6] K. A. Müller, W. Berlinger, and F. Waldner, Phys. Rev. Letters 21, 814 (1968).

[7] G. Shirane and Y. Yamada, Phys. Rev. 177, 858 (1969).

[8] R. A. Cowley, W. J. L. Buyers, and G. Dolling, Solid State Commun. 7, 181 (1969).

[9] B. Alefeld, Z. Physik 222, 155 (1969).

[10] R. O. Bell and G. Rupprecht, Phys. Rev. 129, 90 (1963).

[11] B. Pietrass and E. Hegenbarth, Phys. Status Solidi 34, K 119 (1969).

[12] W. Kaiser and R. Zurek, Phys. Letters 23, 668 (1966).

[13] R. Zurek, thesis, Technische Hochschule München, 1969 (unpublished).

[14] D. C. O'Shea, thesis, Johns Hopkins University, Baltimore, Md., 1968 (unpublished).

[15] S. Geller and V. B. Bala, Acta Cryst. 9, 1019 (1956).

[16] H. Gränicher and K. A. Müller, Nuovo Cimento Suppl. 6, 1216 (1957).

[17] K. A. Müller, E. Brun, B. Derighetti, J. E. Drumheller, and F. Waldner, Phys. Letters 9, 223 (1964).

[18] B. Derigetti, J. E. Drumheller, F. Laves, K. A. Muller, and F. Waldner, Acta Cryst. 18, 557 (1965).

[19] J. D. Axe, G. Shirane, and K. A. Müller, Bull. Am. Phys. Soc. 14, 61 (1969); Phys. Rev. 183, 820 (1969).

[20] J. F. Scott, Phys. Rev. 183, 823 (1969).

[21] V. Platkhy and W. Cochran, Phys. Status Solidi 29, K81 (1968).

[22] V. J. Minkiewicz and G. Shirane, J. Phys. Soc. Japan 26, 674 (1969).

[23] W. Cochran and A. Zia, Phys. Status Solidi 25, 273 (1968).

[24] H. Thomas and K. A. Müller, Phys. Rev. Letters 21, 1256 (1968).

[25] E. Pytte and J. Feder, Phys. Rev. 187, 1077 (1969).

[26] E. Pytte, Phys. Rev. B 1, 924 (1970).

[27] J. C. Slonczewski and H. Thomas, Phys. Rev. B 1, 3599 (1970).

[28] As shown in Ref. 26, this interaction does not affect the values of the soft-mode frequencies at q_R.

[29] See Sec. V of I.

[30] N. Boccara and G. Sarma, Physics 1, 219 (1965).

[31] The free energy used in Ref. 11 has already been minimized with respect to the strains; and the coupling constants of Ref. 11 g_{11} and g_{12} are related to G_{11} and G_{12} by $g_{11}=2[s_{11}G_{11}+2s_{12}G_{12}]$, $g_{12}=2[s_{11}G_{12}+s_{12}(G_{11}+G_{12})]$, where s_{ij} are the elastic compliance constants.

[32] For the Ising model, the transition temperature calculated in the molecular field approximation differs by 25% from the correct value for a cubic ferromagnet. See, for example, R. Brout, *Phase Transitions* (Benjamin, New York, 1965).

[33] Neglecting hybridizations due to interactions with other modes.