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STRUCTURAL PHASE TRANSITIONS IN PEROVSKITE-TYPE CRYSTALS

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We introduce a simple model Hamiltonian for the study of phase transitions in perovskite compounds $AB\text{O}_3$ involving rotations of $B\text{O}_6$ octahedra. Depending on the relative magnitude of the anharmonic coefficients, we find a transition to the tetragonal or to the trigonal phase. We obtain the temperature dependence of the rotation angle below the transition temperature T_a, and of the soft-mode frequencies associated with the transition both above and below T_a. The coupling to an elastic deformation field is briefly discussed.

Recently, considerable experimental progress has been made towards the understanding of purely structural second-order phase transitions occurring in crystals of the perovskite family $AB\text{O}_3$. This concerns structural analysis using EPR methods,[1] Raman scattering,[2] and neutron diffraction.[3] The EPR results demonstrated the essential static characteristic of the transition, which is peculiar to the perovskite structure: The $B\text{O}_6$ octahedra rotate about a tetragonal axis in SrTiO_3 and about a trigonal axis in LaAlO_3, and it was found that the normalized rotation angles vary quantitatively in the same way as a function of reduced temperature below the transition.[1] It was concluded that the rotation angle is the order parameter for this type of transition. Associated with the transition, one expects the occurrence of soft modes[4,5]: The frequencies of those normal modes, which transform like the order parameter, should become zero at the transition temperature T_a. For the case considered, this is the triply degenerate mode at the R corner of the Brillouin zone transforming like the axial vector representation Γ_{15}' if the origin is chosen at the B atom. This choice of origin is more appropriate to the present case than that used by Cowley,[4,6] for which the representation is Γ_{25}. Such a soft mode has recently been observed in neutron diffraction by Shirane[3] in the high-symmetry phase of SrTiO_3. Due to the symmetry breaking at the phase transition, the mode is split below T_a into two branches situated at the zone center and transforming like Γ_1. Both branches are then Raman active and have been seen by Fleury, Scott, and Worlock.[2]

In this note, we study in a simple model the nature of the transition, the behavior of the order parameter, and the dynamics of the soft modes above and below T_a. We consider only the triply degenerate Γ_{15} R-corner mode, and neglect the motion of all other degrees of freedom. This mode can be built up from localized displacement fields $\vec{\text{R}}(l)$ associated with each cell (cell index l), in much the same way as the electron wave functions of a given band can be built up from localized Wannier functions. The experimental results suggest that these $\vec{\text{R}}(l)$ are essentially rotations of $B\text{O}_6$ octahedra about the cell center, with smaller displacements of more distant oxygen atoms (Fig. 1). The three independent rotations about the cube axes permit the

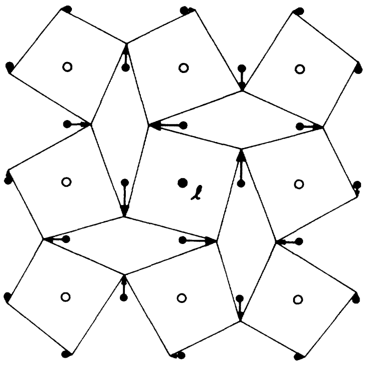

FIG. 1. Displacement field of the Wannier-type function $\vec{\text{R}}(l)$.

construction of three branches as required.

We assume a strong interaction between different $\vec{R}(l)$ favoring alternating rotations in adjacent cells, which is suggested by the fact that adjacent octahedra share an oxygen atom. The resulting rotation will be counterbalanced by anharmonic terms which we describe by a crystal-field-type potential for the $\vec{R}(l)$. We thus have the following Hamiltonian:

$$\mathcal{H}=\mathcal{H}_{\text{kin}}+\mathcal{H}_{\text{pot}}+\mathcal{H}_{\text{int}}. \tag{1}$$

We assume the $\vec{R}(l)$ to be normalized, so that the kinetic energy takes the form

$$\mathcal{H}_{\text{kin}}=\tfrac{1}{2}\sum_l \dot{\vec{R}}^2(l). \tag{2}$$

In the potential energy, we include anharmonic terms of fourth order:

$$\mathcal{H}_{\text{pot}}=\sum_l\{\tfrac{1}{2}\omega_0^2\vec{R}^2(l)+\tfrac{1}{4}B[R_x^4(l)+R_y^4(l)+R_z^4(l)]+\tfrac{1}{2}C[R_x^2(l)R_y^2(l)+R_y^2(l)R_z^2(l)+R_z^2(l)R_x^2(l)]\}. \tag{3}$$

