

## Theory of a Structural Phase Transition Induced by the Jahn-Teller Effect

H. Thomas\*

*Institut für Theoretische Physik, Universität Frankfurt, 6 Frankfurt am Main, Germany*

and

K. A. Müller

*IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland*

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We present theory *a* of structural phase transitions in which the lowering of symmetry originates from a Jahn-Teller effect of the ionic constituents with electronic *E*-type doublets. We consider a model in which the three lowest vibronic states of the Jahn-Teller complexes are well separated from the higher excitations. The static and dynamic properties are studied in an  $S=1$  pseudospin representation.

We consider a crystal containing Jahn-Teller (JT) ions with doublet electronic ground states in octahedral, tetrahedral, or trigonal symmetry. The electronic doublet  $\psi_{11} = |2z_l^2 - x_l^2 - y_l^2\rangle$ ,  $\psi_{12} = |\sqrt{3}(x_l^2 - y_l^2)\rangle$  at lattice site  $l$  is split by the JT coupling with the local normal coordinates  $Q_{13} = \rho_l \cos\theta_l$ ,  $Q_{12} = \rho_l \sin\theta_l$  of the same symmetry. For fixed  $\vec{Q}_l = \{\rho_l \cos\theta_l, \rho_l \sin\theta_l\}$ , the electronic ground state is given by<sup>1</sup>

$$\varphi(\vec{r}_l; \vec{Q}_l) = \psi_{11} \sin^{\frac{1}{2}}\theta_l + \psi_{12} \cos^{\frac{1}{2}}\theta_l. \quad (1)$$

The ground-state energy has  $C_{3v}$  symmetry in the  $Q_{13}$ - $Q_{12}$  plane. The linear JT coupling together with harmonic and anharmonic lattice-energy terms produce an energy surface with minima occurring at  $\rho_l = \rho$  and  $\theta_l = 0, \pm \frac{2}{3}\pi$ , or at  $\theta_l = \pm \frac{1}{3}\pi, \pi$  (corresponding to elongations or contractions of the octahedra along one of the three cubic axes, respectively). The distribution of the ionic complexes over the three valleys is governed by a

competition between the entropy, favoring disorder, and the interaction energy

$$H_{\text{int}} = -\frac{1}{2} \sum_{ll'} \vec{Q}_l \cdot \vec{v}_{ll'} \cdot \vec{Q}_{l'}, \quad (2)$$

favoring order. We assume that "ferrodistor-tive"<sup>2</sup> order with elongation of the octahedra is most favorable.

The above consideration assumes perfect localization of the amplitude  $\chi(\vec{Q}_l)$  of the vibronic wave function

$$\Psi(\vec{Q}_l, \vec{r}_l) = \chi(\vec{Q}_l) \varphi(\vec{r}_l; \vec{Q}_l) \quad (3)$$

in one of the three valleys. Because of the ionic kinetic energy, however, the system can tunnel between the valleys. The vibronic wave functions are then still of the form (3), but with  $\chi$  a superposition of "Wannier" wave packets  $a_n(\theta_l) = a(\theta_l - \frac{2}{3}n\pi)$  centered at  $\theta_l = \frac{2}{3}n\pi$  ( $n=0, \pm 1$ ). Since  $\chi(\vec{Q}_l)$  and  $a(\theta_l)$  transform as a double representation, the Bloch theorem takes the form<sup>3</sup>

$$\chi_\nu(\theta_l) = \frac{1}{\sqrt{3}} \sqrt{3} [a_0(\theta_l) + a_1(\theta_l) \exp(\frac{2}{3}\pi i \nu) + a_{-1}(\theta_l) \exp(-\frac{2}{3}\pi i \nu)], \quad (4)$$

with half-integer "wave numbers"  $\nu = \pm \frac{1}{2}, \frac{3}{2}$ . Thus, one obtains a low-lying doublet  $\nu = \pm \frac{1}{2}$  and a high-lying singlet  $\nu = \frac{3}{2}$ , separated by a tunneling energy  $\frac{3}{2}\Omega$ . We assume that  $\Omega$  is small compared to the excitation energy of higher states, and take only these three lowest states into account.

We make use of an  $S=1$  pseudospin representation. The operators are expressed in the Wannier basis  $(a_1, a_0, a_{-1})$  as linear combinations of the unit matrix, the three spin matrices  $S_x, S_y, S_z$ , and the five matrices

$$E_1 = \frac{1}{3} \sqrt{3} (3S_x^2 - 2), \quad E_2 = S_x^2 - S_y^2, \quad T_1 = S_y S_z + S_z S_y, \quad T_2 = S_z S_x + S_x S_z, \quad T_3 = S_x S_y + S_y S_x. \quad (5)$$

The JT tunneling Hamiltonian is given by

$$H_1^{JT} = -\frac{1}{2} \Omega [\sqrt{2} S_{1x} - (S_{1x}^2 - S_{1y}^2)] = -\frac{1}{2} \Omega (\sqrt{2} S_{1x} - E_{12}). \quad (6)$$

