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Theory of a Structural Phase Transition in Perovskite-Type Crystals

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Structural phase transitions in perovskite crystals involving displacements of the oxygen octahedra due to the condensation of linear combinations of the triply degenerate Γ_{25} modes at the R corner of the Brillouin zone are discussed with the help of a model Hamiltonian. These distortions are essentially rotations. We consider separately the cases of rotations of the octahedra about a cube axis ($SrTiO_3$) and about a cube diagonal ($LaAlO_3$). The temperature dependences of the distortion angle and of the frequencies of the soft Γ_{25} optical modes have been calculated. An approximate self-consistently determined free-energy expression is given from which the internal energy and the specific heat are derived. The theory is compared with the experimental results on the transition from the cubic to the tetragonal phase in $SrTiO_3$ and to the trigonal phase in $LaAlO_3$.

I. INTRODUCTION

THE structural phase transitions in the cubic perovskite compounds ABO_3 involving rotations of the BO_6 octahedra have been the subject of a number of recent investigations.[1–10] These phase transitions are associated with a phonon instability at the R corner of the Brillouin zone, more specifically with the condensation of linear combinations of the triply degenerate Γ_{25} modes.[2,4–6,8,10] One may use as a basic set the three modes corresponding to rotations of the BO_6 octahedra around the three cubic axes.[11] Because of the degeneracy, various structures are possible for the condensed phase. So far, phase transitions of this type are known to occur in $SrTiO_3$, $KMnF_3$, and $LaAlO_3$ at about 105, 184, and 806°K, respectively, each of which exemplifies a different case. In $SrTiO_3$ one of the triply degenerate modes condenses,[1–5] while in $KMnF_3$ a linear combination of two of the modes condenses[6] and in $LaAlO_3$ a linear combination of all three modes.[7–10]

Because the condensation of a linear combination of two modes is more difficult to describe, we consider in this paper only transitions for which one of the modes and a linear combination of all three degenerate modes condense. In $SrTiO_3$ the cubic high-temperature structure undergoes a tetragonal distortion at the transition, corresponding to a rotation of the BO_6 octahedra about a cube axis. In $LaAlO_3$ it undergoes a trigonal distortion to a rhombohedral structure described by a rotation of the oxygen octahedra about a cube diagonal.

By the distortion the primitive unit cell is enlarged and the Brillouin zone is correspondingly reduced. In the distorted structures the (original) R corner and the center of the Brillouin zone are equivalent points. Because of the symmetry breaking of the phase transition the mode splits into two branches in the condensed phase.

These phase transformations were recently discussed by Thomas and Müller,[12] making use of an energy expression in terms of a three-dimensional vector describing rotations about each of the cubic axes through the B ion. Depending on the relative magnitude of the anharmonic coefficients, a transition to tetragonal or trigonal phases was obtained. Using a Landau-type theory of second-order phase transitions, the transition temperature T_a and the temperature dependence of the soft mode frequencies associated with the phase transition both below and above T_a were obtained for temperatures in the immediate neighborhood of the transition point.

In this paper we study these phase transitions with the help of a model Hamiltonian. The Hamiltonian may be constructed directly in terms of a vector describing the rotations of oxygen octahedra as in Ref. 12, or it may be derived starting from the conventional lattice dynamical approach. The model Hamiltonian we use describes only tetragonal and trigonal distortion. It does not allow for the condensation of a linear combination of two modes.

The soft mode frequencies are determined for arbitrary temperatures by calculating equations of motion using the model Hamiltonian and determining the required correlation functions by means of self-consistency conditions. By setting the static part of the equations of motion equal to zero, we obtain a relationship from which the amount of distortion may be determined.

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[11] Although the distortions are, strictly speaking, right-angle displacements, for convenience we shall usually refer to them as rotations.

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These results may be derived alternatively by a variational procedure from an approximate free-energy expression also determined self-consistently. From the free-energy expression the specific heat is obtained in the usual way. In all cases the temperature dependence for $T\approx T_a$ is exhibited explicitly.

II. DERIVATION OF THE MODEL HAMILTONIAN

In the adiabatic approximation an effective potential V exists for the ionic motion.[13] The nonkinetic part of the Hamiltonian may then be expressed as a power series in the ionic displacements of the kth atom in the lth unit cell, $\mathbf{u}(lk)$, from the fixed positions $\mathbf{X}(lk)$. In order to study the structural phase transitions it will be convenient to choose the reference configuration $\{\mathbf{X}(lk)\}$ as the average positions of the ions in the high-temperature phase. It is important to recognize that the reference configuration is only a stationary point of the potential energy. It is not necessarily an absolute minimum and will, in general, be a saddle point. Correspondingly some of the harmonic eigenfrequencies may be purely imaginary. These modes are then stabilized by the anharmonic forces.

Because the potential is stationary for the reference configuration, the Hamiltonian will have no linear terms in the displacement

$$\begin{aligned}H=&\tfrac{1}{2}\sum m_k\dot{u}_\alpha(lk)\dot{u}_\alpha(lk)\\&+\tfrac{1}{2}\sum V_{\alpha_1\alpha_2}(l_1k_1,l_2k_2)u_{\alpha_1}(l_1k_1)u_{\alpha_2}(l_2k_2)\\&+\sum_{n=3}^{\infty}\frac{1}{n!}V_{\alpha_1\cdots\alpha_n}(l_1k_1\cdots l_nk_n)u_{\alpha_1}(l_1k_1)\cdots u_{\alpha_n}(l_nk_n)\,.\end{aligned}\tag{1}$$

Here $V_{\alpha_1\cdots\alpha_n}(l_1k_1\cdots l_nk_n)$ is the nth derivative of the potential with respect to the displacements indicated in the arguments of the function and m_k is the mass of the kth ion in the unit cell. The derivatives $V_{\alpha_1\cdots\alpha_n}(l_1k_1\cdots l_nk_n)$ satisfy symmetry requirements reflecting the symmetry of the reference configuration.

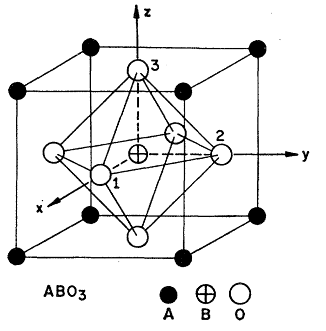

FIG. 1. Unit cell of the cubic perovskite structure with the B ion at the origin.

The perovskite structure has five ions per unit cell and therefore altogether 15 degrees of freedom. The perovskite unit cell with the inscribed oxygen octahedron is shown in Fig. 1. We shall consider three branches which at the R corner describe the triply degenerate Γ_{25} mode and neglect all other degrees of freedom. This mode can be built up from localized displacement fields $\mathbf{R}(l)$ associated with each unit cell describing the rotations of the oxygen octahedra about the cell center.[12] The three independent rotations about the cube axes permit the construction of three branches as required.

The displacements of each of the oxygen ions in the unit cell may be expressed in terms of the vector $\mathbf{R}(l)$. We write[14]

$$\mathbf{u}(lk)=\tfrac{1}{2}\boldsymbol{\xi}(k)\times[\mathbf{R}(l+k)-\mathbf{R}(l)](2m_0a^2)^{-1/2}\,,\tag{2}$$

where $\mathbf{R}(l+k)\equiv\mathbf{R}(\mathbf{X}_l+\boldsymbol{\xi}_k)$, and where $\mathbf{X}_l$ is the position vector of the center of the lth unit cell, while the vectors

$$\boldsymbol{\xi}_1=a(1,0,0)\,,\quad\boldsymbol{\xi}_2=a(0,1,0)\,,\quad\boldsymbol{\xi}_3=a(0,0,1)\,,$$

connect the nearest-neighbor positions l and $l+k$. Further, m_0 is the mass of the oxygen ion and a is the lattice spacing. By definition $\mathbf{R}(l)$ is directed along the axis of rotation. For the particular normalization we have introduced, its magnitude is equal to

$$R=(\tfrac{1}{2}m_0a^2)^{1/2}\tan\varphi\,,\tag{3}$$

where φ is the angular displacement of the oxygen ions.

In terms of these operators the kinetic energy associated with these three degrees of freedom may be written

$$T=\tfrac{1}{2}\sum_{l,l'}\dot{\mathbf{R}}(l)\cdot\boldsymbol{\theta}(l,l')\cdot\dot{\mathbf{R}}(l')\,,\tag{4}$$

where

$$\begin{aligned}\boldsymbol{\theta}(l=l')&=\tfrac{1}{2}\mathbf{1}\,,\\\boldsymbol{\theta}(\boldsymbol{\xi}_k)&=-\tfrac{1}{8}(\mathbf{1}-\hat{\boldsymbol{\xi}}_k\hat{\boldsymbol{\xi}}_k)\,,\end{aligned}\tag{5}$$

while $\boldsymbol{\theta}(l,l')=0$ for higher-order neighbors. Introducing the momentum $\mathbf{P}(l)$ canonically conjugate to $\mathbf{R}(l)$,

$$\mathbf{P}(l)=\sum_{l'}\boldsymbol{\theta}(l,l')\cdot\dot{\mathbf{R}}(l')\,,\tag{6}$$

where $R_\lambda(l)$ and $P_\lambda(l)$ satisfy the commutation relations[15]

$$[R_\lambda(l),P_{\lambda'}(l')]=i\delta_{\lambda\lambda'}\delta_{ll'}\,,\tag{7}$$

the kinetic energy may be written in the alternate form

$$T=\tfrac{1}{2}\sum\mathbf{P}(l)\cdot\boldsymbol{\theta}^{-1}(l,l')\cdot\mathbf{P}(l')\,.\tag{8}$$

We note that $\boldsymbol{\theta}$ plays the role of an effective-mass tensor. From Eq. (5) its Fourier transform

$$\theta_{\lambda\lambda'}(\mathbf{q})=\sum_l\theta_{\lambda\lambda'}(l,l')e^{i\mathbf{q}\cdot[\mathbf{X}(l)-\mathbf{X}(l')]}\,,\quad\lambda,\lambda'=1,2,3\tag{9}$$

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[13] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (The Clarendon Press, Ltd., Oxford, England, 1954).

[14] In the following derivation it will be convenient to use a coordinate system with the B ion as origin, as in Fig. 1. Otherwise, the standard convention with the A ion at the origin has been used throughout.

[15] In this paper $\hbar=1$.

may be written

$$\theta_{\lambda\lambda'}(\mathbf{q})=\tfrac{1}{2}\delta_{\lambda\lambda'}(1+\tfrac{1}{2}\cos q_\lambda a-\tfrac{1}{2}\sum_{\lambda=1}^{3}\cos q_\lambda a). \tag{10}$$

We wish to emphasize, however, that the fact that $\boldsymbol{\theta}(l,l')\neq 0$ only for nearest neighbors does not represent an approximation. Equations (8)–(10) are a completely general representation of the kinetic energy associated with the three degrees of freedom we consider.

