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Interaction of Elastic Strain with the Structural Transition of Strontium Titanate*

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Second-order displacive transitions of a type often observed in crystals of perovskite structure are analyzed by means of a phenomenological model employing optical soft-mode and elastic-strain coordinates. Relations connecting spontaneous distortion, soft-mode vibrational frequencies, and elastic constants of a tetragonal low-temperature phase are derived. These relations are found to be consistent with existing x-ray, neutron, EPR, Raman, Brillouin, and ultrasonic data for $SrTiO_3$. From these data, it is inferred that properties of $SrTiO_3$ are isotropic to a considerable degree and that, of the small anisotropy which determines the symmetry of the low-temperature phase, interaction with strain contributes a large portion. Under certain assumptions, the soft-mode force constant inferred from the data appears to vary fairly smoothly through the transition temperature. Discontinuities in the specific heat and the temperature-derivative of the restoring-force coefficient amounting to 1.3% in $SrTiO_3$ and about 8% in $LaAlO_3$ are predicted.

I. INTRODUCTION

The compound strontium titanate ($SrTiO_3$) exhibits one of the best-behaved and most thoroughly investigated displacive phase transitions. It belongs to a growing list of crystals, including $KMnF_3$, $LaAlO_3$, $PrAlO_3$, and $NdAlO_3$, which have the following characteristics in common: At high temperatures the structure is precisely cubic perovskite. A second-order phase transition occurs at a critical temperature T_c, which varies from one compound to another. At temperatures below T_c the structure changes because of small, cooperative, atomic displacements. These displacements are described by a linear combination of degenerate optic-mode coordinates and an anisotropic macroscopic strain. The vibrational wave vector lies at the point R (the [111] corner) of the cubic Brillouin zone, and the modes subtend the three-dimensional representation Γ_{25}.[1–4]

With respect to the direction of spontaneous distortion these compounds fall into two classes. The distortion of $SrTiO_3$ is precisely tetragonal for all $T<T_c$,[5,6] and that of $KMnF_3$ is tetragonal just below T_c.[7] On the other hand, the distortion of the three aluminates cited has rhombohedral symmetry for $T<T_c$.[8]

In the case of $SrTiO_3$, existing experimental data for the tetragonal phase include the spontaneous optic-mode displacement,[9] spontaneous strain,[5,6] soft-mode frequencies,[1,9,10] plus some information about elastic coefficients.[11–14] Considerable, though less complete, data along these lines are available for the other compounds mentioned.[2–4,15–17]

Thus far, applications of lattice dynamics[18] to such nonferroelectric perovskite transitions have employed optic-mode coordinates only. Here we carry out the program, touched upon previously,[19] of incorporating the effects of strain interactions by adding elastic energy terms plus a term linear in strain and quadratic in optical-mode displacement to the model energy. This phenomenological procedure is time honored in the fields of ferroelectricity[20] and ferromagnetism.[21] The results of its application to the available data for $SrTiO_3$, as given here, make clear the important role that strain interaction plays in the transition. The matter of the proper thermodynamic formulation of the

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soft-mode model, as well as related discontinuities at the transition temperature are discussed in the Appendix.

Note added in proof. Our analysis overlaps recent unpublished work of W. Rehwald.

II. SPONTANEOUS DEFORMATION

In this section we calculate the spontaneous displacement of the soft optic mode and the spontaneous strain which occur below the transition temperature of a cubic crystal. We assume the degenerate set of soft optical-mode coordinates Q_1, Q_2, Q_3 observed in $SrTiO_3$ by means of magnetic resonance,[3,22] optical Raman scattering,[1] and neutron scattering[9,10] experiments. The wave vector for these modes lies at the [111] corner of the cubic Brillouin zone. The atomic displacements represented by one of these modes are illustrated in Fig. 1, taken from the paper of Unoki and Sakudo, who discovered the structure of the tetragonal phase.[22] We remark in passing that magnetic resonance[3] and neutron scattering[16] experiments show that linear combinations of the same modes become spontaneously displaced at the transition in $LaAlO_3$. Neutron scattering[2] reveals the same modes displaced in $KMnF_3$ at the higher of two transition temperatures.

The transformation properties for Q_1, Q_2, Q_3 are easily visualized in Fig. 1. The Ti atoms may be classified into two interpenetrating sublattices A and B, mutually displaced by any one of the three primitive cubic lattice vectors, τ_i $(i=1, 2, 3)$. As illustrated in the figure, a linear displacement Q_k $(k=1, 2 \text{ or } 3)$ represents, in first order, a rotation of the oxygen octahedra surrounding lattices A and B through angles ϕ_k and $-\phi_k$, respectively, both about axes parallel to a cube edge. We normalize the Q_k in such a way that they are numerically equal to the linear oxygen displacements. Then they are related to the ϕ_k by the equation $\tan\phi_k = 2Q_k/a$, where a is the lattice constant. It is evident that Q_1, Q_2, Q_3 transform with respect to point group operations like the components of an axial vector. The translation τ_i for any i reverses the sign of Q_k for all k.

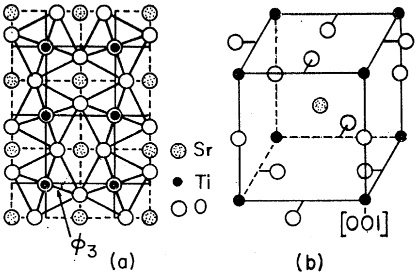

FIG. 1. Based on Unoki and Sakudo. (a) A (001) section of the $SrTiO_3$ lattice illustrating the displacement of oxygen ions described by the soft-mode coordinate Q_3 which is proportional to $\tan\phi_3$. (b) A three-dimensional projection, illustrating the property $\tau_i Q_3 = -Q_3$.

We adopt the abbreviated notation for the components of elastic strain: $e_i \equiv \partial u_i/\partial x_i$ $(i=1, 2, 3)$; and $e_4 \equiv (\partial u_2/\partial x_3) + (\partial u_3/\partial x_2)$, etc. We assume a configurational internal energy per unit volume of the form

$$\begin{aligned} U = {} & \tfrac{1}{2}K(Q_1^2+Q_2^2+Q_3^2) + A(Q_1^2+Q_2^2+Q_3^2)^2 \\ & + A_n(Q_1^2Q_2^2+Q_2^2Q_3^2+Q_3^2Q_1^2) \\ & - B_1(e_1Q_1^2+e_2Q_2^2+e_3Q_3^2) \\ & - B_2[e_1(Q_2^2+Q_3^2)+e_2(Q_1^2+Q_3^2)+e_3(Q_1^2+Q_2^2)] \\ & - B_t(e_4Q_2Q_3+e_5Q_3Q_1+e_6Q_1Q_2) \\ & + \tfrac{1}{2}C_{11}^c(e_1^2+e_2^2+e_3^2) \\ & \quad + C_{11}^c(e_1e_2+e_2e_3+e_3e_1) + \tfrac{1}{2}C_{44}^c(e_4^2+e_5^2+e_6^2), \end{aligned} \tag{1}$$

which is seen to be consistent with crystal symmetry. Equation (1) is an extension of the soft-mode energy employed by Cochran and others[18,19] to include the coupling to the elastic field. The terms with coefficients K and $A(>0)$ represent the isotropic part of the anharmonic optic-mode potential, the term with coefficient A_n the anisotropic part. One can see that Eq. (1) is the simplest expansion, consistent with the crystal symmetry, which gives rise to a transition that couples to strain.

