[†] Work supported in part by the Department of Defense Themis Program through the Office of Naval Research.

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PHYSICAL REVIEW B VOLUME 3, NUMBER 10 15 MAY 1971

Structural Phase Transitions in Spinels Induced by the Jahn-Teller Effect

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(Received 29 April 1970)

A dynamic theory of the cubic-to-tetragonal transformation in spinels containing octahedrally coordinated d^9 and d^4 Jahn-Teller ions is presented. Following Kanamori, the model assumes that the dominant coupling between the doubly degenerate electronic orbital and the lattice is via the elastic strain. The temperature dependence of the splitting of the degenerate electronic level and the changes in the elastic constants due to the interaction is determined. For linear Jahn-Teller coupling, the phase transition is second order. The soft mode is the acoustic shear mode propagating in the [110] direction. The frequency of this mode goes to zero at the transition temperature and remains zero in the distorted structure. Including third-order Jahn-Teller coupling, the phase transition becomes first order. The shear sound velocity changes discontinuously at the transition temperature and then increases with decreasing temperature.

I. INTRODUCTION

This paper considers structural transitions from cubic to tetragonal symmetry in spinel structures containing d^4 and d^9 transition-metal ions. The connection between these phase transitions and the Jahn-Teller effect was first recognized by Dunitz and Orgel[1] and by McClure.[2] Several thermodynamic theories were subsequently constructed. Those by Finch, Sinha, and Sinha[3] and by Wojtowicz[4] considered the case of large local distortion due to the static Jahn-Teller effect. At high temperatures, these distortions are oriented randomly among three equivalent positions. Due to interactions between the distortions, a transition occurs to an ordered structure with all the local distortions aligned in one particular direction. This occurs when the interaction energy gained by aligning the distortions becomes more effective in lowering the free energy than the entropy, which favors a random distribution of the distortions among the equivalent positions. This model corresponds to the case of strong local anisotropy in which the anisotropy energy is much larger than kT_c where T_c is the transition temperature.

The more recent work by Englman and Halperin[5] extends the work by Wojtowicz by taking into account the dynamic Jahn-Teller coupling and the excited vibrational states. Due to the interaction between the Jahn-Teller complexes, the localized vibrational modes associated with a single complex assume the character of propagating optical phonons. However, the interaction was treated in a molecular-field theory and thus only the $q=0$ limit was discussed. Interaction of the electronic system with acoustic phonons was not considered.

A basically different model has been considered by Kanamori.[6] This model describes the spontaneous appearance of a local distortion at the transition temperature. The model implicitly assumes that the interaction between neighboring distortions is sufficiently strong to immediately align the local distortions once these appear. In this model (in its simplest form), there is no local distortion above the transition temperature.

For the case of the normal spinels $FeCr_2O_4$ and FeV_2O_4 with Fe^{2+} Jahn-Teller ions at tetrahedral sites, Mössbauer experiments show that considerable local distortion persists above the transition temperature.[7] However, for Jahn-Teller ions at octahedral sites the amount of local distortion cannot be measured by the Mössbauer effect because field gradients exist at the octahedral site even in the absence of distortion.[8] In $CuFe_2O_4$, an abrupt decrease in the quadrupole splitting at the transition temperature has been reported,[9] whereas in $Mn_xFe_{3-x}O_4$ and $Ge_{0.2}Cu_{1.2}Fe_{1.6}O_4$ no change could be detected.[8]

It is the purpose of the present paper to point out that large elastic anomalies are predicted by the Kanamori model, and that measurements of the elastic constants may provide a simple method of distinguishing between the proposed models.

Whereas Kanamori considered only static effects, the present treatment takes into account the dynamic interactions between the electronic system and the acoustic phonons. However, coupling to the optical phonons will be neglected. In a simple manner, the present treatment also extends the theory to the case of several Jahn-Teller ions per unit cell.

In the high-frequency limit $\omega\tau \gg 1$, where τ is the electron-lattice relaxation time, the elastic constants will be calculated from a coupled set of equations for the electron-phonon system. Due to the interaction the phonon frequencies become temperature dependent exhibiting step discontinuities at the transition temperature. The degenerate electronic level splits due to the interaction with the static strain and becomes dispersive through the interaction with the acoustic phonons.

In the low-frequency limit $\omega\tau \ll 1$ the elastic constants will be calculated thermodynamically. The isothermal elastic constants[10] are obtained in the usual way from the second variation of the free energy in the presence of a static deformation with respect to this deformation.

Because of the short electron-lattice relaxation time[11] the condition $\omega\tau \ll 1$ is expected to apply at usual ultrasonic frequencies. For the very much higher frequencies used in neutron scattering experiments the results for $\omega\tau \gg 1$ may apply.