The harmonic interaction is given similarly by an expression of the form

$$H_2=\tfrac{1}{2}\sum_{l,l'}\mathbf{R}(l)\cdot\mathbf{v}(l,l')\cdot\mathbf{R}(l'). \tag{11}$$

Because $\mathbf{R}(l)$ transforms like a vector, $\mathbf{v}(l=l')$ must, for the cubic perovskite structure, be proportional to the unit matrix. We write

$$v_{\lambda\lambda'}(l=l')=\Omega_0^2\delta_{\lambda\lambda'}. \tag{12}$$

Further, because all the ions remain at rest when the octahedra all rotate in phase, it follows that

$$v_{\lambda\lambda'}(q=0)=\theta_{\lambda\lambda'}(q=0)=0. \tag{13}$$

We require that this Hamiltonian describe at the R corner the Γ_{25} phonon modes. This requirement yields the conditions that

$$\begin{aligned}\theta_{\lambda\lambda'}(\mathbf{q}_R)&=\delta_{\lambda\lambda'},\\ v_{\lambda\lambda'}(\mathbf{q}_R)&=\omega_0^2(\mathbf{q}_R)\delta_{\lambda\lambda'},\end{aligned} \tag{14}$$

where $\omega_0^2(\mathbf{q}_R)$ is the harmonic frequency of the triply degenerate Γ_{25} phonon mode. The normalization for $\mathbf{R}(l)$ in Eq. (2) has been chosen in such a way that the expression for $\theta_{\lambda\lambda'}(\mathbf{q})$ given by Eq. (10) reduces to this form at $\mathbf{q}=\mathbf{q}_R$.

Whereas according to Eq. (10), $\theta_{\lambda\lambda'}(\mathbf{q})$ may everywhere be taken to be diagonal, the interaction $v_{\lambda\lambda'}(\mathbf{q})$ is expected to be anisotropic for an arbitrary point in the Brillouin zone.

For the anharmonic interactions we shall assume a very simple form containing only two anharmonic force constants. The dominant contribution to the potential at the oxygen sites is due to the four nearest-neighbor A sites. Including only this interaction and keeping only the lowest-order terms in the oxygen displacement field $\mathbf{u}(l,k)$ the anharmonic Hamiltonian may be written

$$\begin{aligned}H_4=\tfrac{1}{4}d_1\sum_l\,[&u_y^4(l1)+u_z^4(l1)+u_x^4(l2)+u_z^4(l2)\\ &+u_x^4(l3)+u_y^4(l3)]+\tfrac{1}{2}d_2\sum_l\,[u_y^2(l1)u_z^2(l1)\\ &+u_x^2(l2)u_z^2(l2)+u_x^2(l3)u_y^2(l3)].\end{aligned} \tag{15}$$

In terms of the $\mathbf{R}$ operators this Hamiltonian takes the form

$$\begin{aligned}H_4=\tfrac{1}{4}\sum_{\substack{ll'\\ \lambda\lambda'}}\Gamma_{\lambda\lambda'}(l,l')[R_\lambda(l)-R_\lambda(l')]^2&\\ \times[R_{\lambda'}(l)-R_{\lambda'}(l')]^2,&\end{aligned} \tag{16}$$

where

$$\begin{aligned}\Gamma_{\lambda\lambda'}(l,l')&=\gamma_{\lambda\lambda'}(1-\delta_{\lambda k})(1-\delta_{\lambda' k}), &&\text{for } \mathbf{X}_l-\mathbf{X}_{l'}=\xi_k\\ &=\qquad 0, &&\text{otherwise}\end{aligned} \tag{17}$$

and where in terms of the force constants d_1 and d_2 introduced in Eq. (15),

$$\begin{aligned}\gamma_{\lambda\lambda'}&=\tfrac{1}{64}d_1/m_0^2\equiv\tfrac{1}{32}\Gamma_1, &&\lambda=\lambda'\\ &=\tfrac{1}{64}d_2/m_0^2\equiv\tfrac{1}{16}\Gamma_2, &&\lambda\neq\lambda'.\end{aligned} \tag{18}$$

The Fourier transform of the $\mathbf{\Gamma}$ matrix is given by

$$\mathbf{\Gamma}(\mathbf{q})=\tfrac{1}{16}\begin{bmatrix}\Gamma_1(\cos q_ya+\cos q_za) & 2\Gamma_2\cos q_za & 2\Gamma_2\cos q_ya\\ 2\Gamma_2\cos q_za & \Gamma_1(\cos q_xa+\cos q_za) & 2\Gamma_2\cos q_xa\\ 2\Gamma_2\cos q_ya & 2\Gamma_2\cos q_xa & \Gamma_1(\cos q_xa+\cos q_ya)\end{bmatrix}. \tag{19}$$

Because $[R_\lambda(l)-R_\lambda(l')]\equiv 0$ when all the octahedra rotate in phase, there is no condition analogous to Eq. (13) for the Γ matrix. The particular $\mathbf{q}$ dependence of the $\mathbf{\Gamma}$ matrix given by Eq. (19) depends on the assumption that the dominant contribution to H_4 is due to the four nearest-neighbor A sites.

We discuss in the Appendix how a Hamiltonian of this form may be constructed when one follows the usual procedure of first determining all the eigenmodes of the harmonic Hamiltonian. However, no attempt will be made, in this paper, to relate the model Hamiltonian to a real crystal Hamiltonian.

The model we have just discussed differs from that introduced by Thomas and Müller[12] in two important respects. Firstly, their kinetic energy is local, whereas because the oxygen ions forming a given octahedron belong to more than one unit cell, it must necessarily be nonlocal. Secondly, their Hamiltonian does not vanish when all the octahedra rotate in phase as required on physical grounds.

However, the discussion in Ref. 12 was based not on the model Hamiltonian, but on an energy expression. This expression may be derived by taking the expectation value of either of these model Hamiltonians and approximating the correlation functions of the $\mathbf{R}$ operators by all possible factorizations in terms of lower-order correlations. Thus the fourth-order term in their energy expression is identical to that obtained when each of the operators $R_\lambda(l)$ in the Hamiltonian H_4 is replaced by their expectation values (with $b=2\Gamma_1$, $c=2\Gamma_2$). The coefficient for the second-order term obtained from H_2 and H_4 will depend on correlation functions containing pairs of operators $R_\lambda(l)$. Whereas in a Landau-type theory as considered in Ref. 12, a certain temperature dependence has to be assumed for this coefficient, in the present calculation, the required correlation functions are calculated explicitly, and all the temperature dependences are derived from the model.

III. EQUATIONS OF MOTION: SELF-CONSISTENCY CONDITIONS

The equations of motion for the displacement field $R_\lambda(l)$ $\lambda=1, 2, 3$ are obtained from the model Hamiltonian by means of the commutation relations equation (7),

$$i\frac{\partial}{\partial t}R_\lambda(l)=[R_\lambda(l),H]=i\sum_{\bar\lambda\bar l}(\boldsymbol{\theta}^{-1})_{\lambda\bar\lambda}(l,\bar l)P_{\bar\lambda}(\bar l)\,, \tag{20}$$

$$\begin{aligned}-\frac{\partial^2}{\partial t^2}R_\lambda(l)&=i\sum_{\bar\lambda\bar l}(\boldsymbol{\theta}^{-1})_{\lambda\bar\lambda}(l,\bar l)[P_{\bar\lambda}(l),H]\\&=\sum_{\substack{\bar\lambda\lambda'\\ \bar l l'}}(\boldsymbol{\theta}^{-1})_{\lambda\bar\lambda}(l,\bar l)\{v_{\bar\lambda\lambda'}(\bar l,l')R_{\lambda'}(l')+2\Gamma_{\bar\lambda\lambda'}(\bar l,l')\\&\qquad\times[R_{\bar\lambda}(\bar l)-R_{\bar\lambda}(l')][R_{\lambda'}(\bar l)-R_{\lambda'}(l')]^2\}\,.\end{aligned} \tag{21}$$

Distortion of the crystal from cubic symmetry corresponds to a nonvanishing expectation value of $R_\lambda(l)$. In Eq. (21), we therefore set

$$R_\lambda(l)=\langle R_\lambda(l)\rangle+r_\lambda(l)\,, \tag{22}$$

where the bracket denotes the thermal average, and where $r_\lambda(l)$ describes the fluctuation about this average value.

The expectation value $\langle R_\lambda(l)\rangle$ may be related to the displacement of the individual ions $\langle\mathbf{u}(lk)\rangle$ by Eq. (2). As the direction of the displacement $\langle\mathbf{u}(lk)\rangle$ alternates from one cell to the next, we may write

$$\langle R_\lambda(l)\rangle=A_\lambda e^{i\mathbf{q}_R\cdot\mathbf{x}(l)}\,. \tag{23}$$

The equation of motion for $r_\lambda(l)$ will be linearized by replacing products of pairs of operators $r_\lambda(l)$ with their average values

$$\Delta_{\lambda\lambda'}(l,l')=\langle r_\lambda(l)r_{\lambda'}(l')\rangle\,. \tag{24}$$

Setting the static part of the equation of motion equal to zero then gives a relationship between the expectation values $\langle R_\lambda(l)\rangle$ and the correlation functions $\Delta_{\lambda\lambda'}$. Making use of Eqs. (21)–(24), we obtain

$$\begin{aligned}\omega_0^2(\mathbf{q}_R)A_\lambda&+8\sum_{\lambda'}[\Gamma_{\lambda\lambda'}(0)-\Gamma_{\lambda\lambda'}(\mathbf{q}_R)]A_\lambda A_{\lambda'}^2\\&+4\frac{1}{N}\sum_{\mathbf{q}\lambda'}\{[\Gamma_{\lambda\lambda'}(0)-\Gamma_{\lambda\lambda'}(\mathbf{q}_R)+\Gamma_{\lambda\lambda'}(\mathbf{q}-\mathbf{q}_R)-\Gamma_{\lambda\lambda'}(\mathbf{q})]\\&\qquad\times[A_\lambda\Delta_{\lambda'\lambda'}(\mathbf{q})+2A_{\lambda'}\Delta_{\lambda\lambda'}(\mathbf{q})]\}=0\,,\end{aligned} \tag{25}$$

where $\Delta_{\lambda\lambda'}(\mathbf{q})$ is the Fourier transform of $\Delta_{\lambda\lambda'}(l,l')$. N is the number of unit cells in the volume.