The fact that three independent coefficients B_1, B_2, B_t are required to represent the elastic interaction follows, according to group theory, from the fact that the sets $\{Q_kQ_l\}$ and $\{e_{ij}\}$ subtend the same three irreducible representations A, E, T (in abbreviated notation) of the cubic group. In the cases of $SrTiO_3$ [5,6] and $KMnF_3$,[7] the transition from the cubic phase is accompanied by changes in thermal coefficients of the lattice parameters without an appreciable change in the thermal-expansion coefficient. It is reasonable, therefore, to simplify Eq. (1) by eliminating the coupling to volume strain. This is done by letting

$$B_e \equiv -B_2 = +\tfrac{1}{2}B_1, \tag{2}$$

in which case the coupling terms in Eq. (1) vanish for $e_1=e_2=e_3\neq 0$ and $e_4=e_5=e_6=0$.

Equilibrium states of the crystal in the absence of external constraints are obtained by minimizing Eq. (1) with respect to all Q_i and e_k. Above the transition temperature T_c, we have $K>0$, and then the cubic phase is given by $Q_i=0$ (all i) and $e_k=0$ (all k), assuming that appropriate inequalities are satisfied by the remaining coefficients. Below the transition temperature, we have $K<0$, and the cubic phase cannot be stable. The range of possibilities is conveniently visualized by minimizing U first with respect to all e_k, while keeping all Q_k arbitrary. Setting $\partial U/\partial e_i=0$, we find

$$e_i = B_eC_e^{-1}(3Q_i^2 - Q^2) \quad (i=1, 2, 3), \tag{3}$$

$$e_4 = B_tC_t^{-1}Q_2Q_3, \text{ etc.,} \tag{4}$$

where elastic constants have group-representational subscripts: $C_e \equiv C_{11}^c - C_{12}^c$, and $C_t \equiv C_{44}^c$. Upon substi-

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tution of Eqs. (3) and (4), Eq. (1) becomes

$$\tilde{U}(\mathbf{Q}) \equiv U(\mathbf{Q},\mathbf{e}(\mathbf{Q})) = \tfrac{1}{2}KQ^2 + A'Q^4 + A_n'(Q_1^2Q_2^2 + Q_2^2Q_3^2 + Q_3^2Q_1^2), \quad (5)$$

where

$$A' = A - 3B_e^2/C_e, \quad (6)$$

$$A_n' = A_n + 9B_e^2/C_e - B_t^2/2C_t. \quad (7)$$

These corrections to A and A_n are analogous to the magneto-elastic correction ("ΔK effect") to cubic anisotropy of a ferromagnet.[21]

We emphasize that the function $\tilde{U}$ is meaningful only for finding the equilibrium configuration, but has no dynamical significance, since the strain cannot follow the rapid optical vibrations. By inspection of Eq. (5), it is evident that elastic coupling does not change the transition temperature T_c, which is still governed by the condition $K(T_c) = 0$. The equilibrium displacements, however, are affected because of the corrections (6) and (7) to the potential coefficients. For a constant Q, the expression $Q_1^2Q_2^2 + Q_2^2Q_3^2 + Q_3^2Q_1^2$ has minima at the points $\mathbf{Q} = (\pm Q, 0, 0)$, $(0, \pm Q, 0)$, and $(0, 0, \pm Q)$, and maxima at $\mathbf{Q} = (\pm Q, \pm Q, \pm Q)$ with all sign combinations. Therefore, only tetragonal and trigonal (rhombohedral) symmetries, respectively, are compatible with this model, depending on the sign of A_n'.

Upon minimizing $\tilde{U}$ with respect to Q_i, we find the following, for $K < 0$:

Tetragonal distortion ($A_n' > 0$). To be definite, we take the case $\mathbf{Q} = (0, 0, Q_s)$ with the spontaneous displacement

$$Q_s = (-K/4A')^{1/2}, \quad (8)$$

ground-state energy

$$U^{\text{eq}} = -K^2/16A', \quad (9)$$

and spontaneous strain

$$(e_{1s}, e_{2s}, e_{3s}) = (-1, -1, 2)B_eQ_s^2/C_e \quad (10a)$$

and

$$e_{4s} = e_{5s} = e_{6s} = 0. \quad (10b)$$

The change of crystal-axis ratio defined by

$$\sigma_s \equiv c/a - 1 = e_{3s} - e_{1s} \quad (11)$$

is given by

$$\sigma_s = 3B_eQ_s^2/C_e. \quad (12)$$

Rhombohedral distortion. To be definite, we take $\mathbf{Q} = 3^{-1/2}Q_s(1,1,1)$ with

$$Q_s = [-\tfrac{1}{4}K/(A' + \tfrac{1}{3}A_n')]^{1/2}, \quad (13)$$

$$U^{\text{eq}} = -K^2[16(A' + \tfrac{1}{3}A_n')]^{-1}, \quad (14)$$

$$e_{1s} = e_{2s} = e_{3s} = 0, \quad (15)$$

$$e_{4s} = e_{5s} = e_{6s} = B_tQ_s^2/3C_t = \cos\alpha, \quad (16)$$

where α is the angle included by the rhombohedral crystal axes. The rhombohedral case, which occurs in certain rare-earth aluminates[4,8] will not be considered further in this work.

III. OPTIC FREQUENCIES

The natural angular frequencies ω_i of optic-mode vibration are given by the equations

$$M\omega_i^2\delta_{ij} = \frac{\partial^2 U}{\partial\hat{Q}_i\partial\hat{Q}_j} \quad (i, j = 1, 2, 3), \quad (17)$$

where $\hat{Q}_i$ are principal-axis coordinates of the soft mode and M is the mass density of oxygen atoms participating in each mode, $M = 2m_O/a^3$. The derivative in Eq. (17) is evaluated at the equilibrium points determined in Sec. II. The function U appearing in Eq. (17) must be taken from Eq. (1) rather than (5) because the frequency of uniform-strain oscillation vanishes in principle. Since Raman-scattering experiments involve small but finite wave vectors, optical and acoustic modes do, in fact, mix. The resulting corrections may be important very near the transition temperature, but we leave them out of consideration.