For  $Q_{13}$  and  $Q_{12}$  we find, in the strong localization limit,<sup>4</sup> by neglecting overlap terms

$$Q_{13} = \frac{1}{2} (2 - 3S_{1z}^2) = -\frac{1}{2} \sqrt{3} E_{11}; \quad Q_{12} = \frac{1}{2} \sqrt{3} S_{1z}. \quad (7)$$

Here  $Q_l$  has been assumed to be normalized so that  $\langle \rho_l \rangle = 1$ . We study the linear response to external

forces  $\vec{F}_i^{\text{ext}}$ . The Hamiltonian is then given by

$$H = \sum_i H_i^{\text{JT}} - \frac{1}{2} \sum_{i'} \vec{Q}_i \cdot \vec{\nabla}_{i'} \cdot \vec{Q}_{i'} - \sum_i \vec{F}_i^{\text{ext}} \cdot \vec{Q}_i. \quad (8)$$

The static properties are calculated in the molecular field approximation (MFA) with a density matrix

$$\rho = \prod_i \exp(-\beta H_i^{\text{mol}}) / Z_i, \quad Z_i = \text{tr}_i \exp(-\beta H_i^{\text{mol}}). \quad (9)$$

Here,  $H_i^{\text{mol}}$  is the molecular field Hamiltonian

$$H_i^{\text{mol}} = H_i^{\text{JT}} - \vec{F}_i^{\text{mol}} \cdot \vec{Q}_i; \quad \vec{F}_i^{\text{mol}} = \sum_{i'} \vec{\nabla}_{i'} \cdot \langle \vec{Q}_{i'} \rangle + \vec{F}_i^{\text{ext}}. \quad (10)$$

$Z_i$  is computed from the eigenvalues  $E_{i\alpha}$  of  $H_i^{\text{mol}}$ . For  $F_i^{\text{mol}}$  in the  $Q_3$  direction,

$$E_{11,2} = \frac{1}{4} \left\{ \Omega - F_i^{\text{mol}} \pm [9\Omega^2 + 6\Omega F_i^{\text{mol}} + 9(F_i^{\text{mol}})^2]^{1/2} \right\}; \quad E_{13} = -\frac{1}{2}(\Omega - F_i^{\text{mol}}). \quad (11)$$

The  $\langle \vec{Q}_i \rangle$  are determined by the self-consistency equations

$$\langle \vec{Q}_i \rangle = Z_i^{-1} \partial Z_i / \partial (\beta \vec{F}_i^{\text{mol}}). \quad (12)$$

In the disordered phase,  $\langle \vec{Q}_i \rangle = 0$  for  $\vec{F}_i^{\text{ext}} = 0$ , and one finds the single-particle susceptibility

$$\chi^{(s)} = \left[ \left( \frac{3}{2} \beta \Omega + 2 \right) \exp\left(\frac{1}{2} \beta \Omega\right) - 2 \exp(-\beta \Omega) \right] / 3\Omega \left[ 2 \exp\left(\frac{1}{2} \beta \Omega\right) + \exp(-\beta \Omega) \right]. \quad (13)$$

Assuming one JT ion per unit cell, one obtains after Fourier transformation for the collective susceptibility the feedback expression

$$\vec{\chi}_q = \chi^{(s)} \left[ \vec{1} - \chi^{(s)} \vec{\nabla}_q \right]^{-1}. \quad (14)$$

The disordered phase becomes unstable with respect to ferrodistorptive ordering, if the largest eigenvalue  $v_0$  of  $\vec{\nabla}_q$  occurs for  $q=0$ . The stability limit  $T_1$  is then given by  $1 = v_0 \chi^{(s)}(T_1)$ .

We consider particularly the case  $\Omega \ll v_0$ . Then,  $kT_1 \approx \frac{1}{2} v_0$ . However, also in the opposite case,  $\Omega > v_0$ , there always exists a transition. This is a direct consequence of the JT effect which leads to a ground-state doublet, in contrast to ordinary lattice-dynamical models like the two-valley model of hydrogen-bonded ferroelectrics,<sup>5</sup> which have singlet ground states.

In the ordered phase, one has first to find the order parameter  $\langle Q_3 \rangle$  from Eq. (10) with  $F_i^{\text{ext}} = 0$ . In the limit  $\Omega \ll v_0$ , Eq. (12) takes the form

$$\langle Q_3 \rangle = \left[ \exp(\beta F^{\text{mol}}) - \exp\left(-\frac{1}{2} \beta F^{\text{mol}}\right) \cosh \frac{1}{2} \beta \Omega \right] / Z, \\ Z = \exp(\beta F^{\text{mol}}) + 2 \exp\left(-\frac{1}{2} \beta F^{\text{mol}}\right) \cosh \frac{1}{2} \beta \Omega, \quad (15)$$

where  $F^{\text{mol}} = v_0 \langle Q_3 \rangle$ .