For the Fourier transform of the fluctuation $r_\lambda(l)$, we obtain from Eqs. (21) and (22) the following coupled set of equations:

$$\begin{aligned}-\frac{\partial^2}{\partial t^2}r_\lambda(\mathbf{q})&=\theta_{\lambda\lambda}^{-1}(\mathbf{q})\sum_{\lambda'}v_{\lambda\lambda'}(\mathbf{q})r_{\lambda'}(\mathbf{q})+4\theta_{\lambda\lambda}^{-1}(\mathbf{q})\\&\times\sum_{\lambda'}\{[\Gamma_{\lambda\lambda'}(0)-\Gamma_{\lambda\lambda'}(\mathbf{q}_R)+\Gamma_{\lambda\lambda'}(\mathbf{q}-\mathbf{q}_R)-\Gamma_{\lambda\lambda'}(\mathbf{q})]\\&\times[2A_\lambda A_{\lambda'}r_{\lambda'}(\mathbf{q})+A_{\lambda'}^2r_\lambda(\mathbf{q})]\\&+\frac{1}{N}\sum_{\mathbf{q}'}[\Gamma_{\lambda\lambda'}(0)-\Gamma_{\lambda\lambda'}(\mathbf{q})+\Gamma_{\lambda\lambda'}(\mathbf{q}'-\mathbf{q})-\Gamma_{\lambda\lambda'}(\mathbf{q}')]\\&\qquad\times[2\Delta_{\lambda\lambda'}(\mathbf{q}')r_{\lambda'}(\mathbf{q})+\Delta_{\lambda'\lambda'}(\mathbf{q}')r_\lambda(\mathbf{q})]\}\,.\end{aligned} \tag{26}$$

Introducing a canonical transformation of the form

$$\begin{aligned}r_\lambda(\mathbf{q})&=\sum b_{\lambda\lambda'}(\mathbf{q})s_{\lambda'}(\mathbf{q})\,,\\P_\lambda(\mathbf{q})&=\sum p_{\lambda'}(\mathbf{q})b_{\lambda'\lambda}^{-1}(\mathbf{q})\,,\end{aligned} \tag{27}$$

Eqs. (20) and (26) may be diagonalized and written in the form

$$\begin{aligned}(\partial/\partial t)s_\lambda(\mathbf{q})&=p_\lambda(-\mathbf{q})\,,\\-(\partial^2/\partial t^2)s_\lambda(\mathbf{q})&=\epsilon_\lambda^2(\mathbf{q})s_\lambda(\mathbf{q})\,,\end{aligned} \tag{28}$$

where the coefficients $b_{\lambda\lambda'}(\mathbf{q})$ may be determined from Eqs. (20) and (26). The eigenfrequencies $\epsilon_\lambda^2(\mathbf{q})$ depend on the correlation functions $\Delta_{\lambda\lambda'}(\mathbf{q})$. From Eqs. (24) and (27) the latter may be written

$$\Delta_{\lambda\lambda'}(\mathbf{q})=\sum_{\bar\lambda\bar\lambda'}b_{\lambda\bar\lambda}(\mathbf{q})b_{\lambda'\bar\lambda'}(-\mathbf{q})\langle s_{\bar\lambda}(\mathbf{q})s_{\bar\lambda'}(-\mathbf{q})\rangle\,. \tag{29}$$

Then, making use of the fluctuation-dissipation theorem, we obtain the following self-consistency conditions:

$$\Delta_{\lambda\lambda'}(\mathbf{q})=\sum_{\bar\lambda}b_{\lambda\bar\lambda}(\mathbf{q})b_{\lambda'\bar\lambda}(-\mathbf{q})[2\epsilon_{\bar\lambda}(\mathbf{q})]^{-1}\coth\tfrac{1}{2}\beta\epsilon_{\bar\lambda}(\mathbf{q})\,. \tag{30}$$

For arbitrary values of $\mathbf{q}$ and nondiagonal interaction potentials the determination of $b_{\lambda\lambda'}(\mathbf{q})$ and thus $\epsilon_\lambda^2(\mathbf{q})$ requires the solution of a general cubic equation.

For the subsequent calculations it will be convenient to introduce the following definitions:

$$\begin{aligned}\Delta_{\lambda\lambda'}^{(1)}&=\frac{1}{N}\sum_{\mathbf{q}}\Delta_{\lambda\lambda'}(\mathbf{q})\,,\\ [\Gamma_{\lambda\lambda'}(0)-\Gamma_{\lambda\lambda'}(\mathbf{q}_R)]\Delta_{\lambda\lambda'}^{(2)}&=\frac{1}{N}\sum_{\mathbf{q}}[\Gamma_{\lambda\lambda'}(\mathbf{q}-\mathbf{q}_R)-\Gamma_{\lambda\lambda'}(\mathbf{q})]\Delta_{\lambda\lambda'}(\mathbf{q})\,,\\ \sum_{\lambda'}[\Gamma_{\lambda\lambda'}(0)-\Gamma_{\lambda\lambda'}(\mathbf{q}_R)]\Delta_{\lambda\lambda}^{(3)}&=\frac{1}{N}\sum_{\mathbf{q}\lambda'}[\Gamma_{\lambda\lambda'}(\mathbf{q}-\mathbf{q}_R)-\Gamma_{\lambda\lambda'}(\mathbf{q})]\Delta_{\lambda'\lambda'}(\mathbf{q})\,.\end{aligned} \tag{31}$$

A. Tetragonal Distortion

For tetragonal distortion corresponding to the rotation of the BO_6 octahedra about a cube axis, only one of the components of $\langle\mathbf{R}(l)\rangle$ will be different from zero, We set

$$A_\lambda = A\delta_{\lambda,1}.$$

Further, we may set

$$\Delta_{\lambda\lambda'}{}^{(\alpha)} = 0, \quad \lambda \neq \lambda'$$

and for the diagonal components it follows that

$$\Delta_{11}{}^{(\alpha)} \equiv \Delta_1{}^{(\alpha)},$$
$$\Delta_{22}{}^{(\alpha)} = \Delta_{33}{}^{(\alpha)} \equiv \Delta_2{}^{(\alpha)}.$$

We write the eigenfrequencies in the following form:

$$\epsilon_\lambda{}^2(\mathbf{q}) = \epsilon_\lambda{}^2(\mathbf{q}_R) + [h_\lambda(\mathbf{q}) - h_\lambda(\mathbf{q}_R)]. \tag{32}$$

For $\mathbf{q} = \mathbf{q}_R$, the equations of motion reduce to diagonal form

$$b_{\lambda\lambda'}(\mathbf{q}_R) = \delta_{\lambda\lambda'}, \tag{33}$$

and the eigenfrequencies are given by

$$\begin{aligned}\epsilon_1{}^2(\mathbf{q}_R) = \omega_0{}^2(\mathbf{q}_R) + 3\Gamma_1(2A^2 + \Delta_1{}^{(1)}) + 2\Gamma_2\Delta_2{}^{(1)} \\ + 2\Gamma_1\Delta_1{}^{(2)} + (\Gamma_1 + 2\Gamma_2)\Delta_1{}^{(3)},\end{aligned} \tag{34}$$

$$\begin{aligned}\epsilon_{2,3}{}^2(\mathbf{q}_R) = \omega_0{}^2(\mathbf{q}_R) + \Gamma_2(2A^2 + \Delta_1{}^{(1)}) + (3\Gamma_1 + \Gamma_2)\Delta_2{}^{(1)} \\ + 2\Gamma_1\Delta_2{}^{(2)} + (\Gamma_1 + 2\Gamma_2)\Delta_2{}^{(3)}.\end{aligned} \tag{35}$$

Note that two of the eigenmodes are degenerate at $\mathbf{q} = \mathbf{q}_R$ for all temperatures.

For tetragonal distortion the relationship Eq. (25) takes the form

$$\begin{aligned}A[\omega_0{}^2(\mathbf{q}_R) + \Gamma_1(2A^2 + 3\Delta_1{}^{(1)}) + 2\Gamma_2\Delta_2{}^{(1)} + 2\Gamma_1\Delta_1{}^{(2)} \\ + (\Gamma_1 + 2\Gamma_2)\Delta_1{}^{(3)}] = 0.\end{aligned} \tag{36}$$

This equation has a solution $A = 0$ corresponding to the undistorted phase. By symmetry it follows that in this phase

$$\Delta_1{}^{(\alpha)} = \Delta_2{}^{(\alpha)} \equiv \Delta^{(\alpha)},$$

and that all three eigenmodes are degenerate at the R corner. For $A \neq 0$, Eq. (36) provides a relationship between A and the correlation functions $\Delta_{1,2}{}^{(\alpha)}$. The transition temperature is defined by taking the limit $A \to 0$, $\Delta_{1,2}{}^{(\alpha)} \to \Delta^{(\alpha)}$ when $T \to T_a$. We obtain

$$\begin{aligned}\omega_0{}^2(\mathbf{q}_R) + (3\Gamma_1 + 2\Gamma_2)\Delta^{(1)}(T_a) + 2\Gamma_1\Delta^{(2)}(T_a) \\ + (\Gamma_1 + 2\Gamma_2)\Delta^{(3)}(T_a) = 0.\end{aligned} \tag{37}$$

For $T < T_a$ we make use of Eq. (36) to write the eigenmodes in the following form:

$$\begin{aligned}\epsilon_1{}^2(\mathbf{q}_R) &= 4\Gamma_1 A^2, \\ \epsilon_{2,3}{}^2(\mathbf{q}_R) &= 2(\Gamma_2 - \Gamma_1)A^2 + (\Gamma_2 - 3\Gamma_1)(\Delta_1{}^{(1)} - \Delta_2{}^{(1)}) \\ &\quad + 2\Gamma_1(\Delta_2{}^{(2)} - \Delta_1{}^{(2)}) + 2\Gamma_2(\Delta_2{}^{(3)} - \Delta_1{}^{(3)}).\end{aligned} \tag{38}$$

From the definition of T_a it follows that as $T \to T_a$ then $A \to 0$, $\Delta_2{}^{(\alpha)} \to \Delta_1{}^{(\alpha)}$, and the eigenmodes $\epsilon_\lambda{}^2(\mathbf{q})$ all go to zero at the R corner. For $T > T_a$ the modes take the form

$$\begin{aligned}\epsilon_\lambda{}^2(\mathbf{q}_R) = \omega_0{}^2(\mathbf{q}_R) + (3\Gamma_1 + 2\Gamma_2)\Delta^{(1)} \\ + 2\Gamma_1\Delta^{(2)} + (\Gamma_1 + 2\Gamma_2)\Delta^{(3)},\end{aligned} \tag{39}$$

or, alternatively, making use of the definition of T_a, Eq. (37),

$$\begin{aligned}\epsilon_\lambda{}^2(\mathbf{q}_R) = (3\Gamma_1 + 2\Gamma_2)[\Delta^{(1)}(T) - \Delta^{(1)}(T_a)] \\ + 2\Gamma_1[\Delta^{(2)}(T) - \Delta^{(2)}(T_a)] \\ + (\Gamma_1 + 2\Gamma_2)[\Delta^{(3)}(T) - \Delta^{(3)}(T_a)].\end{aligned} \tag{40}$$

The latter expression explicitly exhibits the fact that $\epsilon_\lambda{}^2(\mathbf{q}_R) \to 0$ as $T \to T_a$ also for $T > T_a$.