II. MODEL HAMILTONIAN

In the case of octahedral coordination, the linear Jahn-Teller coupling between the doubly degenerate electronic level and the local elastic strain may be written[6]

$$H_1 = -A' \sum_{lk} [u_3(lk)\sigma_3(lk) + u_1(lk)\sigma_1(lk)] \; . \qquad (1)$$

Here, we have

$$\begin{aligned} u_1(lk) &= (1/\sqrt{2})[e_{11}(lk) - e_{22}(lk)] \;, \\ u_3(lk) &= (1/\sqrt{6})[2e_{33}(lk) - e_{11}(lk) - e_{22}(lk)] \;, \end{aligned} \qquad (2)$$

where $e_{ij}(lk)$ are the elastic strain components at the kth Jahn-Teller ion in the lth unit cell. The operators $\sigma_i(lk)$ are Pauli spin operators describing the doubly degenerate electronic level.[12] It is assumed that the electronic levels are nondispersive in the absence of the coupling to the elastic strain.

Similarly the third-order anharmonic interaction and Jahn-Teller coupling may be written[6]

$$\begin{aligned} H_2 = &-K_1' \sum_{lk} [u_3^3(lk) - 3u_3(lk)u_1^2(lk)] \\ &-K_2' \sum_{lk} \{[u_3^2(lk) - u_1^2(lk)]\sigma_3(lk) \\ &- 2u_1(lk)u_3(lk)\sigma_1(lk)\} \; . \end{aligned} \qquad (3)$$

As long as we are interested only in the linear phonon spectrum, the k dependence of the strain may be neglected. The interaction Hamiltonian then takes the form

$$\begin{aligned} H_1 &= -A \sum_l [u_3(l)S_3(l) + u_1(l)S_1(l), \\ H_2 &= -K_1 \sum_l [u_3^3(l) - 3u_3(l)u_1^2(l)] \\ &\quad -K_2 \sum_l \{[u_3^2(l) - u_1^2(l)]\, S_3(l) - 2u_1(l)u_3(l)S_1(l)\} \;, \end{aligned} \qquad (4)$$

where

$$S_i(l) = \tfrac{1}{2} \sum_k \sigma_i(lk) \; .$$

The spin associated with each unit cell depends on the number of Jahn-Teller ions. $CuFe_2O_4$ has two Cu^{2+} ions at octahedral sites per primitive unit cell, whereas Mn_3O_4 has four Mn^{3+} ions per unit cell.

For cubic symmetry the Hamiltonian describing static elastic strain and acoustic phonons with a linear spectrum may be written

$$\begin{aligned} H_e = \tfrac{1}{2} \sum_l M\dot{R}^2(l) &+ \tfrac{1}{2}C_{11} \sum_l [e_{11}^2(l) + e_{22}^2(l) + e_{33}^2(l)] \\ &+ C_{12} \sum_l [e_{11}(l)e_{22}(l) + e_{11}(l)e_{33}(l) + e_{22}(l)e_{33}(l)] \\ &+ 2C_{44} \sum_l [e_{12}^2(l) + e_{13}^2(l) + e_{23}^2(l)] \;, \end{aligned} \qquad (5)$$

where $R(l)$ is the center-of-mass coordinate for the lth unit cell and M the mass of the unit cell. The constants C_{ij} have units of energy and are related to the usual elastic constant c_{ij} by $C_{ij} = (V/N)c_{ij}$, where V is the volume of the crystal and N the number of unit cells.

Deviations from cubic symmetry are described by nonvanishing thermal expectation values of the strains $e_{ij}(l)$ and the spin operators $S_i(l)$. We set

$$e_{ij}(l) = \langle e_{ij}(l)\rangle + b_{ij}(l) \;, \qquad (6)$$

$$S_i(l) = \langle S_i(l)\rangle + s_i(l) \; . \qquad (7)$$

We shall consider only the case of tetragonal distortion in which case

$$\langle e_{ij}\rangle = 0, \quad i \neq j$$

$$\langle e_{11}\rangle = \langle e_{22}\rangle = e_a \;,$$

$$\langle e_{33}\rangle = e_c \;,$$

$$\langle S_i \rangle = 0 \quad \text{for } i \neq 3 , \tag{8}$$

where the 3 axis has been taken as the c axis. The fluctuations about the average values of the strain may be expressed in terms of the normal-mode coordinates of the acoustic phonons in the usual way:

$$b_{ij}(l) = \frac{i}{2} \frac{1}{\sqrt{N}} \sum_{\lambda \vec{q}} e^{i \vec{q} \cdot \vec{X}(l)} [q_i e_j(\lambda \vec{q}) + q_j e_i(\lambda \vec{q})] \, Q_\lambda(\vec{q}) , \tag{9}$$

where $Q(\lambda \vec{q})$ is the normal-mode coordinate for the λth acoustic branch of frequency $\omega(\lambda \vec{q})$, wave vector $\vec{q}$, and polarization vector $\vec{e}(\lambda \vec{q})$. $\vec{X}(l)$ is the center of the lth unit cell.