Cubic phase. In the cubic phase, all e_i vanish and

$$\omega_1^2 = \omega_2^2 = \omega_3^2 = K/M \quad \text{(cubic)}. \quad (18)$$

Tetragonal phase. In the tetragonal phase [Eqs. (8–12)] we let $\hat{Q}_i \equiv Q_i$, and one finds

$$\omega_1^2 = \omega_2^2 = -K(A_n + 9B_e^2C_e^{-1})/2M(A - 3B_e^2C_e^{-1}) = -K(A_n' + \tfrac{1}{2}B_t^2C_t^{-1})/2MA', \quad (19)$$

$$\omega_3^2 = -2KM^{-1}[1 - 3B_e^2/AC_e]^{-1} = -2KM^{-1}A/A', \quad (20)$$

where A' and A_n' are given in Eqs. (6) and (7). If we make the special simplifying assumption that K is linear in temperature, then by combining (18) and (20), we find the relation

$$\frac{\omega_3(T = T_c - \Delta)}{\omega_i(T = T_c + \Delta)} = 2^{1/2}\left(1 - \frac{3B_e^2}{AC_e}\right)^{-1/2} = \left(\frac{2A}{A'}\right)^{1/2}, \quad (21)$$

which reduces to $2^{1/2}$ in the limit of vanishing elastic coupling ($B_e = 0$), in agreement with Thomas and Müller.[19] Equation (21) may be expressed in terms of measurable quantities by eliminating B_e and A through Eqs. (6), (8), and (12) to find

$$\omega_3^2(T = T_c - \Delta) = 2\omega_i^2(T = T_c + \Delta) + 8\sigma_s^2(C_{11}^c - C_{12}^c)(3MQ_s^2)^{-1}. \quad (22)$$

We remark that the relationships (21) and (22) are apt to be of limited usefulness because, as we show in Sec. V, it is not clear that $K(T)$ varies smoothly through the point $T = T_c$.

Since the quantity A_n, appearing in Eq. (19), is not independently determinable, $\omega_{1,2}(T = T_c - \Delta)$ cannot be generally related on a similar basis. However, the optic-mode anisotropy A_n may be expressed in the form

$$A_n = (M\omega_1^2/2Q_s^2) - \sigma_s^2Q_s^{-4}(C_{11}^c - C_{12}^c), \quad (23)$$

which permits its determination from measurable quantities.

IV. ELASTICITY

Suppose a given strain **e** is imposed at a low frequency on the crystal. The optic coordinates **Q** will be displaced to nearly static-equilibrium values under the action of the optic-elastic interaction, thereby affecting the apparent elasticity. The resulting adiabatic elastic coefficients may be written in the form

$$C_{ij}=\frac{\partial^2\hat{U}}{\partial e_i \partial e_j},\quad \hat{U}(e)\equiv U[\mathbf{Q}(\mathbf{e}),\mathbf{e}],\tag{24}$$

where U is the energy function (1), and $\mathbf{Q}(\mathbf{e})$ satisfies the equation set

$$\frac{\partial U}{\partial Q_k}[\mathbf{Q},\mathbf{e}]=0,\quad (k=1,2,3)\tag{25}$$

for arbitrary **e**. In contrast to $\tilde{U}(\mathbf{Q})$, the function $\hat{U}(\mathbf{e})$ does have dynamical significance because **Q** follows **e** quasistatically at acoustic frequencies. By carrying out the differentiations in Eq. (24), and combining with Eq. (25) and its first partial derivative with respect to e_i, we find

$$C_{ij}=C_{ij}^c-\sum_{kl}\frac{\partial^2 U}{\partial e_i \partial Q_k}R_{kl}\frac{\partial^2 U}{\partial Q_l \partial e_j},\tag{26}$$

where C_{ij}^c are the "bare" cubic elastic constants appearing in Eq. (1) and where the matrix R_{kl} satisfies the equation

$$\sum_l R_{kl}\frac{\partial^2 U}{\partial Q_l \partial Q_m}=\delta_{km}.\tag{27}$$

If vibrational principal-axis coordinates $\hat{Q}_k$ are used, Eqs. (26) and (27) reduce, in view of Eq. (17), to

$$C_{ij}=C_{ij}^c-M^{-1}\sum_k \frac{\partial^2 U}{\partial e_i \partial \hat{Q}_k}\omega_k^{-2}\frac{\partial^2 U}{\partial \hat{Q}_k \partial e_j}.\tag{28}$$

Cubic phase. Substituting Eq. (1) into Eq. (25) one finds a solution $\mathbf{Q}=0$ valid for all **e**. Thus, at any temperature and with any applied strain, the state $\mathbf{Q}=0$ (cubic phase) is in equilibrium, though not always stable. In this case, Eq. (24), when applied to Eq. (1), reduces to

$$C_{ij}=C_{ij}^c,$$

as it must by definition of C_{ij}^c.

Tetragonal phase. Applying Eq. (28) to the six independent elastic constants of the tetragonal phase which may be stable for $K<0$ as described in the preceding sections, we find

$$\begin{aligned}&C_{11}=C_{11}^c-D,\quad C_{33}=C_{11}^c-4D,\quad C_{12}=C_{12}^c-D,\\ &C_{13}=C_{12}^c+2D,\quad C_{44}=C_{44}^c-E,\quad C_{66}=C_{44}^c,\end{aligned}\tag{29}$$

where

$$D=4B_e^2Q_s^2/M\omega_3^2,\quad E=B_t^2Q_s^2/M\omega_1^2.\tag{30}$$

At this point we remark that we may regard M and the cubic C's as independently known. We have, therefore, five fundamental parameters K, A, A_n, B_e, B_t and six measurables Q_s, σ_s, ω_1, ω_3, D ($\equiv C_{11}^c-C_{11}$, say), E ($\equiv C_{44}^c-C_{44}$). Thus, experiment permits the complete determination of the parameters. In particular, eliminating B_e through Eq. (12), we find the elastic change

$$D=4\sigma_s^2(C_{11}^c-C_{12}^c)^2/9Q_s^2M\omega_3^2\tag{31}$$

expressed in terms of independently measurable parameters.

We note that σ_s, Q_s^2, ω_1^2, and ω_3^2, when expressed in terms of fundamental parameters [Eqs. (8), (12), (19), and (20)], are simply proportional to K. Thus, according to Eqs. (30) and (31), D and E do not depend on K and the elasticity has step-discontinuities at the transition temperature.