The model parameter must satisfy the stability conditions

$$\epsilon_\lambda{}^2(\mathbf{q}_R) \geq 0.$$

For the $\mathbf{q}$ dependence of the modes given by Eq. (32) we require that

$$h_\lambda(\mathbf{q}) > h_\lambda(\mathbf{q}_R) \tag{41}$$

for all $\mathbf{q} \neq \mathbf{q}_R$. For $\mathbf{q} \approx \mathbf{q}_R$,

$$h_\lambda(\mathbf{q}) \approx h_\lambda(\mathbf{q}_R) + \sum \alpha_{ij}{}^\lambda(\mathbf{q}_R)(\mathbf{q} - \mathbf{q}_R)_i(\mathbf{q} - \mathbf{q}_R)_j. \tag{42}$$

Then for $T = T_a$ the eigenmodes take the form

$$\epsilon_\lambda{}^2(T_a, \mathbf{q} \approx \mathbf{q}_R) = \sum_{ij} \alpha_{ij}{}^\lambda(\mathbf{q}_R)(\mathbf{q} - \mathbf{q}_R)_i(\mathbf{q} - \mathbf{q}_R)_j. \tag{43}$$

The eigenfrequencies have a linear dependence in the neighborhood of the R corner and are, in general, anisotropic.

B. Trigonal Distortion

For trigonal distortion the octahedra rotate about a cube diagonal and the components of $\langle \mathbf{R}(l) \rangle$ are all equal. We set

$$A_\lambda{}^2 = \tfrac{1}{3}A^2$$

and

$$\begin{aligned}\Delta_{\lambda\lambda'}{}^{(\alpha)} &= \Delta_1{}^{(\alpha)}, \quad \lambda = \lambda', \quad \Delta_1{}^{(3)} = \Delta^{(3)} \\ &= \Delta_2{}^{(\alpha)}, \quad \lambda \neq \lambda', \quad \Delta_2{}^{(3)} = 0.\end{aligned}$$

The condition [Eq. (25)] that the static parts of the equations of motion vanish now takes the form

$$\begin{aligned}A[\omega_0{}^2(\mathbf{q}_R) + (\Gamma_1 + 2\Gamma_2)(\tfrac{2}{3}A^2 + \Delta_1{}^{(1)} + \Delta^{(3)}) \\ + 2\Gamma_1(\Delta_1{}^{(1)} + \Delta_1{}^{(2)}) + 4\Gamma_2(\Delta_2{}^{(1)} + \Delta_2{}^{(2)})] = 0.\end{aligned} \tag{44}$$

Again for $A \neq 0$ this gives a relationship between A and the correlation functions $\Delta_1{}^{(\alpha)}$ and $\Delta_2{}^{(\alpha)}$. As $T \to T_a$, $A \to 0$, $\Delta_2{}^{(\alpha)} \to 0$, and $\Delta_1{}^{(\alpha)} \to \Delta^{(\alpha)}$, where by definition $\Delta_1{}^{(\alpha)} = \Delta^{(\alpha)}$ for $T \geq T_a$. The equation for the transition temperature is seen to be the same as for the tetragonal case.

From Eq. (26) the equations of motion for $\mathbf{q} = \mathbf{q}_R$ may be written

$$(-\partial^2/\partial t^2) r_\lambda(\mathbf{q}_R) = X r_\lambda(\mathbf{q}_R) + Y \sum_{\lambda' \neq \lambda} r_{\lambda'}(\mathbf{q}_R), \tag{45}$$

where

$$\begin{aligned}X = \omega_0{}^2(\mathbf{q}_R) + (3\Gamma_1 + 2\Gamma_2)(\tfrac{2}{3}A^2 + \Delta_1{}^{(1)}) \\ + 2\Gamma_1\Delta_1{}^{(2)} + (\Gamma_1 + 2\Gamma_2)\Delta^{(3)},\end{aligned} \tag{46}$$

$$Y = 2\Gamma_2(\tfrac{2}{3}A^2 + \Delta_2{}^{(1)} + \Delta_3{}^{(2)}).$$

Solving the secular determinant for Eq. (45) we obtain a singlet mode

$$\epsilon_1^2(\mathbf{q}_R)=X+2Y$$

and a doubly degenerate mode

$$\epsilon_{2,3}^2(\mathbf{q}_R)=X-Y.$$

The matrix $b_{\lambda\lambda'}(\mathbf{q}_R)$ which is diagonal for the tetragonal case now takes the form

$$b_{\lambda\lambda'}(\mathbf{q}_R)=\begin{bmatrix} 1/\sqrt{3} & -\frac{1}{2}(1/\sqrt{3}+1) & -\frac{1}{2}(1/\sqrt{3}-1) \\ 1/\sqrt{3} & -\frac{1}{2}(1/\sqrt{3}-1) & -\frac{1}{2}(1/\sqrt{3}+1) \\ 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \end{bmatrix}. \tag{47}$$

As might be expected, this represents a rotation such that the (1) axis in the rotated coordinate system is parallel to the rotation axis.

For $T<T_a$ we make use of Eq. (44) in order to rewrite the expressions for the eigenmodes. We obtain

$$\begin{aligned} \epsilon_1^2(\mathbf{q}_R)&=4(\Gamma_1+2\Gamma_2)\tfrac{1}{3}A^2, \\ \epsilon_{2,3}^2(\mathbf{q}_R)&=4(\Gamma_1-\Gamma_2)\tfrac{1}{3}A^2-6\Gamma_2(\Delta_2^{(1)}+\Delta_2^{(2)}). \end{aligned} \tag{48}$$

From the definition of T_a it follows that

$$\epsilon_\lambda^2(\mathbf{q}_R)\rightarrow 0, \quad \text{as} \quad T\rightarrow T_a.$$

For $T>T_a$, then, $A=\Delta_2^{(1)}=\Delta_2^{(2)}=0$ and the eigenmodes $\epsilon_1^2(\mathbf{q}_R)=\epsilon_{2,3}^2(\mathbf{q}_R)$ are given by either Eq. (39) or (40). For $T>T_a$ there is, of course, no difference between the tetragonal and trigonal cases.

IV. MOLECULAR FIELD CALCULATION

In the previous section we derived a set of self-consistency equations from which A, $\Delta_1^{(\alpha)}$, and $\Delta_2^{(\alpha)}$ may be calculated. However, in order to avoid complicated summations over the Brillouin zone we have instead, as a first approximation, determined the thermal expectation values A, $\Delta_1^{(\alpha)}$, and $\Delta_2^{(\alpha)}$ explicitly only for the case in which the interaction between the different cells is treated in the molecular field approximation.

The molecular field equations are obtained by replacing the interaction tensors $\theta_{\lambda\lambda'}(\mathbf{q})$, $v_{\lambda\lambda'}(\mathbf{q})$, and $\Gamma_{\lambda\lambda'}(\mathbf{q})$ by their averaged values over the Brillouin zone.[16] From Eqs. (10), (12), and (19) it follows that

$$\begin{aligned} \frac{1}{N}\sum_{\mathbf{q}} \theta_{\lambda\lambda'}(\mathbf{q})&=\tfrac{1}{2}\delta_{\lambda\lambda'}, \\ \frac{1}{N}\sum_{\mathbf{q}} v_{\lambda\lambda'}(\mathbf{q})&=\Omega_0^2\delta_{\lambda\lambda'}, \\ \frac{1}{N}\sum_{\mathbf{q}} \Gamma_{\lambda\lambda'}(\mathbf{q})&=0. \end{aligned} \tag{49}$$

We obtain the immediate simplification that

$$\Delta_{\lambda\lambda'}^{(2)}\equiv 0 \quad \text{and} \quad \Delta_{\lambda\lambda'}^{(3)}\equiv 0, \tag{50}$$

as seen from their definitions, Eqs. (31). Consequently, we drop the superscript on $\Delta_{\lambda\lambda'}^{(1)}$,

$$\Delta_{\lambda\lambda'}\equiv\Delta_{\lambda\lambda'}^{(1)}=\langle r_\lambda(lt)r_{\lambda'}(lt)\rangle. \tag{51}$$

We note the molecular field equations are independent of the particular form of $\Gamma_{\lambda\lambda'}(\mathbf{q})$ given by Eq. (19) provided certain conditions, such as Eq. (49), are satisfied. The now $\mathbf{q}$-independent coefficients $b_{\lambda\lambda'}$ are equal to $\sqrt{2}$ times the $\mathbf{q}$-dependent coefficients evaluated at $\mathbf{q}=\mathbf{q}_R$, which are given by Eqs. (33) and (47) for the tetragonal and trigonal cases, respectively.

For $T>T_a$ the molecular field equations take the form

$$\begin{aligned} \Delta&=\omega^{-1}\coth\tfrac{1}{2}\beta\omega, \\ \omega^2&=2\Omega_0^2+(3\Gamma_1+2\Gamma_2)\Delta. \end{aligned} \tag{52}$$

For $T<T_a$ we obtain for the tetragonal case

$$\Delta_1=\omega_1^{-1}\coth\tfrac{1}{2}\beta\omega_1, \quad \Delta_2=\omega_2^{-1}\coth\tfrac{1}{2}\beta\omega_2, \tag{53}$$

where

$$\begin{aligned} \omega_1^2&=4\Gamma_1A^2+[2\Omega_0^2-\omega_0^2(\mathbf{q}_R)], \\ \omega_2^2&=2(\Gamma_2-\Gamma_1)A^2+(\Gamma_2-3\Gamma_1)(\Delta_1-\Delta_2) \\ &\qquad +[2\Omega_0^2-\omega_0^2(\mathbf{q}_R)], \end{aligned} \tag{54}$$

and where A^2 is determined by

$$\omega_0^2(\mathbf{q}_R)+\Gamma_1(2A^2+3\Delta_1)+2\Gamma_2\Delta_2=0. \tag{55}$$

For the trigonal case we obtain

$$\begin{aligned} \Delta_1&=\tfrac{1}{3}[\omega_1^{-1}\coth\tfrac{1}{2}\beta\omega_1+(2/\omega_2)\coth\tfrac{1}{2}\beta\omega_2], \\ \Delta_2&=\tfrac{1}{3}[\omega_1^{-1}\coth\tfrac{1}{2}\beta\omega_1-\omega_2^{-1}\coth\tfrac{1}{2}\beta\omega_2], \end{aligned} \tag{56}$$

$$\begin{aligned} \omega_1^2&=4(\Gamma_1+2\Gamma_2)\tfrac{1}{3}A^2+[2\Omega_0^2-\omega_0^2(\mathbf{q}_R)], \\ \omega_2^2&=4(\Gamma_1-\Gamma_2)\tfrac{1}{3}A^2-6\Gamma_2\Delta_2+[2\Omega_0^2-\omega_0^2(\mathbf{q}_R)], \\ &\omega_0^2(\mathbf{q}_R)+(\Gamma_1+2\Gamma_2)(\tfrac{2}{3}A^2+\Delta_1)+2\Gamma_1\Delta_1+4\Gamma_2\Delta_2=0. \end{aligned} \tag{57}$$

We note that if in the set of equations for the trigonal case we replace $\frac{1}{3}(\Gamma_1+2\Gamma_2)$ by $\tilde{\Gamma}_1$, and Γ_1 by $\tilde{\Gamma}_2$, then these equations become identical to those for the tetragonal case with Γ_1, Γ_2 replaced by $\tilde{\Gamma}_1$, $\tilde{\Gamma}_2$.