For the interaction, we assume the form[7]

$$\mathcal{H}_{\text{int}}=\tfrac{1}{2}\sum_{ll'}{}' v(l,l')\vec{R}(l)\cdot\vec{R}(l'), \tag{4}$$

where the Fourier transform of $v(l,l')$ takes on its minimum value v_R at the R corner of the zone,

$$v_R=\sum_l v(l-l')\exp[i\vec{q}_R\cdot(\vec{x}_l-\vec{x}_l')];\quad q_R=\left(\frac{\pi}{a},\frac{\pi}{a},\frac{\pi}{a}\right). \tag{5}$$

The model will show a phase transition only if the energy gain due to this interaction is larger than the harmonic part of the potential energy:

$$-v_R>\omega_0^2. \tag{6}$$

In order to study the nature of the transition, we obtain the internal energy for given average values $\langle\vec{R}(l)\rangle$ of the form

$$\langle\vec{R}(l)\rangle=\vec{\Phi}\exp(i\vec{q}_R\cdot\vec{x}_l)=(-1)^{l_1+l_2+l_3}\vec{\Phi}. \tag{7}$$

Up to fourth order in $\vec{\Phi}$, we find

$$\mathcal{E}=(1/N)\langle\mathcal{H}\rangle=\mathcal{E}_0(T)+\tfrac{1}{2}a(T)(\Phi_x^2+\Phi_y^2+\Phi_z^2)+\tfrac{1}{4}b(T)(\Phi_x^4+\Phi_y^4+\Phi_z^4)$$
$$+\tfrac{1}{2}c(T)(\Phi_x^2\Phi_y^2+\Phi_y^2\Phi_t^2+\Phi_z^2\Phi_x^2) \tag{8}$$

with temperature-dependent coefficients to be determined from the correlation functions.[8] The coefficient $a(T)$ in particular consists of the negative part $\omega_0^2+v_R$, and a positive contribution coming from the fluctuation of the $\vec{R}(l)$ in the anharmonic terms of $\mathcal{H}_{\text{pot}}$ which will increase with temperature. The transition temperature is defined by $a(T_a)=0$, and for temperatures close to T_a, we can assume that

$$a(T)=\alpha(T-T_a),\quad \alpha>0, \tag{9}$$

and neglect the temperature dependence of b and c. Here, we shall not attempt to calculate the correlation functions, but rather consider α, b, c, and T_a as model parameters to be determined from a comparison with experiment. Disregarding the difference between adiabatic and isothermal changes, we obtain the equilibrium value of $\vec{\Phi}$ by minimizing the energy.[9] Above T_a, we have $\vec{\Phi}=0$. Below T_a, we find two cases, depending on the relative values of b and c (Fig. 2).[10]

1. $0<b<c$.—The energy has a minimum at

$$\Phi_x=\Phi^{\text{tetr}}(T)\equiv\left[\frac{-a(T)}{b}\right]^{1/2}\approx\left[\frac{\alpha}{b}(T_a-T)\right]^{1/2},$$
$$\Phi_y=\Phi_z=0, \tag{10}$$

and five other points related by symmetry, of depth $-a^2/4b$. This corresponds to a rotation of the $B\text{O}_6$ octahedra about a tetragonal axis.

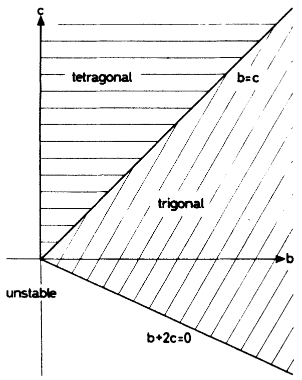

FIG. 2. Ranges of the anharmonic coefficients b and c leading to a transition into the tetragonal and the trigonal states, respectively.