When Eq. (6) is substituted in Eq. (5), the Hamiltonian H_e separates into static terms, terms which are linear in the fluctuations $b_{ij}(l)$ and terms which are quadratic in the fluctuations. For tetragonal distortion, the static part of the Hamiltonian takes the form

$$H_e^{(s)} = N [C_{11}(e_a^2 + \tfrac{1}{2} e_c^2) + C_{12}(e_a^2 + 2 e_a e_c)] . \tag{10}$$

The linear term may be written

$$H_e^{(l)} = [(C_{11} + C_{12}) e_a + C_{12} e_c] \textstyle\sum_l [b_{11}(l) + b_{22}(l)] + (C_{11} e_c + 2 C_{12} e_a) \sum_l b_{33}(l) . \tag{11}$$

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

$$H_e^{(f)} = \frac{1}{2M} \sum_{\lambda \vec{q}} P_\lambda(\vec{q}) P_\lambda(-\vec{q}) + \tfrac{1}{2} M \sum_{\lambda \vec{q}} \omega_0^2(\lambda \vec{q}) Q_\lambda(\vec{q}) Q_\lambda(-\vec{q}) , \tag{12}$$

where $P_\lambda(\vec{q})$ is the canonical conjugate momentum to $Q_\lambda(\vec{q})$,

$$[Q_\lambda(\vec{q}), P_\lambda(\vec{q}\,')] = i \delta_{\lambda \lambda'} \delta_{\vec{q} \vec{q}'} . \tag{13}$$

Similarly, making use of Eqs. (6) and (7), the Hamiltonians H_1 and H_2 may be separated into their static and fluctuating parts.

III. COUPLED-MODE FREQUENCIES

From the Hamiltonian we calculate the equations of motion for the acoustic normal-mode coordinates $Q_\lambda(\lambda \vec{q})$ and the spin operators $S_i(l)$. We set the static parts of the equations of motion equal to zero and linearize the equations of motion by keeping only terms linear in the fluctuations b_{ij} and s_i. Setting the static parts of the acoustic-phonon equations of motion equal to zero gives the following two relations among the static parts:

$$(C_{11} + C_{12}) e_a + C_{12} e_c + \frac{A}{\sqrt{6}} \langle S_3 \rangle + \frac{3K_1}{\sqrt{6}} \langle u_3 \rangle^2 + \frac{2K_2}{\sqrt{6}} \langle S_3 \rangle \langle u_3 \rangle = 0 , \tag{14}$$

$$C_{11} e_c + 2 C_{12} e_a - 2 \left(\frac{A}{\sqrt{6}} \langle S_3 \rangle + \frac{3K_1}{\sqrt{6}} \langle u_3 \rangle^2 + \frac{2K_2}{\sqrt{6}} \langle S_3 \rangle \langle u_3 \rangle \right) = 0 ,$$

where

$$\langle u_3 \rangle = (2/\sqrt{6})(e_c - e_a) . \tag{15}$$

The $S_i(l)$ equations have no static parts.

From these equations, we obtain

$$e_a = -\tfrac{1}{2} e_c , \tag{16}$$

$$(C_{11} - C_{12}) \langle u_3 \rangle - 3K_1 \langle u_3 \rangle^2 = (A + 2K_2 \langle u_3 \rangle) \langle S_3 \rangle . \tag{17}$$

Making use of Eq. (16) the static part of the Hamiltonian H_e may be written

$$H_e^{(s)} = N \tfrac{1}{2} (C_{11} - C_{12}) \langle u_3 \rangle^2 . \tag{18}$$

For the linearized equations of motion, we obtain

$$\frac{\partial}{\partial t} s_1(\vec{q}) = \Omega_1 s_2(\vec{q}), \tag{19}$$

$$\frac{\partial}{\partial t} s_2(\vec{q}) = -\Omega_1 s_1(\vec{q}) + \frac{i}{\sqrt{2}} \langle S_3 \rangle \times \Omega_2 \sum_\lambda [q_1 e_1(\lambda \vec{q}) - q_2 e_2(\lambda \vec{q})] \, Q_\lambda(\vec{q}) , \tag{20}$$

$$\frac{\partial}{\partial t} s_3(\vec{q}) = 0, \qquad s_3 = 0 \tag{21}$$

$$\frac{-\partial^2}{\partial t^2} Q_\lambda(\vec{q}) = \omega^2(\lambda \vec{q}) \, Q_\lambda(\vec{q}) + \frac{i}{\sqrt{2}} \frac{\Omega_2}{M} \times [q_1 e_1(\lambda \vec{q}) - q_2 e_2(\lambda \vec{q})] \, s_1(\vec{q}), \tag{22}$$

where

$$\Omega_1 = \langle u_3 \rangle \ (A + K_2 \langle u_3 \rangle), \tag{23}$$

$$\Omega_2 = (A - 2 K_2 \langle u_3 \rangle), \tag{24}$$

$$\omega^2(\lambda \vec{q}) = \omega_0^2(\lambda \vec{q}) + (1/M) \ (3 K_1 \langle u_3 \rangle + K_2 \langle S_3 \rangle \times \{ [q_1 e_1 (\lambda \vec{q}) - q_2 e_2 (\lambda \vec{q})]^2 - \tfrac{1}{3} [2 \, q_3 e_3(\lambda \vec{q}) - q_1 e_1(\lambda \vec{q}) - q_2 e_2(\lambda \vec{q})]^2 \} . \tag{25}$$