The transition temperature is in both cases given by

$$\omega_0^2(\mathbf{q}_R)+(3\Gamma_1+2\Gamma_2)\Delta(T_a)=0. \tag{58}$$

Because $\Delta(T)$ is a positive and monotonically increasing function of temperature there will be no phase transition unless

$$\omega_0^2(\mathbf{q}_R)+(3\Gamma_1+2\Gamma_2)\Delta(0)<0. \tag{59}$$

It should be emphasized that the molecular field equations are used only to determine the expectation values A, Δ_1, and Δ_2. The wave-vector-dependent excitation spectra $\epsilon_\lambda(\mathbf{q},A,\Delta_1,\Delta_2)$ describe the fluctuations about these average values. The frequencies ω_λ^2 do not represent, even approximately, the excitations of the

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[16] An alternate derivation of the molecular field equations is outlined in Sec. V.

system. This is a situation familiar from the study of exchange models in the theory of magnetism, where the molecular field energy is quite different from the **q**-dependent low-lying spin-wave excitations.

The requirement that $\epsilon_\lambda^2(\mathbf{q}_R)>0$, gives the following stability conditions for the tetragonal phase:

$$\Gamma_1>0\,,\quad 2(\Gamma_2-\Gamma_1)A^2+(\Delta_2-3\Delta_1)(\Gamma_1-\Gamma_2)>0\,. \tag{60}$$

Similarly, for the trigonal phase we obtain

$$\Gamma_1+2\Gamma_2>0\,,\quad 2(\Gamma_1-\Gamma_2)A^2-9\Gamma_2\Delta_2>0\,. \tag{61}$$

These conditions differ from those given in Ref. 12 by the presence of the correlation functions Δ_1 and Δ_2. From Eqs. (40) and (50) the stability of the cubic phase requires

$$3\Gamma_1+2\Gamma_2>0\,. \tag{62}$$

This condition together with Eq. (59) shows that the harmonic soft-mode frequency $\omega_0(\mathbf{q}_R)$ must be purely imaginary with a certain minimum absolute value, in order for a phase transition to be possible.[17]

The limiting behavior for $T\approx T_a$ and for $T\to\infty$ is easily extracted from these molecular field equations. For $T\leq T_a$ we obtain

$$A^2=a_1(T_a-T)$$

with a different constant a_1 for the tetragonal and trigonal cases.[18] For the tetragonal case,

$$(\Delta_1-\Delta_2)=a_2A^2\,,$$

while the for trigonal case we find

$$\Delta_2=a_2'A^2\,.$$

From Eqs. (38), (48), and (50) the eigenmodes may then be written

$$\epsilon_\lambda^2(\mathbf{q}_R)=b_\lambda(T_a-T)\,,$$

where $b_1\neq b_2=b_3$, and where these constants are different for tetragonal and trigonal distortions. For $T\gtrsim T_a$ we find

$$\Delta(T)-\Delta(T_a)=a_3(T-T_a)\,,$$

where

$$\Delta(T_a)=\Delta_1(T_a)=\Delta_2(T_a)=\omega_0^2/(3\Gamma_1+2\Gamma_2)\,.$$

For the triply degenerate eigenmodes $\epsilon_\lambda^2(\mathbf{q}_R)$ we therefore obtain the usually assumed Curie-Weiss behavior

$$\epsilon_\lambda^2(\mathbf{q}_R)=c(T-T_a)\,.$$

We note that the molecular field approximation gives the limiting behavior assumed in Ref. 12, for A and for the eigenfrequencies $\epsilon_\lambda^2(\mathbf{q}_R)$.

In the high-temperature limit $T\to\infty$, we obtain from Eqs. (40), (50), and (52)

$$\Delta\to(3\Gamma_1+2\Gamma_2)^{-1/2}(kT)^{1/2}\,,$$
$$\epsilon_\lambda^2(\mathbf{q}_R)\to(3\Gamma_1+2\Gamma_2)^{1/2}(kT)^{1/2}\,.$$

In this limit the eigenfrequencies depend only on the anharmonic terms in the interaction potential. This temperature dependence differs from the modified Curie-Weiss law,

$$1/\epsilon_\lambda^2=a/(T-T_a)+b\,,$$

which has been proposed in order to fit the neutron scattering data.[4] The latter expression yields a constant value for ϵ_λ^2 in the high-temperature limit. The data were, however, taken only over a limited temperature range, and the observed deviation from Curie-Weiss law is compatible with the high-temperature limit predicted by the model. With increasing temperature, higher-order anharmonic terms neglected in this model will, of course, also become increasingly more important.

For arbitrary temperatures the molecular field equations may be solved numerically by iteration for given values of the model parameters. We have made use of the experimental information available to test the predictions of the model. The value of A is related to the measured rotation angle by Eq. (3). We obtain

$$\varphi=\sqrt{2}A/(m_0a^2)^{1/2} \tag{63}$$

for small angles such that $\tan\varphi\approx\varphi$. This relationship may be derived alternatively from Eq. (A18), making use of the known position vectors $\mathbf{X}_k$ of the oxygen ions and the polarization vectors $\mathbf{e}(\mathbf{q}_R\lambda\mathbf{X}_k)$ for the Γ_{25} modes.

For $SrTiO_3$ the temperature dependence of the rotation angle has been measured by electron paramagnetic resonance (EPR),[3] the soft-mode frequencies by neutron scattering,[4,5] and for $T<T_a$, also by Raman scattering.[2] These experimental results are qualitatively in good agreement with the predictions of the model. A singlet-mode frequency is obtained which, within experimental error, is proportional to the order parameter A, in agreement with Eq. (38), whereas the frequency of the doubly degenerate mode is found to have a more complicated temperature dependence as allowed by the theoretical expression Eq. (38). In the neighborhood of the transition temperature A^2 and ϵ_λ^2 are well fitted by a linear dependence with the possible exception of $\epsilon_{2,3}^2$ for $T\lesssim T_a$ where the experimental uncertainties are largest. This indicates that the data in the temperature range considered are well described by the molecular field approximation. An improved statistical mechanical treatment of the model[19] will presumably give deviations from the linear behavior sufficiently close to T_a. However, more sophisticated calculations do not seem to be justified by the experimental data currently available.

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[17] In model calculations for $SrTiO_3$ such purely imaginary harmonic Γ_{25} phonon modes have been obtained by R. A. Cowley, Phys. Rev. **134**, A981 (1964). See in particular Fig. 8, model V.

[18] These coefficients are rather complicated functions of the model parameters and will not be given explicitly.

[19] Any calculation going beyond the molecular field approximation would require a specific model form also for $v_{\lambda\lambda'}(\mathbf{q})$. This may be constructed in a straightforward manner by arguments analogous to those used to obtain $\Gamma_{\lambda\lambda'}(\mathbf{q})$.

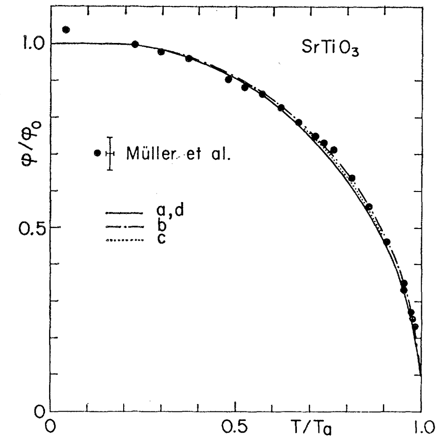

FIG. 2. Angle of rotation of the oxygen octahedron in $SrTiO_3$ normalized to its value at $T=0$, as a function of reduced temperature. ● Experimental points obtained by EPR. (a) Theoretical curve giving best fit to all the available data. b: Theoretical curve giving best fit to the observed temperature dependence of the angle. (c) Predicted curve based on a fit to the neutron data. (d) Predicted curve based on a fit to the Raman data.

The molecular field equations contain four model parameters, two harmonic interaction parameters $\omega_0^2(\mathbf{q}_R)$ and Ω_0^2, and two anharmonic constants Γ_1 and Γ_2. These parameters are well overdetermined by the data available. Making use only of the value of the transition temperature T_a, the order parameter and the soft-mode frequencies at $T=0$, $A(0)$, $\epsilon_1(0)$, $\epsilon_{2,3}(0)$ and the slopes of these quantities for $T\approx T_a$, a_1, b_1, $b_{2,3}$ and c, alone provide eight experimental values.

We determined the model parameters by a best-fit procedure using all the available data.[20] However, only relative values of the rotation angle were used for reasons discussed below. To demonstrate the extent to which the model parameters are overdetermined, we have also obtained the model parameters by using in turn only the neutron data, Raman data, and the temperature dependence of the angle of rotation, and then predicted the behavior of the remaining quantities.

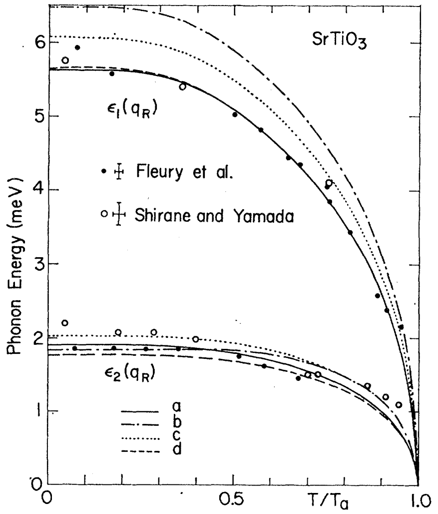

FIG. 3. Γ_{25} optical-phonon frequencies in $SrTiO_3$ as a function of reduced temperature in the distorted phase. ○ Experimental points obtained by neutron scattering. ● Experimental points obtained by Raman scattering. (a) Theoretical curve giving best fit to all the available data. (b) Predicted curves based on a fit to the EPR data. (c) Theoretical curve giving best fit to the neutron data. (d) Theoretical curve giving best fit to the Raman data.