V. APPLICATION TO STRONTIUM TITANATE

Some experimental information about all of the measurables Q_s, σ_s, ω_1, ω_3, C_{ij} derived above is available for the tetragonal phase of $SrTiO_3$ which exists at temperatures below 108°K. First of all, the structural parameter describing the spontaneous deformation from cubic symmetry has been determined at 78°K by neutron diffraction,[9] yielding a spontaneous oxygen displacement of the form described in Fig. 1, given by $Q_s=(0.0060\pm0.0015)\times 2a=0.047\pm0.012$ Å. (Here, a is the lattice parameter.) At other temperatures one may assume, with Unoki and Sakudo,[22] that Q_s is proportional to the angle $\bar{\phi}$ of rotation of the tetragonal component of the crystal field of the Fe^{3+}-$V_{O^{2-}}$ complex.[3,22]

The spontaneous tetragonal strain σ_s has been measured by neutron backscattering in the temperature range 77–150°K.[6] It has the value $\sigma_s=(4.0\pm0.5)\times10^{-4}$ (error assigned by ourselves on the basis of the published data) at 78°K and varies linearly with temperature to zero at the transition temperature of 108°K, as shown in Fig. 2.

To obtain values of σ_s (and of Q_s in a different way) at other temperatures we argue as follows: We assume that only K of the free-energy parameters [Eq. (1)] varies with temperature. Since our relations in Sec. I show that Q_s^2, σ_s, and ω_3^2 are each simply proportional to $|K|$ in the tetragonal phase, we expect these quantities to be mutually proportional. Moreover, the spontaneous distortion gives rise to a quadrupolar crystalline electrostatic potential $\sum_{ij}V_{ij}X_iX_j$ at impurity sites which one would calculate, say in the point-charge approximation, from the spontaneous displacements of ions from their cubic positions. Since the quantities V_{ij}, e_{ij}, and Q_iQ_j are all second-rank symmetric tensors, the leading term in the spontaneous tetragonal component V_s ($\equiv 2V_{33}-V_{11}-V_{22}$) of V_{ij} is a linear function of σ_s and Q_s^2.

Accordingly, EPR or optical measurements of ω_3, V_s, or $\bar{\phi}$ should serve to extend the temperature range of

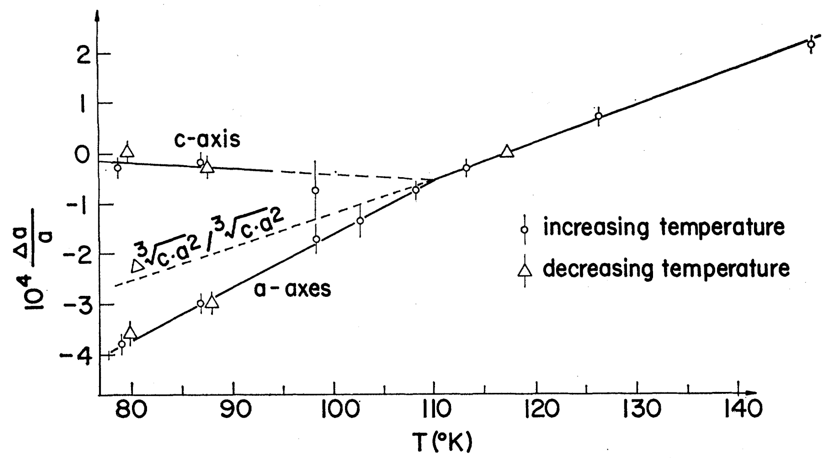

FIG. 2. Lattice parameter changes of $SrTiO_3$ versus temperature, showing tetragonal distortion below the transition temperature. Taken from the work of Alefeld.

measured σ_s and Q_s values through simple proportionalities. The validity of these procedures is tested in Fig. 3, which shows plots of ω_3^2, V_s, and $\bar{\phi}^2$, which should all be in constant proportions, versus temperature in the tetragonal phase of $SrTiO_3$. For ω_3 we take the Raman-effect data of Fleury *et al.*,[1] which agree well with neutron scattering results.[9,10] For V_s we have three sets of data: (i) the axial splitting of the Gd^{3+} EPR spectrum by Rimai and deMars,[23] (ii) the axial splitting of *R*-line fluorescence of Cr^{3+} by Stokowski and Schawlow,[24] and (iii) the rhombic component of the spin Hamiltonian of the Fe^{3+}-$V_{O^{2-}}$ complex by Kirkpatrick and co-workers[25] and Müller.[26] The rotation angle $\bar{\phi}$ is taken from Müller

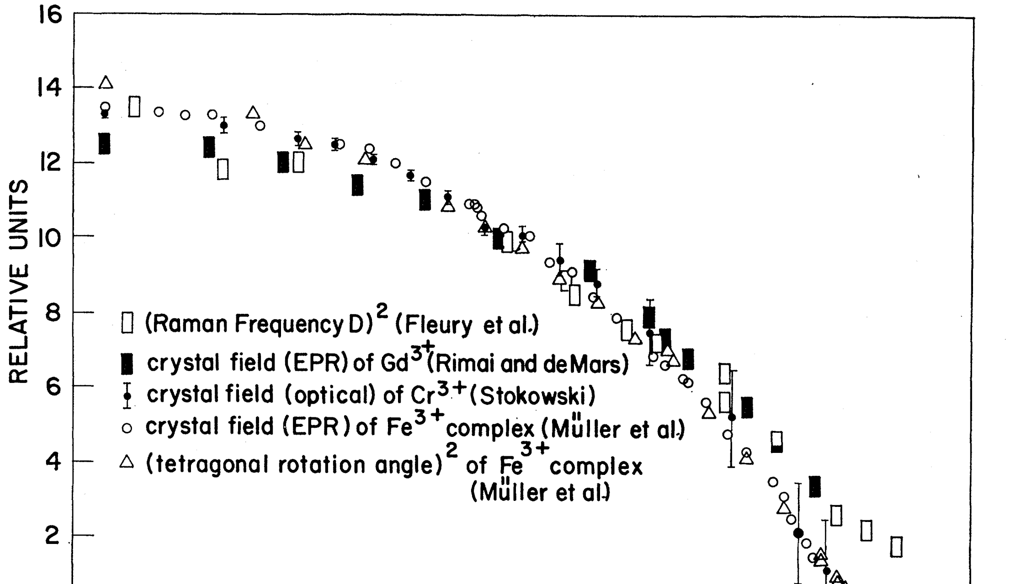

FIG. 3. Comparison of temperature dependences in the tetragonal phase of $SrTiO_3$. Each plot is normalized to the same area under a least-squares polynomial of third degree.

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et al.,[3] whose results agree well with the earlier but less extensive results of Unoki and Sakudo.[22]

In Fig. 3, vertical scale factors were adjusted to give equal areas under third-degree polynomials fitted by least squares to each set of data. To the extent that these plots agree, they indicate the insensitivity to temperature of the energy parameters other than K. A recent microscopic theory of the phase transition[27] supports the proportionality of Q_s to ω_3 but not to ω_1, although both are inherent to the soft-mode model if only K varies with temperature. Although we do not rule out the possibility that a sufficiently refined theory will show deviations from soft-mode model relations, we accept them provisionally.