2. $b > c$ and $b > -2c$.—The energy has a minimum at

$$\Phi_x = \Phi_y = \Phi_z = 3^{-\frac{1}{2}} \Phi^{\mathrm{trig}}(T),$$

where

$$\Phi^{\mathrm{trig}}(T) = \left(\frac{-3a}{b+2c}\right)^{1/2} \approx \left[\frac{3\alpha}{b+2c}(T_a - T)\right]^{1/2}, \quad (11)$$

and seven other points related by symmetry, of depth $-3a^2/4(b+2c)$. This corresponds to a rotation of the BO_6 octahedra about a trigonal axis.

Outside the region $b > 0$ and $b + 2c > 0$, there exists no minimum of the energy.

Depending on the relative magnitudes of b and c, we thus obtain a phase transition either into a tetragonal or into a trigonal phase. The first case is realized in $SrTiO_3$, and the second one in $LaAlO_3$.

The frequencies of the normal modes are most conveniently obtained as the poles of the response to an external field $\vec{f}(l,t) = \vec{f}(l)\exp(i\omega t)$ coupling to the $\vec{R}(l)$. The equations of motion are

$$\ddot{\vec{R}}(l) = -\frac{\partial}{\partial \vec{R}(l)}(\mathcal{H}_{\mathrm{pot}} + \mathcal{H}_{\mathrm{int}}) + \vec{f}(l,t). \quad (12)$$

We restrict the discussion to the motion of the R-corner mode itself and set

$$\vec{f}(l) = (-1)^{l_1 + l_2 + l_3} \vec{f}. \quad (13)$$

The average of $\vec{R}(l)$ will then be of the form (7) with a time-dependent $\vec{\Phi}$. If we neglect the difference between the static and the dynamic averages of $\mathcal{H}_{\mathrm{pot}} + \mathcal{H}_{\mathrm{int}}$, we find for $\vec{\Phi}$ the equation of motion

$$\ddot{\vec{\Phi}} = -\partial\mathcal{E}/\partial\vec{\Phi} + \vec{f}. \quad (14)$$

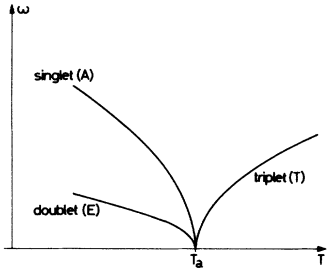

FIG. 3. Temperature dependence of the soft modes above and below T_a (schematic).

The linear response to $\vec{f}$ is obtained by setting

$$\vec{\Phi} = \vec{\Phi}^{\mathrm{eq}} + \vec{\varphi}, \quad (15)$$

and linearizing with respect to $\vec{\varphi}$. One finds

$$\ddot{\vec{\varphi}} = -\mathsf{D} \cdot \vec{\varphi} + \vec{f},$$

where

$$D_{ij} = (\partial^2\mathcal{E}/\partial\Phi_i \partial\Phi_j)_{\mathrm{eq}}. \quad (16)$$

The squares of the normal-mode frequencies are thus the eigenvalues of the Hessian matrix of the energy:

$$\det[(\partial^2\mathcal{E}/\partial\Phi_i\partial\Phi_j)_{\mathrm{eq}} - \omega_\lambda^2 \delta_{ij}] = 0. \quad (17)$$

We find above the phase transition the triply degenerate mode

$$\omega_T = [a(T)]^{1/2} \approx [\alpha(T - T_a)]^{1/2}. \quad (18)$$

Below the phase transition, it splits into a doublet and a singlet (Fig. 3): For the tetragonal case,

$$\omega_E = (c-b)^{\frac{1}{2}} \Phi^{\mathrm{tetr}}(T), \quad \omega_A = (2b)^{\frac{1}{2}} \Phi^{\mathrm{tetr}}(T);$$

for the trigonal case,

$$\omega_E = [\tfrac{2}{3}(b-2c)]^{\frac{1}{2}} \Phi^{\mathrm{trig}}(T),$$

$$\omega_A = [\tfrac{2}{3}(b+2c)]^{\frac{1}{2}} \Phi^{\mathrm{trig}}(T). \quad (19)$$

In both cases, there exists a relation

$$\omega_A(T_a - \Delta)/\omega_T(T_a + \Delta) = \sqrt{2} \quad (20)$$

between the singlet mode below T_a and the triplet mode above T_a.