The results of the numerical calculations are shown in Figs. 2–4 and in Table I. The only predicted curve which lies clearly outside the experimental error is $\epsilon_1(\mathbf{q}_R)$ when the model parameters were determined by the temperature dependence of the rotation angle alone.

In these calculations we have, however, made no use of the absolute magnitude of the rotation angle. We see from Table I that the predicted value of $\varphi(T=0)=\varphi_0$ is always much larger than the experimental value $\varphi_0=2.0\pm0.1°$.[1,3] It was not possible to obtain a good fit both for the absolute magnitude of φ and its temperature dependence. Any attempt to fit the value of φ_0 seriously distorted the shape of the $\varphi(T)$ as well as the $\epsilon_{1,2}$ curves.

This suggests that additional anharmonic forces neglected in the simple model may be very important in order to stabilize the crystal and to determine the minimum of the free energy as a function of angle. The good agreement for the temperature dependence of φ and the soft mode frequencies indicates that the shape of the free-energy minimum is well described by the model although the location of the minimum is not.

For $LaAlO_3$, the displacements have been measured by EPR,[3] and the behavior of the soft mode in the cubic phase has been studied by neutron scattering.[10] It is reasonable to assume that additional anharmonic interactions may be important also for $LaAlO_3$. Thus, we

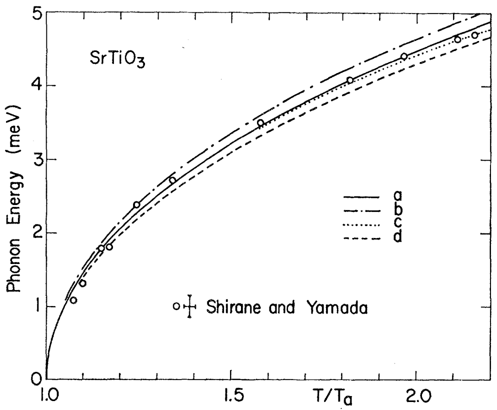

FIG. 4. Γ_{25} optical-phonon frequency in $SrTiO_3$ as a function of reduced temperature in the high-temperature phase. ○ Experimental points obtained by neutron scattering. (a) Theoretical curve giving best fit to all the available data. (b) Predicted curve based on a fit to the EPR data. (c) Theoretical curve giving best fit to the neutron data. (d) Predicted curve based on a fit to the Raman data.

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[20] The data reported in Ref. 5 were not available to us prior to completion of the numerical calculations.

TABLE I. Model parameters giving best fit of theory to experiments with the transition temperature and the angle of rotation $\varphi(T=0)$ at best fit.

Material	Data used for fit	Ω_0^2 (meV)^2	$-\omega_0^2(q_R)$ (meV)^2	Γ_1 (meV)^3	Γ_2 (meV)^3	T_a °K	$\varphi(T=0)$ (degrees)
$SrTiO_3$	EPR,[a] neutron and Raman scattering	51	34	41	49	105	4.7
	Rotation angle EPR[a]	34	40	40	45	105	5.4
	Neutron scattering	35	34	33	39	104	5.5
	Raman scattering	41	32	33	39	104[b]	5.2
$LaAlO_3$	Rotation angle EPR[a] Neutron scattering	244	178	272	20	794	9.0

[a] Using only the relative values for the rotation angle.

[b] The temperature scale for the Raman scattering data of Ref. 2 has been multiplied by 0.91 in order to give a transition temperature equal to that obtained for the neutron data.

have used only the relative values of $\varphi(T)$ together with the neutron data in order to determine the model parameters. The fit for $\varphi(T)$ is shown in Fig. 5. The values obtained for the model parameters are given in Table I. The soft mode frequencies are shown in Fig. 6 together with the experimental results of Axe *et al.*[10] It should be noted that the modes for $T<T_a$, particularly ϵ_2, are very sensitive to small changes in the model parameters, and that the neutron data have fairly large uncertainties due to the fact that the modes are overdamped in the neighborhood of the transition temperature.[10]

For φ_0 we obtain 9.0° as compared with the experimental value of 6.3°. The agreement is somewhat better than in the case of $SrTiO_3$. We note that for $SrTiO_3$ the values obtained for Γ_1 and Γ_2 lie very close to the stability limit.[21] For $T=0$ the stability condition for the tetragonal phase, Eq. (60), reads $\Gamma_2>\Gamma_1$ when we neglect zero-point motion corrections, whereas according to Table I, $\Gamma_2\approx 1.2\Gamma_1$. The corresponding stability condition for trigonal distortion $\Gamma_1>\Gamma_2$ is seen to be well satisfied for $LaAlO_3$. We expect therefore that the additional anharmonic interactions will be more important in stabilizing the crystal for $SrTiO_3$ than for $LaAlO_3$.

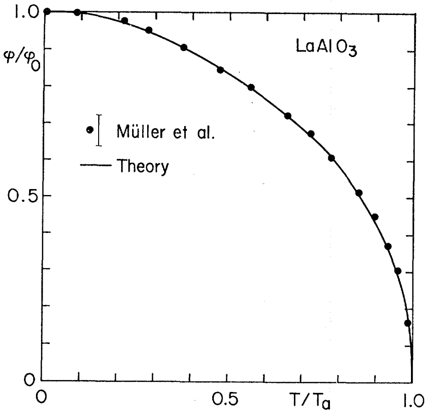

FIG. 5. Angle of rotation in $LaAlO_3$ normalized to its value at $T=0$ as a function of reduced temperature. ● Experimental points obtained by EPR. Theoretical curve giving best fit to the EPR and neutron data.

The interactions with the strains and the importance of the sixth-order anharmonic interactions are currently being investigated.

V. FREE ENERGY AND THE SPECIFIC HEAT

The results presented in Sec. III may be derived alternatively by a variational procedure. We introduce a trial density matrix of the form

$$\rho_{\mathrm{eff}}=e^{-\beta H_{\mathrm{eff}}}/\mathrm{Tr}e^{-\beta H_{\mathrm{eff}}}, \tag{64}$$

where H_{eff} is a diagonal Hamiltonian

$$H_{\mathrm{eff}}=E_0+\sum_{\mathbf{q}\lambda}\epsilon_\lambda(\mathbf{q})a_\lambda^\dagger(\mathbf{q})a_\lambda(\mathbf{q}) \tag{65}$$

expressed in terms of temperature-dependent energies E_0, and $\epsilon_\lambda(\mathbf{q})$. By definition, a_λ and $a_\lambda^\dagger$ are linear combinations of the set of operators $\{r_\lambda,P_\lambda\}$ satisfying Bose commutation relations

$$[a_\lambda(\mathbf{q}),a_{\lambda'}^\dagger(\mathbf{q}')]=\delta_{\lambda\lambda'}\delta_{\mathbf{q}\mathbf{q}'}.$$

In terms of this density matrix the free energy may be

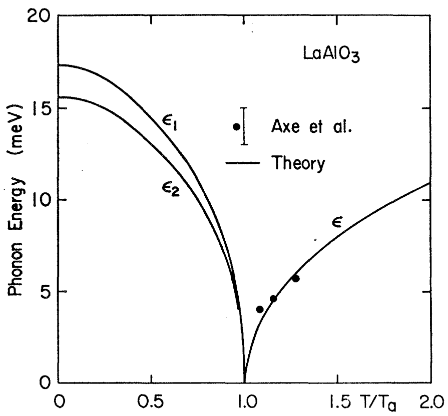

FIG. 6. Γ_{25} optical-phonon modes in $LaAlO_3$ as a function of reduced temperature. ● Experimental points obtained by neutron scattering. Theoretical curve giving best fit to the EPR and neutron data.

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[21] In fact, using a best-fit procedure including the magnitude of the rotation angle led to values of Γ_1 and Γ_2 outside the stability region for tetragonal distortion.

written

$$F=\mathrm{Tr}(\rho_{\mathrm{eff}}H+\beta^{-1}\rho_{\mathrm{eff}}\ln\rho_{\mathrm{eff}}). \tag{66}$$

Here H is the original Hamiltonian given by Eqs. (8), (11), and (16). The effective Hamiltonian is used only to define a density-matrix diagonal in the occupation-number representation of the excitations $\epsilon_\lambda(\mathbf{q})$. We note that ρ_{eff} and F are independent of $E_0(T)$ introduced in Eq. (65).

For noninteracting Bose excitations the entropy contribution to the free energy,

$$S=-k_B\,\mathrm{Tr}\rho_{\mathrm{eff}}\ln\rho_{\mathrm{eff}},$$

may be written in the form

$$S=k_B\sum_{\mathbf{q}\lambda}\{[1+n_\lambda(\mathbf{q})]\times\ln[1+n_\lambda(\mathbf{q})]-n_\lambda(\mathbf{q})\ln n_\lambda(\mathbf{q})\}, \tag{67}$$

where $n_\lambda(\mathbf{q})$ is the Bose occupation number factor

$$n_\lambda(\mathbf{q})=1/(e^{\beta\epsilon_\lambda(\mathbf{q})}-1).$$

In order to evaluate $\langle H\rangle$ we express $\{r_\lambda,P_\lambda\}$ in terms of the new normal-mode coordinates a_λ and $a_\lambda{}^\dagger$. It will be convenient to make use of the operators $s_\lambda(\mathbf{q})$ introduced in Eq. (27). We assume that s_λ may be expressed in terms of a_λ and $a_\lambda{}^\dagger$ with equal amplitudes for forward and backward propagating waves,[22]

$$s_\lambda(\mathbf{q})=[2\epsilon_\lambda(\mathbf{q})]^{-1/2}[a_\lambda(\mathbf{q})+a_\lambda{}^\dagger(-\mathbf{q})]. \tag{68}$$

The form of $P_\lambda(\mathbf{q})$ follows from the requirement that the transformations be canonical. For this choice of $s_\lambda(\mathbf{q})$ the expectation value of the kinetic energy takes the simple form

$$\langle T\rangle=\tfrac{1}{2}\sum_{\mathbf{q}\lambda}\epsilon_\lambda(\mathbf{q})[n_\lambda(\mathbf{q})+\tfrac{1}{2}]. \tag{69}$$