The approximate proportionality of ω_3^2 to the other quantities in Fig. 3 is particularly reassuring in the face of the valid objection that Eq. (17) is not generally correct, as will be discussed in the Appendix. The importance of this consideration should be reflected by departures of ω_3^2 from other quantities in Fig. 3, which are not great except near $T=T_c$.

It has been noted that the special viewpoint, according to which rigid TiO_6^{-2} octahedra rotate to produce the deformation,[3,6,22] accounts for roughly three-fourths of the tetragonal strain, with the remainder attributable to the tetragonal deformation of the individual octahedra.[6] Neglecting the latter deformation would imply the relation $\sigma_s Q_s^{-2}=2/a^2$, which, in turn, would imply a purely geometric origin of the interaction coefficient B_e, according to Eq. (12). In spite of the merit of this view we will continue to regard B_e simply as an adjustable parameter.

We can now test the correction to the optic vibration frequency ω_3 expressed in Eq. (20) by computing the harmonic force constant K (or K/M) from the available data by means of the equation

$$K/M=-\tfrac{1}{2}\omega_3^2+4\sigma_s^2(C_{11}^c-C_{12}^c)(3Q_s^2M)^{-1}, \qquad (T<T_c) \quad (32)$$

$$K/M=\omega_1^2=\omega_2^2=\omega_3^2, \quad (T>T_c).$$

Consistency of the elementary soft-mode theory requires the computed K to be a smooth function of T without a break at $T=T_c$. Figures 4(a) and 4(b) show K computed in the tetragonal phase both without and with the strain correction. In these computations, the elastic constants C_{11}^c and C_{12}^c were taken from ultrasonic measurements[11] in the cubic phase, while Q_s^2 and σ_s were taken proportional to the rhombic crystal field of the Fe^{3+} complex (Fig. 3) and normalized to the direct measurements cited at 78°K. In Fig. 4(a), $\omega_3(T)$ was taken from the Raman spectrum[1] in the tetragonal phase, while in Fig. 4(b), $\omega_3(78°\mathrm{K})=35\ \mathrm{cm}^{-1}$ was taken from the same source, but at other temperatures $\omega_3(T)$ was assumed to vary in proportion to the rhombic splitting of Fe^{3+}-$V_{O^{2-}}$ (Fig. 3). The values with the strain correction are shown as bands corresponding to the experimental latitudes in the absolute measurements of Q_s and σ_s. In the cubic phase ($T>\approx 108°$K), one curve represents the empirical formula

$$(\hbar\omega)^{-2}=0.0081+4.22/(T-108)\ \mathrm{meV}^{-2},$$

fitted by Shirane and Yamada to their neutron data.[9] The other curve is a straight line obtained from the formula

$$\nu_R^2=1.125\times10^{22}(T-107.4)\ \mathrm{Hz}^2, \qquad (32')$$

fitted by Cowley *et al.*, to their independent neutron data.[10]

We see that neither Fig. 4(a) nor Fig. 4(b) supports the soft-mode model conclusively, though the curves based on the temperature dependence of the Fe^{3+}-complex spectrum (which we see in Fig. 3 is highly consistent with $\bar{\phi}^2$ and Cr^{3+} splitting) look better, and the strain correction is in the right direction. It should also be noted that Fig. 4(b) is more consistent with the third-law requirement and that the temperature derivative of any thermodynamic parameter must vanish at $T=0$°K. Nonanalytic behavior of K at T_c is foreshadowed by the microscopic theory.[27] The Appendix also deals with this point.

VI. ELASTIC CONSTANTS OF STRONTIUM TITANATE

We discuss now ultrasonic and Brillouin-scattering measurements of sound velocity in $SrTiO_3$. The calculation of sound velocity requires, in principle, knowledge of adiabatic elastic coefficients. We ignore the difference between adiabatic and isothermal processes because the results in our Appendix indicate that it is small in $SrTiO_3$.

According to Eqs. (29), we can predict the discontinuities in C_{11}, C_{33}, C_{12}, and C_{13} by evaluating D from Eq. (31). Substituting the already cited experimental values at 78°K into Eq. (31), we find $D=(0.04\pm0.02)\times10^{12}$ dyn/cm². Since the velocities of longitudinal waves propagating along the principal axes are proportional to $C_{11}^{1/2}$ and $C_{33}^{1/2}$ we expect, from Eqs. (29), longitudinal [100]-wave velocity reductions lying between 0.3% and 0.9%, and between 1.2% and 3.7%, respectively, as compared to the cubic phase. This prediction is to be compared with the observation of a single reduction of about 4%, for this case, reported in a brief communication on Brillouin scattering.[13,28] A similar reduction was observed by O'Shea.[29]

In addition, Rupprecht and Winter[12] have studied the temperature variation of the compliance coefficient S_{11} (cubic indices) in $SrTiO_3$ by observing electromechanical

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[27] E. Pytte and J. Feder, Phys. Rev. **187**, 1077 (1969); J. Feder and E. Pytte (unpublished). See also K. Tani, J. Phys. Soc. Japan **26**, 93 (1969); K. Tani and N. Tsuda, J. Phys. Soc. Japan **26**, 113 (1969).

[28] Professor W. Kaiser indicated in a private communication that the higher predicted shift falls within his experimental accuracy.