Equations (19) and (20) may be combined to give

$$\frac{\partial^2}{\partial t^2} s_1(\vec{q}) = -\Omega_1^2 \, s_1(\vec{q}) + \frac{i}{\sqrt{2}} \langle S_3 \rangle \times \Omega_1 \Omega_2 \sum_\lambda [q_1 e_1(\lambda \vec{q}) - q_2 e_2(\lambda \vec{q})] \, Q(\vec{q}). \tag{26}$$

We note that this equation contains a sum over the acoustic modes. For simplicity we shall consider the coupling of one acoustic mode λ to the electronic system. From Eqs. (22) and (26), the secular equation then takes the form

$$[\omega^2-\omega^2(\lambda\vec{q})]\,(\omega^2-\Omega_1^2)$$

$$-(1/2M)\,\langle S_3\rangle\,\Omega_1\Omega_2^2\,[q_1e_1(\lambda\vec{q})-q_2e_2(\lambda\vec{q})]^2=0, \quad (27)$$

with the solution

$$\omega_{1,2}^2(\vec{q})=\tfrac{1}{2}[\Omega_1^2+\omega^2(\lambda\vec{q})]\pm\{\tfrac{1}{4}[\Omega_1^2+\omega^2(\lambda\vec{q})]^2-\Omega_1^2\omega^2(\lambda\vec{q})$$

$$+(1/2M)\,\langle S_3\rangle\,\Omega_1\Omega_2^2\,[q_1e_1(\lambda\vec{q})-q_2e_2(\lambda\vec{q})]^2\}^{1/2}. \quad (28)$$

We note from Eq. (27) that there is no coupling between the modes for $T>T_c$. If we expand for small q, we obtain for the minus sign an acoustic mode

$$\omega_2^2=\omega^2(\lambda\vec{q})-(1/2M)\,\langle S_3\rangle$$

$$\times(\Omega_2^2/\Omega_1)\,[q_1e_1(\lambda\vec{q})-q_2e_2(\lambda\vec{q})]^2\,; \quad (29)$$

for the plus sign, we obtain

$$\omega_1^2=\Omega_1^2+(1/2M)\langle S_3\rangle\,(\Omega_2^2/\Omega_1)\,[q_1e_1(\lambda\vec{q})-q_2e_2(\lambda\vec{q})]^2. \quad (30)$$

This latter mode describes the splitting of the doubly degenerate electronic level due to the static distortion and the interaction with the acoustic phonons. This expansion is only valid for $\omega(\lambda q)\ll\Omega_1$ and is therefore restricted to the distorted structure.

Making use of the relationship between the sound velocities and the elastic constants we may deduce from Eq. (29) the corresponding changes in the high-frequency elastic constants for $T<T_c$. We obtain

$$\tilde{C}_{11}^a=C_{11}-\alpha+\tfrac{2}{3}\beta\ ,\qquad \tilde{C}_{44}^a=C_{44}\ ,$$

$$\tilde{C}_{33}^a=C_{11}-\tfrac{4}{3}\beta\ ,\qquad \tilde{C}_{66}^a=C_{66}\ , \quad (31)$$

$$\tilde{C}_{12}^a=C_{12}+\alpha-\tfrac{4}{3}\beta\ ,\qquad \tilde{C}_{13}^a=C_{12}+\tfrac{2}{3}\beta\ ,$$

where C_{ij} are the elastic constants for the cubic structure assumed to be temperature independent and where

$$\alpha=\tfrac{1}{2}\langle S_3\rangle\frac{\Omega_2^2}{\Omega_1}\ ,$$

$$\beta=3K_1\langle u_3\rangle+K_2\langle S_3\rangle\ . \quad (32)$$

Equation (17) provides a relationship between $\langle S_3\rangle$ and $\langle u_3\rangle$. In order to calculate these expectation values explicitly as functions of temperature and the model parameters, an additional relationship is required. We make use of the molecular-field approximation. From the Hamiltonians, Eqs. (4), the effective field acting on the spin $\vec{S}(l)$ may be written