We have thus obtained a $|T - T_a|^{1/2}$ temperature dependence in the critical region for the order parameter below T_a, and for the normal-mode frequencies both above and below T_a. A more refined statistical mechanical treatment may, however, lead to a power different from $\frac{1}{2}$. The temperature dependence of the order parameter is in qualitative agreement with the EPR results[1] on $SrTiO_3$ and $LaAlO_3$; no quantitative power law $(T_a-T)^n$ was derived from the measured values because we find that a change of 1° in $T_a = 103°$ results in a variation of n of over 30%. For the soft modes determined by Raman scattering, a value of $n = 0.3$ has been mentioned[2] using $T_a = 110°K$. However, due to the uncertainty in T_a, not too much weight should be attached to this value of n.

It is well known that phases of slightly distorted ABO_3 compounds, different from the tetragonal $I4/mcm$ and the trigonal $R\bar{3}c$ ones, exist, for instance in $GdAlO_3$[11] at 300°K, and in the mineral perovskite $CaTiO_3$.[12] Consequently, in these compounds other modes at the corner, faces, or edges of the large zone must become soft because the unit cell is at least doubled. However, investigations of the phase transitions of mixed crystals like $(Sr, Ca)TiO_3$ have shown[13] that on reducing the temperature, the phase associated with the R-corner mode appears first. Also, the highest noncubic phase of $PrAlO_3$ or $NdAlO_3$ is probably isomorphic to that of $LaAlO_3$.[14] This view is further supported by the recent structure study in $SrZrO_3$,[15] which is orthorhombic at room temperature, but the phase below the first transition at $T_a = 1170°C$ is very probably the same as occurring in $SrTiO_3$. In pure $CaTiO_3$, in addition to the TiO_6 rotational mode, others may collapse at the same or nearly the same temperature,[12,5] probably due to the small size of the Ca ion.

We should like to emphasize that, in contrast to the structural phase transitions discussed in the present note, displacive ferroelectric phase transitions occur in other structures as well (e.g., PbTe) and are not typical of the perovskite structure.

So far, we have neglected all other degrees of freedom of the crystal. We expect important effects from the coupling of the coordinates $\vec{R}(l)$ with the long-wavelength acoustic phonons, and in particular with a static elastic deformation of the crystal. Symmetry considerations show that such a coupling can be described in lowest order by an interaction energy of the form

$$\mathcal{E}_{\rm int} = \gamma[(\Phi_x^2-\tfrac{1}{3}\Phi^2)\epsilon_{xx} + (\Phi_y^2-\tfrac{1}{3}\Phi^2)\epsilon_{yy} + (\Phi_z^2-\tfrac{1}{3}\Phi^2)\epsilon_{zz}] + \delta(\Phi_x\Phi_y\epsilon_{xy} + \Phi_y\Phi_z\epsilon_{yz} + \Phi_z\Phi_x\epsilon_{zx}), \tag{21}$$

where the ϵ_{ik} are the components of the strain tensor. By minimizing the total energy consisting of Eqs. (8) and (21), and the elastic energy of the crystal, we find below the phase transition a spontaneous strain of tetragonal or trigonal symmetry, respectively, which varies as T_a-T in the critical region, and a small change in the order parameter Φ. Below T_a, the interaction term (21) gives rise to a resonance interaction between the soft rotational mode and transverse acoustic phonons, and the normal modes of the system consist of a coupled motion of the $\vec{R}(l)$ and the elastic displacement field.

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[6] In fact, some of the lattice dynamical models studied by Cowley (Ref. 4) showed an instability against exactly these modes, but were discarded as being unrealistic.

[7] We have actually included part of the interaction in $\mathcal{H}_{\rm pot}$; the term belonging to a given l is defined as the energy of the state with all $\vec{R}(l')$ with $l' \neq l$ kept at zero.

[8] This approach is related to the one used by P. C. Kwok and P. B. Miller [Phys. Rev. 151, 387 (1966)] for displacive ferroelectrics.

[9] By this procedure, we obtain the equilibrium for a given value of the entropy S. Strictly speaking, we should use S as the independent variable, and obtain the temperature at thermodynamic equilibrium as $T = \partial\mathcal{E}/\partial S$.

[10] After completion of this work we learned that J. Axe (private communication) has obtained the same results from an energy expression of form (8).

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