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

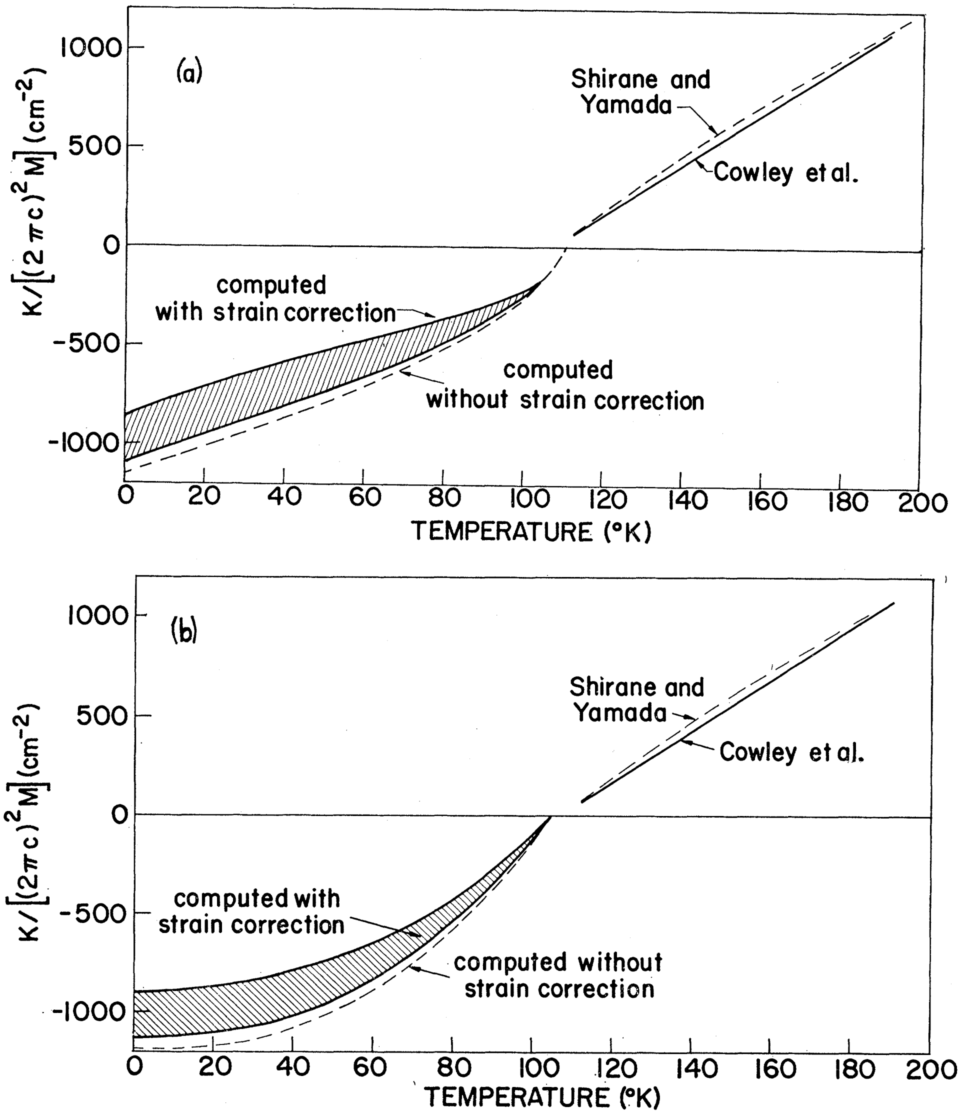

FIG. 4. Harmonic force constant for soft-mode of $SrTiO_3$ versus temperature, as computed from experimental data using Eq. (32): (a) based on experimental temperature dependence of ω_3; (b) assuming $\omega_3{}^2$ is proportional to rhombic crystal field of Fe^{3+} complex.

resonances in a sample of 1.53-cm length. They found an increase of 54% near 80°K, as compared to the cubic phase, which is far more than the maximum of 4% increase allowed by the application of the elastic constants in the present theory. Although a bias field of 15.93 kV/cm was present during this measurement, it is unreasonable to attribute such a large discrepancy to it.

The discrepancy may well be caused by domain-wall displacements which would naturally have the effect of increasing the apparent S_{11} in a multidomain sample. Presence of domain walls should not similarly dominate the Brillouin scattering, because the phonon wavelength of 0.2 μ is far less than the typical domain width of 20–50 μ found in some crystal regions.[5,30] We note in passing that other crystal regions with domain widths of 2–5 μ, which is but one order of magnitude greater than the wavelength, are also observed.[5]

A further test of the relations (29) is provided by comparing the Brillouin-effect determination of the transverse velocities V_t for propagation along the pseudocubic [100] axes,[13,14] with the ultrasonic observation of the longitudinal velocity V_l for propagation along a [111] direction.[11] These velocities are easily shown to be

$$V_t=(C_{44}/\rho)^{1/2},\quad \text{and}\quad V_t'=(C_{66}/\rho)^{1/2},\qquad \text{([100] transverse)}\qquad (33)$$

$$V_l=(C+8C_{44}+4C_{66})^{1/2}/(3\rho^{1/2}),\qquad \text{([111] longitudinal)},\qquad (34)$$

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[30] E. Sawaguchi, A. Kikuchi, and Y. Kodera, J. Phys. Soc. Japan 18, 459 (1963).

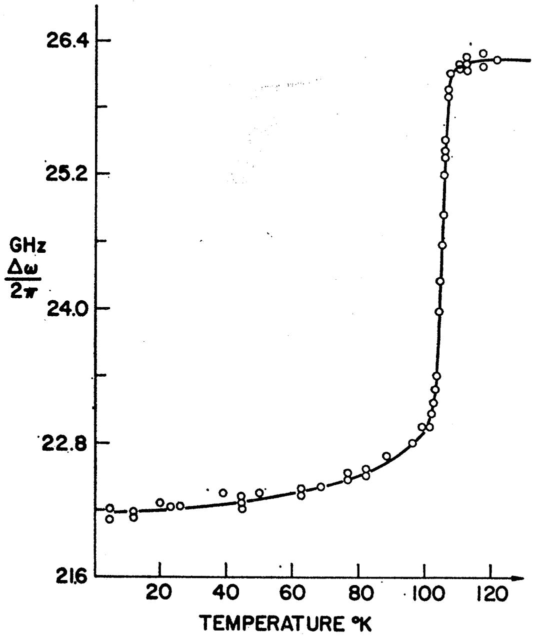

FIG. 5. Frequency shift due to Brillouin scattering from transverse [100] acoustic phonons in $SrTiO_3$, versus temperature. Based on Zurek.

where C is proportional to the bulk modulus

$$C \equiv 2C_{11}+C_{33}+2C_{12}+4C_{13}. \qquad (35)$$

Two expressions for transverse velocity are given for the two possible domain orientations. According to Eq. (29), the bulk modulus does not change at the transition. (This is a consequence of our original assumption that volume strain does not interact with the soft modes.) The changes in V_t and V_l at the transition are, therefore, simply related because they depend on E, but not on D. Eliminating E, and combining Eqs. (29), (33), and (34), we find

$$V_l=\tfrac{1}{3}[(3C_{11}{}^c+6C_{12}{}^c+4C_{44}{}^c)\rho^{-1}+8V_t{}^2]^{1/2}. \qquad (36)$$

The Brillouin data for the frequency shift proportional to V_t, as reported in Ref. 13, clearly show one velocity above $T_c=108$°K, and two below this temperature. One of the latter is substantially undisplaced and the second is displaced downward as predicted.

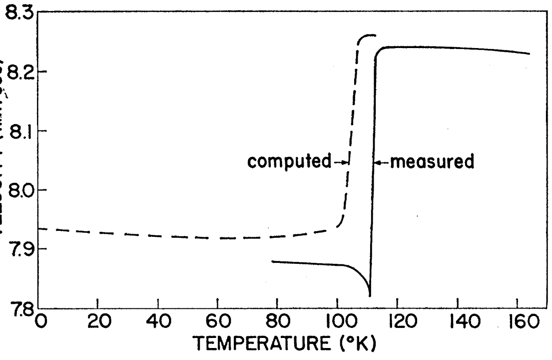

FIG. 6. Velocity of longitudinal wave propagating along [111] axis versus temperature. The measured curve is ultrasonic data of Bell and Rupprecht. Computed curve is based on Eq. (36) and Brillouin data of Zurek (Fig. 5).