$$\vec{F}=(0,0,A\,\langle u_3\rangle+K_2\langle u_3\rangle^2)\ . \quad (33)$$

The expectation value of S_3 is therefore given by

$$\langle S_3\rangle=\tfrac{1}{2}N_S\tanh y\ , \quad (34)$$

where $y=F/2k_BT$ and N_S is the number of Jahn-Teller ions per unit cell. The free energy may be written

$$F/N=\tfrac{1}{2}(C_{11}-C_{12})\langle u_3\rangle^2-A\,\langle u_3\rangle\langle S_3\rangle-K_1\langle u_3\rangle^2-K_2\langle u_3\rangle^2\langle S_3\rangle$$

$$+k_BT\,\tfrac{1}{2}N_S\big([1+(2/N_S)\langle S_3\rangle]\ln\{\tfrac{1}{2}[1+(2/N_S)\langle S_3\rangle]\}+[1-(2/N_S)\langle S_3\rangle]\ln\{\tfrac{1}{2}[1-(2/N_S)\langle S_3\rangle]\}\big)\ . \quad (35)$$

These molecular-field equations have previously been derived (for $N_S=1$) by Kanamori who discussed their solutions for different relative values of A, K_1, and K_2. For $K_1=K_2=0$, Eqs. (17) and (34) may be written

$$(C_{11}-C_{12})\langle u_3\rangle=A\,\langle S_3\rangle\ , \quad (36)$$

$$\langle S_3\rangle=\tfrac{1}{2}N_S\ \tanh[A^2/(C_{11}-C_{12})]\langle S_3\rangle/2k_BT\ . \quad (37)$$

It follows from Eq. (37) that the phase transition is of second order. The transition temperature is given by

$$k_BT=\tfrac{1}{4}N_SA^2/(C_{11}-C_{12})\ . \quad (38)$$

In the molecular-field approximation, we have

$$\langle u_3\rangle,\ \langle S_3\rangle\propto(T_c-T)^{1/2}\ \text{ for } T\lesssim T_C\ .$$

For K_1, $K_2\neq0$ the transition is of first order. The transition temperature is obtained by setting the free energy of the two phases equal.

By calculating the changes in the free energy in the presence of static external deformation the isothermal elastic constants are obtained in the usual way. We obtain

$$\tilde{C}_{11}^i=C_{11}-\alpha+\tfrac{2}{3}\beta-\tfrac{1}{6}\gamma\ ,$$

$$\tilde{C}_{33}^i=C_{11}-\tfrac{4}{3}\alpha-\tfrac{1}{6}\gamma\ ,$$

$$\tilde{C}_{12}^i=C_{12}+\alpha-\tfrac{4}{3}\beta-\tfrac{2}{3}\gamma\ , \quad (39)$$

$$\tilde{C}_{13}^i=C_{12}+\tfrac{2}{3}\beta+\tfrac{1}{3}\gamma\ ,$$

where

$$\gamma=\frac{N_S}{4kT}\,(A+2K_2\langle u_3\rangle)^2\left(1-\frac{4}{N_S^2}\langle S_3\rangle\right)^2\ . \quad (40)$$

These expressions are valid for all values of the temperature. For $T>T_c$, we have

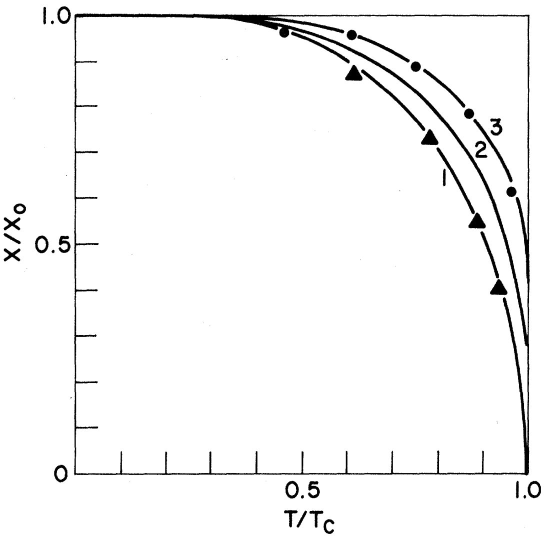

FIG. 1. Temperature dependence of the tetragonal distortion. Curve 1: $k_1=k_2=0$; curve 2: $k_1=0.15$, $k_2=0$; curve 3: $k_1=0$, $k_2=0.10$. ●: $CuFe_2O_4$; ▲: $CuFe_{1.7}Cr_{0.3}O_4$.

$$\alpha=\tfrac{1}{8}N_S\,A^2/kT\ ,\quad \beta=0\ ,\quad \gamma=\tfrac{1}{4}N_S\,A^2/kT\ . \tag{41}$$

The sound velocity of a shear mode propagating in a [110] direction polarized in the $[1\bar{1}0]$ direction is given by

$$\tilde{v}_s^2=(\tilde{C}_{11}-\tilde{C}_{12})/2M\ . \tag{42}$$

From the preceding expressions, it follows that for a second-order transition $\tilde{v}_s^a$ goes to zero discontinuously, whereas $\tilde{v}_s^i$ vanishes continuously. In both cases, $\tilde{v}_s$ remains zero for all temperatures $T<T_c$. It is of interest to note the frequency as calculated by the equation-of-motion method vanishes discontinuously in spite of the fact that the phase transition is of second order in which the order parameter $\langle u_3\rangle$ or $\langle S_3\rangle$ goes to zero continuously as T approaches T_c from below.