For $\langle H_2\rangle$ we obtain

$$\langle H_2\rangle=\tfrac{1}{2}N\sum_{\lambda\lambda'}v_{\lambda\lambda'}(\mathbf{q}_R)A_\lambda A_{\lambda'}+\tfrac{1}{2}\sum_{\mathbf{q},\lambda\lambda'}v_{\lambda\lambda'}(\mathbf{q})\Delta_{\lambda\lambda'}(\mathbf{q}), \tag{70}$$

where $\Delta_{\lambda\lambda'}(\mathbf{q})$ is defined by Eq. (30). Because the density matrix is diagonal, the fourth-order correlation functions involving a_λ and $a_\lambda{}^\dagger$ which occur in $\langle H_4\rangle$ may be decomposed using Wick's theorem. We obtain

$$\begin{aligned}\langle H_4\rangle={}&2N\sum_{\lambda\lambda'}[\Gamma_{\lambda\lambda'}(0)-\Gamma_{\lambda\lambda'}(\mathbf{q}_R)]A_\lambda{}^2A_{\lambda'}{}^2\\&+2\sum_{\mathbf{q},\lambda\lambda'}[\Gamma_{\lambda\lambda'}(0)-\Gamma_{\lambda\lambda'}(\mathbf{q}_R)+\Gamma_{\lambda\lambda'}(\mathbf{q}-\mathbf{q}_R)-\Gamma_{\lambda\lambda'}(\mathbf{q})]\\&\times[A_\lambda{}^2\Delta_{\lambda'\lambda'}(\mathbf{q})+2A_\lambda A_{\lambda'}\Delta_{\lambda\lambda'}(\mathbf{q})]\\&+\frac{1}{N}\sum_{\mathbf{q}\mathbf{q}'\lambda\lambda'}[\Gamma_{\lambda\lambda'}(0)-\Gamma_{\lambda\lambda'}(\mathbf{q})+\Gamma_{\lambda\lambda'}(\mathbf{q}'-\mathbf{q})-\Gamma_{\lambda\lambda'}(\mathbf{q}')]\\&\times[\Delta_{\lambda\lambda}(\mathbf{q}')\Delta_{\lambda'\lambda'}(\mathbf{q})+2\Delta_{\lambda\lambda'}(\mathbf{q}')\Delta_{\lambda\lambda'}(\mathbf{q})].\end{aligned} \tag{71}$$

The expectation value A_λ and the excitation energies will be determined by requiring that the free energy, $F=\langle H\rangle-TS$, be stationary with respect to variations of these parameters. The condition

$$\partial F/\partial A_\lambda=0 \tag{72}$$

immediately gives the relationship Eq. (25), whereas the functional variation

$$\partial F/\partial\epsilon_\lambda(\mathbf{q})=0 \tag{73}$$

yields the following expression for $\epsilon_\lambda(\mathbf{q})$:

$$\begin{aligned}\epsilon_\lambda{}^2(\mathbf{q})={}&\sum_{\bar\lambda\lambda'}v_{\bar\lambda\lambda'}(\mathbf{q})b_{\bar\lambda\lambda}(\mathbf{q})b_{\lambda'\lambda}(-\mathbf{q})\\&+4\sum_{\bar\lambda\lambda'}[\Gamma_{\bar\lambda\lambda'}(0)-\Gamma_{\bar\lambda\lambda'}(\mathbf{q}_R)+\Gamma_{\bar\lambda\lambda'}(\mathbf{q}-\mathbf{q}_R)-\Gamma_{\bar\lambda\lambda'}(\mathbf{q})]\\&\times[2A_{\bar\lambda}A_{\lambda'}b_{\bar\lambda\lambda}(\mathbf{q})b_{\lambda'\lambda}(-\mathbf{q})+A_{\bar\lambda}{}^2b_{\lambda'\lambda}(\mathbf{q})b_{\lambda'\lambda}(-\mathbf{q})]\\&+4\frac{1}{N}\sum_{\mathbf{q}'\bar\lambda\lambda'}[\Gamma_{\bar\lambda\lambda'}(0)-\Gamma_{\bar\lambda\lambda'}(\mathbf{q})+\Gamma_{\bar\lambda\lambda'}(\mathbf{q}'-\mathbf{q})-\Gamma_{\bar\lambda\lambda'}(\mathbf{q}')]\\&\times[2\Delta_{\bar\lambda\lambda'}(\mathbf{q}')b_{\bar\lambda\lambda}(\mathbf{q})b_{\lambda'\lambda}(-\mathbf{q})\\&\qquad+\Delta_{\bar\lambda\bar\lambda}(\mathbf{q}')b_{\lambda'\lambda}(\mathbf{q})b_{\lambda'\lambda}(-\mathbf{q})].\end{aligned} \tag{74}$$

This corresponds to Eqs. (26)–(28), and we have rederived the result obtained by the equation of motion method in Sec. III.

The molecular field equations may be obtained similarly. To define the density matrix ρ_{eff} we use an effective Hamiltonian of the form

$$H_{\mathrm{eff}}=E_0+\sum_\lambda\omega_\lambda a_\lambda{}^\dagger(\mathbf{q})a_\lambda(\mathbf{q})$$

with a flat spectrum ω_λ. Introducing the corresponding canonical transformations to Eqs. (27) and (68) with wave-vector-independent coefficients $b_{\lambda\lambda'}$, the extremum conditions

$$\partial F/\partial A=0,\quad \partial F/\partial\omega_\lambda=0$$

give the molecular field equations discussed in Sec. IV.

We choose the arbitrary function $E_0(T)$ in Eq. (65) such that the self-consistency condition

$$\langle H\rangle=\langle H_{\mathrm{eff}}\rangle$$

is satisfied. Then we may write

$$\langle H\rangle=E_0(T)+\sum_{\lambda\mathbf{q}}\epsilon_\lambda(\mathbf{q})n_\lambda(\mathbf{q}), \tag{75}$$

$$F=E_0(T)+k_BT\sum_{\mathbf{q}\lambda}\ln(1-e^{-\beta\epsilon_\lambda(\mathbf{q})}). \tag{76}$$

The specific heat is obtained either from the free energy or the internal energy in the usual way,

$$C_v=-T\frac{d^2F}{dT^2}=\frac{d}{dT}\langle H\rangle.$$

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[22] A more general canonical transformation would introduce additional variational parameters but would yield the same final result.

When we make use of the conditions Eq. (72) and (73) we obtain either from Eq. (75) or (76);

$$C_v=\frac{1}{k_BT^2}\sum_{\lambda\mathbf{q}}\epsilon_\lambda(\mathbf{q})n_\lambda(\mathbf{q})[1+n_\lambda(\mathbf{q})]\times\left[\epsilon_\lambda(\mathbf{q})-T\frac{d}{dT}\epsilon_\lambda(\mathbf{q})\right]. \tag{77}$$

The form of the **q**-dependent modes is given by Eq. (32), where in the molecular field approximation,

$$e_\lambda^2(\mathbf{q}_R)\rightarrow a_\lambda(T_a)\,|T-T_a|$$

as $T\rightarrow T_a$ from either side of the transition point with a_λ in general different for $T>T_a$ and $T<T_a$. For the **q** dependence given by Eqs. (41) and (42) a finite discontinuity is then obtained for the specific heat, given by

$$\Delta C_v=\frac{N}{2k_BT}\sum_\lambda\left[I_\lambda(T_c)\frac{d}{dT}\epsilon_\lambda^2(T)\Bigg|\begin{matrix}T\rightarrow T_a{}^+\\ T\rightarrow T_a{}^-\end{matrix}\right], \tag{78}$$

where I_λ is the nondivergent integral

$$I_\lambda=\frac{1}{N}\sum_{\mathbf{q}}n_\lambda(\mathbf{q})[1+n_\lambda(\mathbf{q})].$$

VI. CONCLUSION

From the altogether 15 degrees of freedom per unit cell in the perovskite structure, we have separated out the three degrees of freedom directly connected with the structural phase transition, and constructed a model Hamiltonian describing these three degrees of freedom. The anharmonic interactions were approximated by a simple form containing only two anharmonic force constants. With this model good agreement with the experimental results for $SrTiO_3$ and $LaAlO_3$ could be obtained except for the magnitude of the angular distortion. For $SrTiO_3$, the model parameters were overdetermined in the sense that when part of the available data was used to determine the model parameters, the predictions for the remaining quantities were in good agreement with the experimental results.

The disagreement for the magnitude of the rotation angle suggests that additional anharmonic interactions need be taken into account.

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APPENDIX

The Hamiltonian, Eq. (1), may be expressed in terms of the harmonic normal mode coordinates in the usual way,[13]

$$H=\tfrac{1}{2}\sum_{\lambda\mathbf{q}}[P_\lambda(\mathbf{q})P_\lambda(-\mathbf{q})+\omega_0{}^2(\lambda\mathbf{q})Q_\lambda(\mathbf{q})Q_\lambda(-\mathbf{q})]+\sum_n\frac{1}{n!}\sum U^{(n)}(\lambda_1\mathbf{q}_1\cdots\lambda_n\mathbf{q}_n)Q_{\lambda_1}(\mathbf{q}_1)\cdots Q_{\lambda_n}(\mathbf{q}_n), \tag{A1}$$

where

$$Q_\lambda(\mathbf{q})=1/\sqrt{N}\sum_{\alpha,k,l}(\sqrt{m_k})e_\alpha{}^*(\lambda\mathbf{q}k)u_\alpha(lk)e^{-i\mathbf{q}\cdot\mathbf{X}(lk)},$$

$$P_\lambda(\mathbf{q})=1/\sqrt{N}\sum_{\alpha,k,l}(\sqrt{m_k})e_\alpha(\lambda\mathbf{q}k)\dot{u}_\alpha(lk)e^{i\mathbf{q}\cdot\mathbf{X}(lk)},$$

$$\begin{aligned}U^{(n)}(\lambda_1\mathbf{q}_1\cdots\lambda_n\mathbf{q}_n)&=N^{-n/2}\sum\frac{V_{\alpha_1\cdots\alpha_n}(l_1k_1\cdots l_nk_n)}{(m_{k_1}\cdots m_{k_n})^{1/2}}\delta(\sum_{i=1}^{n}\mathbf{q}_i)\\&\times e_{\alpha_1}(\lambda_1k_1\mathbf{q}_1)\cdots e_{\alpha_n}(\lambda_nk_n\mathbf{q}_n)\\&\times\exp[i\mathbf{q}_1\cdot\mathbf{X}(l_1k_1)+\cdots+i\mathbf{q}_n\cdot\mathbf{X}(l_nk_n)].\end{aligned} \tag{A2}$$