Subsequent work[14] on another sample did not detect the undisplaced velocity V_t' because of highly anisotropic distribution of domains, but provided revised data for the frequency shift proportional to V_t shown in Fig. 5. Quite similar results were obtained by O'Shea.[29] Figure 6 compares the velocity V_l computed from the results of Zurek, using Eq. (36), with ultrasonic measurements of Bell and Rupprecht.[11] A more detailed analysis of the Brillouin data for $SrTiO_3$ will appear in a forthcoming paper by Lauberau.[31] In this computation we used cubic elastic constants extrapolated downward to 78°K by means of Bell and Rupprecht's empirical cubic-phase formulas [Eqs. (4) of Ref. **11**], with the transition-related $(T-T_a)^{-1}$ terms omitted.

Note added in proof. Recent Brillouin scattering results for C_{ij} [D. C. O'Shea, Bull. Am. Phys. Soc. **15**, 383 (1970)] support our predictions in considerable detail.

VII. ANISOTROPY

The experimental data available to date permit estimates of the three separate contributions to the effective anisotropy A_n' whose sign determines whether the low-temperature phase is tetragonal or trigonal. According to Eq. (7) it is given by

$$A_n'=A_n+A_e+A_t, \qquad (37)$$

where A_n is the intrinsic anisotropy of the vibrational potential, $A_e=9B_e^2/C_e$ is the contribution from strains of E symmetry (tetragonal), and $A_t=-B_t^2/(2C_t)$ is the contribution from strains of T symmetry (trigonal). From Eq. (12), A_e may be written in the form

$$A_e=\sigma_s{}^2(C_{11}-C_{12})/Q_s{}^4. \qquad (38)$$

From cited experimental values at 78°K, we estimate

$$A_e=(0.5\text{–}0.2)\times M\omega_1{}^2/Q_s{}^2, \qquad (39)$$

where the range given corresponds to experimental errors in σ_s and Q_s. From Eq. (23), the intrinsic contribution may be written

$$A_n=M\omega_1{}^2/2Q_s{}^2-A_e=(0.0\text{–}0.3)\times M\omega_1{}^2/Q_s{}^2, \qquad (40)$$

the last equality following from Eq. (39), with the range again corresponding to errors. From Eqs. (29) and (30) the T-strain contribution is

$$A_t=-(M\omega_1{}^2/Q_s{}^2)\,|\Delta C_{44}|/2C_{44}\cong-0.15M\omega_1{}^2/Q_s{}^2, \qquad (41)$$

where $|\Delta C_{44}|/2C_{44}$ is taken directly from the relative frequency step in Fig. 5.

The values for A_n, A_e, and A_t given above are consistent with tetragonal distortion to the extent that the total $A_n'\approx 0.35M\omega_1{}^2/Q_s{}^2$ is positive. It is interesting to

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[31] A. Lauberau (unpublished).

note that A_e is at least one-half of A_n' and that the present data do not exclude the possibility that the intrinsic anisotropy A_n has a negligible bearing on the symmetry of the low-temperature state.

VIII. SUMMARY

The following conclusions are drawn from our analysis of the interaction of strain with soft optical corner modes of the type observed in $SrTiO_3$:

(i) The transition temperature, its order, and the permitted symmetries (tetragonal and rhombohedral) of the lower symmetry phase remain unchanged.

(ii) The strain interaction contributes to the energy difference between the rhombohedral and tetragonal states. In the case of $SrTiO_3$, the strain contribution accounts for at least one-half of the total difference.

(iii) A premise of the elementary soft-mode model is that the restoring-force constant $K(T)$ varies smoothly through $T=T_c$. This premise is fairly consistent with experiment if the square of the higher Raman frequency ω_3 is taken proportional to the tetragonal crystal field for temperatures just below T_c. The consistency is weaker if the experimental values of ω_3 are used at all temperatures.

(iv) We might reasonably interpret conclusion (iii) as supporting the applicability of the Landau theory to $SrTiO_3$, but not the extension of it required to derive soft-mode frequencies at temperatures removed from T_c. The Landau theory is founded on *quasistatic* thermodynamic variables (Q and e, in our case) and its validity rests on the analyticity of the configurational energy U. But vibrations of soft modes involve time-dependent forces which might not be well represented by $\partial U/\partial Q_i$ (see Appendix). Indeed, the observables of a recent microscopic theory do not all vary with T in the simple proportions of the soft-mode model.[27]

(v) Our Eqs. (29) and (31) express four of the six tetragonal-phase elastic coefficients in terms of other measurables without adjustable parameters, providing consistency checks. The scant elastic data presently available for $SrTiO_3$ are consistent with our calculations, but additional measurements are needed.

(vi) If one ignores the elastic anomalies close to T_c arising from fluctuations, the elastic coefficients exhibit step discontinuities at T_c between essentially temperature-independent values, as borne out by ultrasonic and Brillouin-scattering data for $SrTiO_3$.

(vii) We remark that $SrTiO_3$ is a fairly isotropic material, both elastically and with respect to the soft-mode potential. The relation $C_{11}=C_{12}+2C_{44}$ satisfied by an isotropic medium is in error only by 7% in the cubic phase. The energy difference $\frac{1}{3}A_n'Q_s^4$, between rhombohedral and tetragonal states is about 20% of the isotropic anharmonic energy $A'Q_s^4$. Thus we may describe the configurational free energy as isotropic and not involving strain in first order. Only in second order do the anisotropic soft-mode potential and elastic interactions take part in comparable proportions. In this respect $SrTiO_3$ is quite different from the ferroelectric $BaTiO_3$, in which the anisotropic part of the ferroelectric mode potential is as great as the isotropic part.[20]

(viii) Discontinuities in specific heat and the quantity dK/dT at the transition point are predicted, as shown in the Appendix.

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APPENDIX

We discuss here questions of thermodynamics and discontinuities related to displacive transitions.

The dynamic properties of a system are more directly related to the internal energy of the system than to its free energy. For this reason, we have formulated the theory so that it applies to a closed system, and the appropriate thermodynamic potential is the internal energy W expressed as a function of entropy S and those coordinates X_k to be studied explicitly:

$$W=W(S,\mathbf{X}). \tag{A1}$$

Stable equilibrium configurations are characterized by having minimum energy compared to neighbor configurations with the same entropy. Thus, for every value of the entropy, the equilibrium values $X_k^{\text{eq}}(S)$ of the coordinates X_k are found by minimizing $W(S,\mathbf{X})$ with respect to the X_k. At equilibrium, the energy becomes a function of the entropy alone,

$$W^{\text{eq}}(S)=W(S,\mathbf{X}^{\text{eq}}(S)), \tag{A2}$$

and the temperature is defined by

$$T=\frac{dW^{\text{eq}}}{dS}=\left(\frac{\partial W}{\partial S}\right)_{\mathbf{X}=\mathbf{X}^{\text{eq}}}, \tag{A3}$$

where the last equality follows from the minimum property of $W(S,\mathbf{X})$.