When the transition is first order (K_1 or $K_2\neq 0$) $\tilde{v}_s$ exhibits a step discontinuity at $T=T_c$ to a nonzero value and then increases with decreasing temperature.

The requirement that $\tilde{v}_s>0$ yields a stability condition for the tetragonal structure. In the limit of small anisotropies, it takes the form

$$A\,K_1/(C_{11}-C_{12})+K_2>0\ .$$

This condition has previously been derived by Kanamori (for $N_S=1$) using the free-energy expression.[6]

IV. NUMERICAL CALCULATIONS

It will be convenient to introduce the dimensionless variables

$$x=\frac{2(C_{11}-C_{12})}{A\,N_S}\langle u_3\rangle\ ,\quad t=\frac{4(C_{11}-C_{12})}{A^2N_S}k_BT\ ,$$

$$k_1=\frac{3A^2N_SK_1}{2(C_{11}-C_{12})}\ ,\quad k_2=\frac{N_SK_2}{2(C_{11}-C_{12})}\ . \tag{43}$$

Then Eq. (17) determining the strain distortion may be written

$$x-k_1x^2=(1+2k_2x)\tanh y\ , \tag{44}$$

where

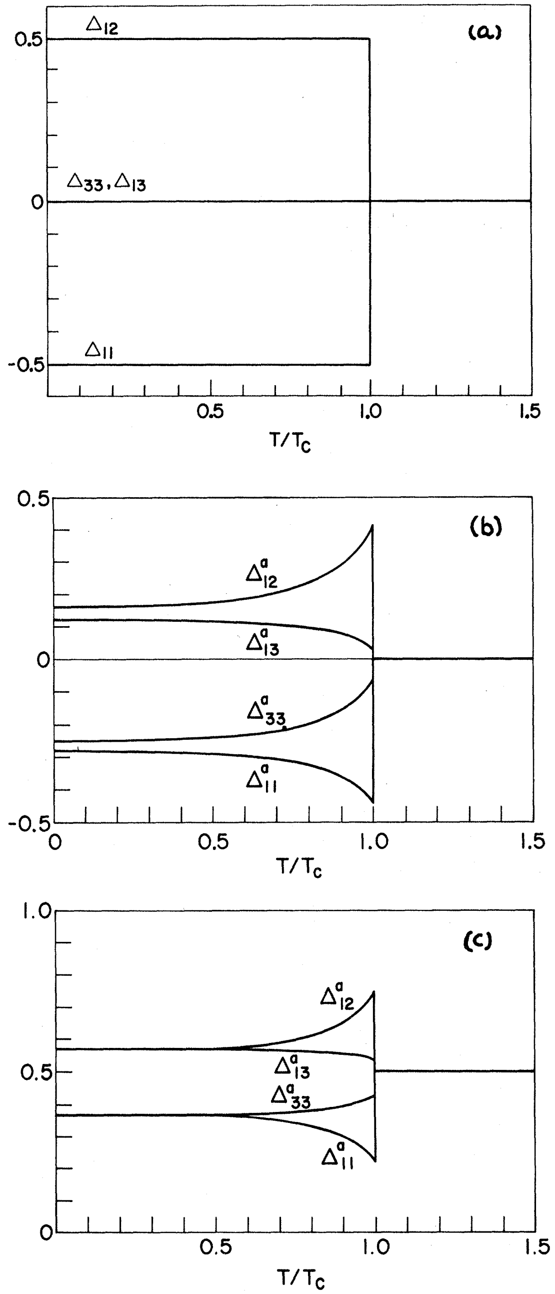

FIG. 2. Temperature dependence of the changes in the relative high-frequency elastic constants Δ_{ij}^a defined by Eq. (47). (a) $k_1=k_2=0$; (b) $k_1=0.15$, $k_2=0$; (c) $k_1=0$, $k_2=0.10$.