Further, $\omega_0{}^2(\lambda\mathbf{q})$ are the $3h$ eigenvalues of the harmonic dynamical matrix, where h is the number of ions per unit cell and $\mathbf{e}(\lambda k\mathbf{q})$ are the corresponding polarization vectors for branch λ and momentum **q** which satisfy the completeness and orthogonality relations

$$\begin{aligned}&\sum_\lambda e_\alpha{}^*(\lambda\mathbf{q}k)e_{\alpha'}(\lambda\mathbf{q}k')=\delta_{\alpha\alpha'}\delta_{kk'},\\&\sum_{\alpha k}e_\alpha{}^*(\lambda\mathbf{q}k)e_\alpha(\lambda'\mathbf{q}k)=\delta_{\lambda\lambda'}.\end{aligned} \tag{A3}$$

The operators $Q_\lambda(\mathbf{q})$ and $P_\lambda(\mathbf{q})$ are canonical conjugate variables,

$$[Q_\lambda(\mathbf{q}),P_{\lambda'}(\mathbf{q}')]=i\delta_{\mathbf{q}\mathbf{q}'}\delta_{\lambda\lambda'}. \tag{A4}$$

We introduce space-dependent normal-mode coordinates defined by

$$\begin{aligned}P_\lambda(l)&=\frac{1}{\sqrt{N}}\sum_{\mathbf{q}\lambda'}e^{-i\mathbf{q}\cdot\mathbf{X}(l)}T_{\lambda\lambda'}(\mathbf{q})P_{\lambda'}(\mathbf{q})\\R_\lambda(l)&=\frac{1}{\sqrt{N}}\sum_{\mathbf{q}\lambda'}e^{i\mathbf{q}\cdot\mathbf{X}(l)}Q_{\lambda'}(\mathbf{q})(T^{-1})_{\lambda\lambda'}(\mathbf{q}).\end{aligned} \tag{A5}$$

The matrix $T_{\lambda\lambda'}$ has been introduced to account for degeneracies of the $\omega_0{}^2(\lambda\mathbf{q})$ eigenfrequencies. If there is no crossing of the harmonic eigenfrequencies anywhere in the Brillouin zone, then **T** may be replaced by the unit matrix. This procedure is analogous to that used to construct Wannier wave functions for degenerate energy bands.[23] In addition, the introduction of the matrix **T** permits the imposition of desired symmetry properties on the operators $R_\lambda(l)$ and $P_\lambda(l)$. In order

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[23] See, for example, E. I. Blount, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 13, p. 306.

for $P_\lambda(l)$ and $R_\lambda(l)$ to be Hermetian we require that

$$T_{\lambda\lambda'}(\mathbf{q})=T_{\lambda\lambda'}{}^*(-\mathbf{q}). \tag{A6}$$

By construction, $R_\lambda(l)$ and $P_\lambda(l)$ satisfy the canonical commutation relations

$$[R_\lambda(l),P_{\lambda'}(l')]=i\delta_{\lambda\lambda'}\delta_{ll'}. \tag{A7}$$

In terms of these operators the Hamiltonian may be written

$$\begin{aligned}H=\tfrac{1}{2}\sum_{\substack{ll'\\ \lambda\lambda'}} P_\lambda(l)(\theta^{-1})_{\lambda\lambda'}(l,l')P_{\lambda'}(l')
&+\tfrac{1}{2}\sum_{\substack{ll'\\ \lambda\lambda'}} R_\lambda(l)v_{\lambda\lambda'}(l,l')R_{\lambda'}(l')\\
&+\sum_{n=3}^{\infty}\frac{1}{n!}\Gamma^{(n)}(\lambda_1l_1\cdots\lambda_nl_n)R_{\lambda_1}(l_1)\cdots R_{\lambda_n}(l_n),\end{aligned} \tag{A8}$$

where

$$\begin{aligned}(\theta^{-1})_{\lambda\lambda'}(l,l')&=\frac{1}{N}\sum_{\mathbf{q}\bar\lambda} e^{-i\mathbf{q}\cdot[\mathbf{X}(l)-\mathbf{X}(l')]}(T^{-1})_{\bar\lambda\lambda}(\mathbf{q})\times(T^{-1})_{\bar\lambda\lambda'}(\mathbf{q}),\\
v_{\lambda\lambda'}(l,l')&=\frac{1}{N}\sum_{\mathbf{q}\bar\lambda} e^{-i\mathbf{q}\cdot[\mathbf{X}(l)-\mathbf{X}(l')]}T_{\lambda\bar\lambda}(\mathbf{q})\times\omega_0{}^2(\mathbf{q}\bar\lambda)T_{\lambda'\bar\lambda}(-\mathbf{q}),\end{aligned} \tag{A9}$$

and

$$\begin{aligned}\Gamma^{(n)}(\lambda_1l_1\cdots\lambda_nl_n)=N^{-n/2}\sum T_{\lambda_1\bar\lambda_1}(\mathbf{q}_1)\cdots
&\times T_{\lambda_n\bar\lambda_n}(\mathbf{q}_n)U^{(n)}(\bar\lambda_1\mathbf{q}_1\cdots\bar\lambda_n\mathbf{q}_n)\\
&\times e^{-[\mathbf{q}_1\cdot\mathbf{X}(l_1)+\cdots+\mathbf{q}_n\cdot\mathbf{X}(l_n)]}.\end{aligned} \tag{A10}$$

From the definition Eq. (A5) the Fourier transform of $R_\lambda(l)$ is given by

$$R_\lambda(\mathbf{q})=\sum_{\lambda'} Q_\lambda(\mathbf{q})(T^{-1})_{\lambda\lambda'}(\mathbf{q}). \tag{A11}$$

We choose the matrix $\mathbf{T}$ equal to the unit matrix at the R corner such that

$$R_\lambda(\mathbf{q}_R)=Q_\lambda(\mathbf{q}_R). \tag{A12}$$

However, for an arbitrary point in the Brillouin zone, $R_\lambda(\mathbf{q})$ will in general be a linear combination of all the harmonic normal-mode coordinates as indicated by Eq. (A11).

In order to obtain from the Hamiltonian equation (A8) a reduced Hamiltonian which describes only the three degrees of freedom in which we are interested, we separate out all the terms which contain only the operators $\{R_\lambda(l),P_\lambda(l)\}$, $\lambda=1, 2, 3$ for which $R_\lambda(\mathbf{q}_R)$ is equal to the normal-mode coordinate $Q(\mathbf{q}_R)$ of the three degenerate Γ_{25} modes. Further, we choose the matrix $T_{\lambda\lambda'}(\mathbf{q})$ such that the two three-component objects

$$\begin{aligned}\mathbf{R}(l)&\equiv(R_1(l),R_2(l),R_3(l)),\\
\mathbf{P}(l)&\equiv(P_1(l),P_2(l),P_3(l)),\end{aligned} \tag{A13}$$

transform like vectors, and identify these with the vectors introduced in Eqs. (2) and (6). For the anharmonic terms we assume as before that the dominant interaction is described by Eq. (16), and we obtain the Hamiltonian given by Eqs. (8), (11), and (16).

From the symmetry requirements on the harmonic terms

$$v_{\lambda\lambda'}(l=l')=\Omega_0{}^2\delta_{\lambda\lambda'},\quad \theta_{\lambda\lambda'}(l=l')=\theta\delta_{\lambda\lambda'},$$

we obtain from Eqs. (A9) and (A6) the following conditions on the matrix $T_{\lambda\lambda'}(\mathbf{q})$:

$$\begin{aligned}\frac{1}{N}\sum_{\mathbf{q}\bar\lambda} T_{\lambda\bar\lambda}(\mathbf{q})\omega_0{}^2(\bar\lambda\mathbf{q})(T^+)_{\bar\lambda\lambda'}(\mathbf{q})&=\Omega_0{}^2\delta_{\lambda\lambda'},\\
\frac{1}{N}\sum_{\mathbf{q}\bar\lambda} T_{\lambda\bar\lambda}(\mathbf{q})(T^+)_{\bar\lambda\lambda'}(\mathbf{q})&=\theta\delta_{\lambda\lambda'},\end{aligned} \tag{A14}$$

where furthermore, according to Eq. (10), we may choose $\theta=\frac{1}{2}$. From Eq. (13) it follows that

$$\begin{aligned}\sum_{\bar\lambda} T_{\lambda\bar\lambda}(0)(T^+)_{\bar\lambda\lambda'}(0)&=0,\\
\sum_{\bar\lambda} T_{\lambda\bar\lambda}(0)\omega_0{}^2(\bar\lambda0)T_{\bar\lambda\lambda'}(0)&=0.\end{aligned} \tag{A15}$$

In Eqs. (A14) and (A15) the sum $\bar\lambda$ is over all the 15 modes, whereas λ, λ' are restricted to the values λ, $\lambda'=1, 2, 3$.

Because of the choice that $T_{\lambda\lambda'}(\mathbf{q}_R)=\delta_{\lambda\lambda'}$ we obtain from Eq. (A9),

$$\theta_{\lambda\lambda'}(\mathbf{q}_R)=\delta_{\lambda\lambda'},\quad v_{\lambda\lambda'}(\mathbf{q}_R)=\omega_0{}^2(\mathbf{q}_R)\delta_{\lambda\lambda'}, \tag{A16}$$

when we note that the harmonic frequencies $\omega_0{}^2(\lambda\mathbf{q}_R)$ of the Γ_{25} phonon modes are independent of λ. From Eqs. (A2) and (A5), $R_\lambda(l)$ may be related to the displacement of the individual ions $u_\alpha(lk)$ by

$$R_\lambda(l)=\frac{1}{N}\sum_{\mathbf{q}\lambda'} e^{i\mathbf{q}\cdot\mathbf{X}(l)}\sum_{\alpha kl'}(\sqrt{m_0})e_\alpha{}^*(\lambda'\mathbf{q}k)\times(T^{-1})_{\lambda'\lambda}(\mathbf{q})e^{-i\mathbf{q}\cdot[\mathbf{X}(l')+\mathbf{X}(k)]}u_\alpha(l'k). \tag{A17}$$

This very complicated relationship involving two Fourier transforms and a dependence on the matrix $T_{\lambda\lambda'}(\mathbf{q})$ should be compared with the equivalent very direct relationship given by Eq. (2) in the text.

The expectation values are related by

$$A_\lambda=\sum_{k\alpha}\sqrt{(m_k)}e^{-i\mathbf{q}\cdot[\mathbf{X}(l')+\mathbf{X}(k)]}e_\alpha{}^*(\lambda\mathbf{q}_Rk)A_\alpha(k), \tag{A18}$$

where

$$\begin{aligned}\langle R_\lambda(l)\rangle&=A_\lambda e^{i\mathbf{q}_R\cdot\mathbf{X}(l)},\\
\langle u_\alpha(kl)\rangle&=A_\alpha(k)e^{i\mathbf{q}_R\cdot\mathbf{X}(l)}.\end{aligned} \tag{A19}$$