For the case discussed in the present paper, the set of explicit coordinates consists of the three optic-mode coordinates $Q_k(=1, 2, 3)$ and the six strain components e_i $(i=1, \ldots, 6)$. We consider an internal energy

$$W(S,\mathbf{Q},\mathbf{e})=U(S,\mathbf{Q},\mathbf{e})+W_0(S), \tag{A4}$$

where the first term has the form of Eq. (1) with coefficients depending on the *entropy*, and the last term is the contribution from all "internal" degrees of freedom. Since the temperature at equilibrium is a more accessible parameter than the entropy of the system, one may solve Eq. (A3) for $S(T)$ and substitute into U to express the coefficients in U as functions of T. Thus, we obtain a justification of the procedure followed in the text for the static properties. It has to be noted, however, that a smooth dependence of the coefficients on entropy will yield a discontinuity of their derivatives with respect to T.

To estimate the amount of the discontinuity for the coefficient K, we consider the thermodynamic relation

$$\frac{dS}{dT}=\frac{c}{T}, \tag{A5}$$

where c is the specific heat at equilibrium.

This permits us to write

$$\frac{dK}{dT}=\frac{dK}{dS}\frac{c}{T}. \tag{A6}$$

If dK/dS is continuous in S at the critical entropy S_c, then discontinuities of c and dK/dT are mutually proportional. Therefore, we define the relative discontinuity

$$\Delta=\frac{c_{-}-c_{+}}{c_{+}}=\left[\left(\frac{dK}{dT}\right)_{-}-\left(\frac{dK}{dT}\right)_{+}\right]\left(\frac{dK}{dT}\right)_{+}^{-1}, \tag{A7}$$

where the subscripts $+$ and $-$ refer to limits taken above and below T_c, respectively.

We derive an expression for Δ by a method similar to that of Landau and Lipshitz.[32] Combining Eqs. (A3) and (A5) we find the general relation

$$c=T\left(\frac{d^2W^{\mathrm{eq}}}{dS^2}\right)^{-1}. \tag{A8}$$

Substituting this expression into Eq. (A7), we obtain to first order

$$\Delta=\frac{c_{+}}{T}\left[\left(\frac{d^2W^{\mathrm{eq}}}{dS^2}\right)_{+}-\left(\frac{d^2W^{\mathrm{eq}}}{dS^2}\right)_{-}\right]. \tag{A9}$$

We now assume that the nonconfigurational part $W_0(S)$ of the energy is smooth at S_c, and that all coefficients except K can be considered constant. The configuration energy $U^{\mathrm{eq}}(S)$ is given by Eq. (9) below S_c and vanishes above S_c. Application of the condition $K(S_c)=0$ thus leads to

$$\Delta=c_{+}\left(\frac{dK}{dS}\right)^2\bigg/(8A'T). \tag{A10}$$

The parameters K and A' are eliminated through Eqs. (8) and (18) to give, with the help of Eq. (A5), the final expression

$$\Delta=\frac{-MT_c}{2c}\left(\frac{d(\omega_i^2)}{dT}\right)_{+}\left(\frac{d(Q_s^2)}{dT}\right)_{-} \tag{A11}$$

in terms of measurable quantities.

To evaluate Δ in $SrTiO_3$, we take for c the value 11.4 cal/deg mol at 105°K from data of Todd and Lorenson[33]; for $[d(\omega_i^2)/dT]_{+}$ we take $(2\pi)^2$ times the coefficient of the experimental relation (32′); and we estimate $[d(Q_s^2)/dT]_{-}\approx -Q_s^2(78°\mathrm{K})/(105-78)$, where $Q_s(78°\mathrm{K})=0.047\pm0.012$ Å, from neutron diffraction.[9] The resulting discontinuity $\Delta=1.3\times10^{-2}$ is too small to materially affect our discussion of $K(T)$ in Sec. V. It is large enough to be observed in specific-heat measurements as precise as those of Todd and Lorenson,[32] whose data scatter by little more than one part in 10^3. However, the existence of the transition was not known at the time and our analysis of their tabulated data does not reveal a discontinuity. It would be worthwhile to repeat the experiment at more closely spaced temperatures to settle this question conclusively.

One can verify that Eq. (A11) is valid for trigonal as well as tetragonal distortions. Thus, we can estimate Δ for the trigonal compound $LaAlO_3$. We estimate c from the equipartition theorem; we take $T_c=800°\mathrm{K}$ and $[d(\omega_i^2)/dT]_{+}$ from the Raman data of Scott[4] by applying the factor $\frac{1}{2}$ to his data at $T<T_c$ [i.e., neglecting the elastic coupling correction in Eq. (21)]; we take $[d(Q_s^2)/dT]_{-}$ from the data of Müller *et al.*[3] The result is $\Delta\approx8\%$, considerably larger than in $SrTiO_3$, which might make $LaAlO_3$ a better substance to measure.

The smallness of Δ in $SrTiO_3$ indicates that the distinction between free energy and internal energy is in this case not very important. A more difficult question concerns the propriety of calculating optic-mode frequencies from any thermodynamic potential. The equations of motion (17) would be justified if the internal equilibrium with respect to all other degrees of freedom were not upset by the motion of the Q_i, i.e., if the "isolated response," in the sense of Wilcox,[34] of the system equals its "adiabatic response." This condition is satisfied either if the statistical distribution over the internal degrees of freedom remains canonical for an isolated change of the Q_i, or if it relaxes towards a canonical distribution with a relaxation time shorter than the reciprocal soft-mode frequencies.

For T sufficiently close to 0°K, the statistical distribution is canonical because only the ground state is populated. For T sufficiently close to T_c, the relaxation-time condition should be satisfied because the soft-mode frequencies tend to zero. For intermediate T, however, the soft-mode frequency is so large (~30 cm^{-1}) that modes appreciably occupied for $kT<kT_c(=73$ cm$^{-1})$ could not conceivably have even higher relaxation frequencies without being unrealistically overdamped. Thus, our employment of Eq. (17) remains to be justified.

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[32] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1958), p. 434.

[33] S. S. Todd and R. E. Lorenson, J. Am. Chem. Soc. **74**, 2043 (1952).

[34] R. M. Wilcox, Phys. Rev. **174**, 624 (1968).