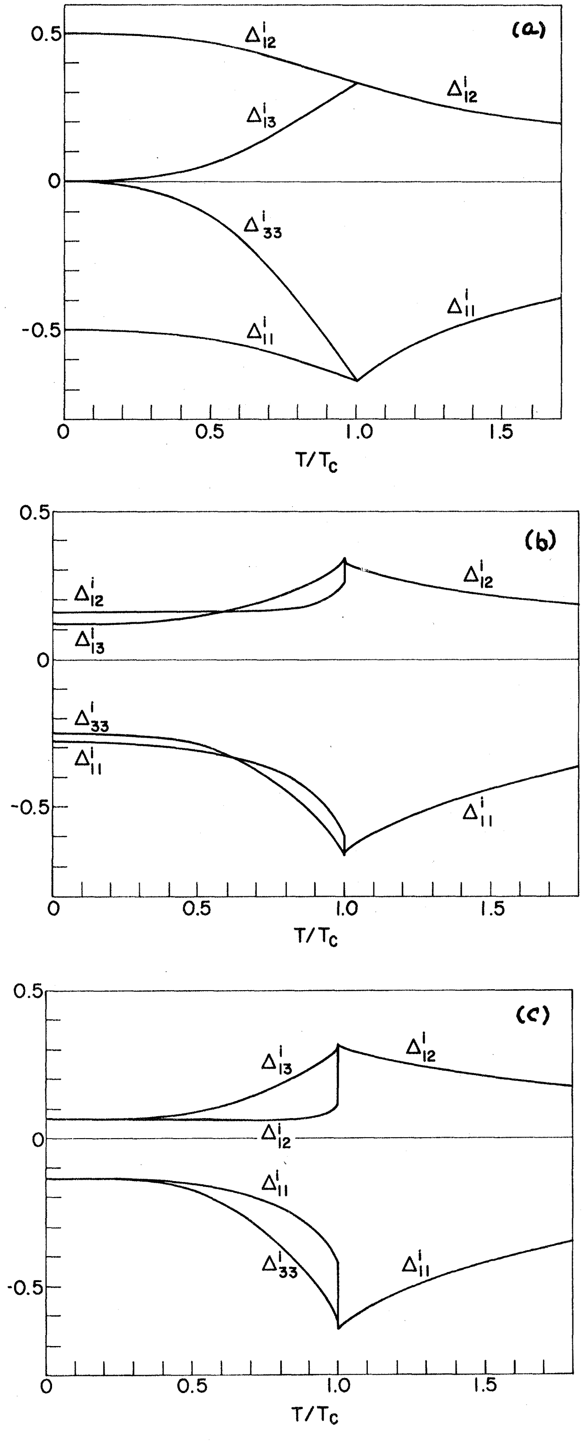

FIG. 3. Temperature dependence of the changes in the relative isothermal elastic constants Δ^i_{ij}. Parts (a), (b), and (c) of the figure correspond to the same values of k_1 and k_2 as in Fig. 2.

$$y = (x + k_2 x^2)/t \quad .$$

The equation for the transition temperature takes the form

$$\tfrac{1}{2}x^2 - x\tanh y - \tfrac{1}{3}k_1 x^3 - k_2 x^2 \tanh y + \tfrac{1}{2}t\{(1+\tanh y)\ln[\tfrac{1}{2}(1+\tanh y)] + (1-\tanh y) \times \ln[\tfrac{1}{2}(1-\tanh y)] + 2\ln 2\}\Big|_{t=t_c} = 0 \quad . \tag{45}$$

Further, if we define

$$\Delta_{ij} = (\tilde{C}_{ij} - C_{ij})/(C_{11} - C_{12}) \quad , \tag{46}$$

the changes in the elastic constants may be written

$$\begin{aligned}
&\Delta^a_{11} = -\alpha' + \tfrac{2}{3}\beta', &&\Delta^a_{33} = -\tfrac{4}{3}\beta' , \\
&\Delta^a_{12} = \alpha' - \tfrac{4}{3}\beta' , &&\Delta^a_{13} = \tfrac{2}{3}\beta' , \\
&\Delta^i_{11} = -\alpha' + \tfrac{2}{3}\beta' - \tfrac{1}{6}\gamma' , &&\Delta^i_{33} = -\tfrac{4}{3}\beta' - \tfrac{2}{3}\gamma' , \\
&\Delta^i_{12} = \alpha' - \tfrac{4}{3}\beta' - \tfrac{1}{6}\gamma' , &&\Delta^i_{13} = \tfrac{2}{3}\beta' + \tfrac{1}{3}\gamma' , \\
&\Delta^a_{44} = \Delta^i_{44} = 0 , &&\Delta^a_{66} = \Delta^i_{66} = 0 ,
\end{aligned} \tag{47}$$

where

$$\alpha' = \frac{(1-2k_2 x)^2}{1+k_2 x}\,\frac{\tanh y}{2x} , \tag{48}$$

$$\beta' = k_1 x + k_2 \tanh y,$$

$$\gamma' = (1 + 2k_2 x)^2 \operatorname{sech}^2 y/t \; .$$

The splitting of the degenerate electronic level due to the interaction with the static strain and the acoustic mode λ takes the form

$$\omega_1^2 = \Omega_1^2 + v^2[q_1 e_2(\lambda\vec{q}) - q_2 e_1(\lambda\vec{q})]^2 , \tag{49}$$

with

$$\Omega_1 = \frac{A^2 N_s}{2(C_{11} - C_{12})}\, x(1 + k_2 x) , \qquad v^2 = 2\alpha' v_s^2 , \tag{50}$$

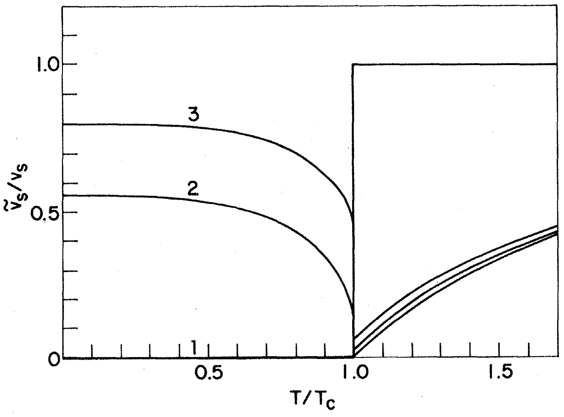

FIG. 4. Shear sound velocity $\tilde{v}_s$ defined by Eq. (42) as a function of temperature. For $T < T_c$, $\tilde{v}^a_s = \tilde{v}^i_s$. For $T > T_c$, $\tilde{v}^a_s = v_s$. Curves 1, 2, and 3 correspond to the same values of k_1 and k_2 as in Fig. 1.

where v_s is the sound velocity of the shear mode propagating in the $[1,1,0]$ direction and polarized in the $[1\bar{1}0]$ direction in the undistorted structure.

Figures 1–4 show the results of numerical calculations based on these expressions for $N_s = 2$. Figure 1 shows the temperature dependence of the tetragonal distortion for different values of k_1 and k_2 together with experimental points for $CuFe_2O_4$ and $CuFe_{1.7}Cr_{0.3}O_4$. The values of k_1 and k_2 have been chosen to give curves in the neighborhood of the experimental points. No attempt was made to determine k_1 or k_2 as a satisfactory fit could be obtained for different combinations of k_1 and k_2. The strain distortion depends somewhat more strongly on k_2 than on k_1. Figures 2–4 show the temperature dependence of the elastic constants and of the sound velocity v_s for the same values of k_1 and k_2. No measurements of the elastic properties of these spinels have as yet been reported.

The splitting of the electronic level is proportional to x for $k_2 = 0$. For the value of $k_2 = 0.10$ used in Fig. 1 the curve showing the temperature dependence of Ω_1 is slightly below the corresponding curve for x.

For given values of k_1 and k_2, the constants A and $C_{11} - C_{12}$ may be determined from the transition temperature T_c and the low-temperature value of the c/a ratio. The c/a ratio is related to $\langle u_3 \rangle$ by Eq. (15):

$$(c/a - 1) = e_c - e_a = \tfrac{1}{2}\sqrt{6}\,\langle u_3 \rangle$$

For $CuFe_2O_4$, we have $T_c \approx 630\,^\circ K$ and[13] $(c/a - 1) = 0.06$.

The values of A and v_s obtained for different values of k_1 and k_2 is shown in Table I together with t_c, $x_0 = x(t=0)$, $x_c = x(t_c)$ and the splitting of the electronic level $\Omega_1(t=0)$.

TABLE I. Predicted values of v_s and Ω_1 for different values of the anisotropy constants k_1 and k_2.

Anisotropy	t_c	x_0	x_c/x_0	v_s (10^5 cm/sec)	A (10^{-12} ergs)	Ω_1 (10^2 cm^{-1})
$k_1=0$, $k_2=0$	1.0	1.0	0	2.1	3.5	8.8
$k_1=0.15$, $k_2=0$	1.02	1.23	0.27	2.6	4.4	11
$k_1=0.25$, $k_2=0$	1.06	2.0	0.38	4.3	7.1	17
$k_1=0$, $k_2=0.10$	1.06	1.25	0.49	2.7	4.4	13
$k_1=0$, $k_2=0.175$	1.21	1.54	0.72	3.3	5.5	17

The mass of the $CuFe_2O_4$ unit cell has been taken as $M = 8.010^{-22}$ G.

V. CONCLUSIONS

In this paper, the interaction between the static strain and acoustic phonons with the doubly degenerate electronic orbital level in the spinel structure exhibiting a collective Jahn-Teller effect has been studied. The model predicts anomalous behavior of the elastic constants at the phase transition. A study of the elastic properties of these materials may therefore give valuable information concerning the relative merits of the theories that have been proposed for these phase transitions.

ACKNOWLEDGMENTS

I am indebted to K. A. Müller, H. Thomas, R. Englman, and J. C. Slonczewski for informative discussions.

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