In the uniform-field case  $q=0$ , one finds for the collective susceptibility

$$\chi_{33} = \chi_{33}^{(s)} / (1 - v_0 \chi_{33}^{(s)}), \quad \chi_{22} = \chi_{22}^{(s)} / (1 - v_0 \chi_{22}^{(s)}). \quad (16)$$

In the limit  $\Omega \ll v_0$ ,

$$\chi_{33}^{(s)} = (9/2kTZ^2) \exp\left(\frac{1}{2} \beta F^{\text{mol}}\right) \cosh \frac{1}{2} \beta \Omega, \\ \chi_{22}^{(s)} = (3/\Omega Z) \exp\left(-\frac{1}{2} \beta F^{\text{mol}}\right) \sinh \frac{1}{2} \beta \Omega. \quad (17)$$

One finds a stability limit  $T_2 > T_1$  which is determined by  $\chi_{33}$ . The transition is of first order, as expected from symmetry. The thermodynamic phase boundary  $T_c$  is found from the condition that the free energies of the two phases become equal. Figure 1 gives the order parameter as a function of temperature.

The dynamic behavior is determined by the equations of motion for the eight operators  $S_{1x}$ ,  $S_{1y}$ ,  $S_{1z}$ ,  $E_{11}$ ,  $E_{12}$ ,  $T_{11}$ ,  $T_{12}$ , and  $T_{13}$ . In the random-phase approximation (RPA), we obtain from the static parts

$$\frac{1}{2} \sqrt{2} (\Omega + 3F^{\text{mol}}) \langle S_x \rangle + \sqrt{3} \Omega \langle E_1 \rangle + \Omega \langle E_2 \rangle = 0. \quad (18)$$

This relation is easily seen to be satisfied by the MFA equilibrium state. For linear deviations from the equilibrium state, the eight equations decompose into two sets of four. The first set describes the

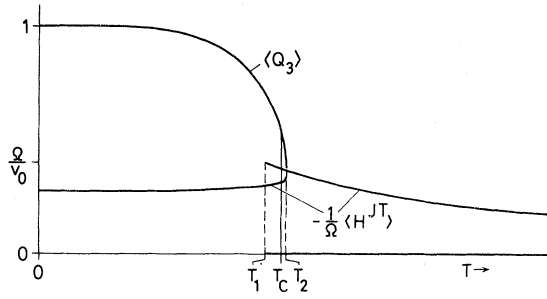


FIG. 1. Temperature dependence of the order parameter  $\langle Q_3 \rangle$  and of the JT energy.

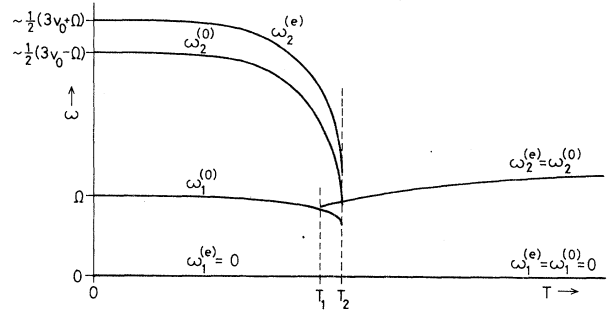


FIG. 2. Temperature dependence of the normal-mode frequencies for  $q=0$ .

motion of the operators which are even under the reflection  $Q_3 \rightarrow -Q_3$ ,

$$\begin{bmatrix} -i\omega & 0 & 0 & -\frac{1}{2}(3F^{\text{mol}} + \Omega) \\ 0 & -i\omega & 0 & -(\frac{3}{2})^{1/2}\Omega \\ 0 & 0 & -i\omega & -\Omega/\sqrt{2} \\ \frac{1}{2}(3F^{\text{mol}} + \Omega) & \sqrt{3}(\Omega/\sqrt{2} - \frac{3}{4}v_q \langle S_x \rangle) & \Omega/\sqrt{2} & -i\omega \end{bmatrix} \begin{bmatrix} \delta S_x \\ \delta E_1 \\ \delta E_2 \\ \delta T_1 \end{bmatrix} = 0; \quad (19)$$

and the second set that of the operators odd under reflection,

$$\begin{bmatrix} -i\omega & \Omega/\sqrt{2} - \frac{3}{4}v_q \langle S_x \rangle & \frac{1}{2}(3F^{\text{mol}} - \Omega) & 0 \\ -\Omega/\sqrt{2} & -i\omega & 0 & \Omega \\ -\frac{1}{2}(3F^{\text{mol}} - \Omega) & 0 & -i\omega & -\Omega/\sqrt{2} \\ 0 & -\Omega - \frac{3}{2}v_q \langle E_2 \rangle & \Omega/\sqrt{2} & -i\omega \end{bmatrix} \begin{bmatrix} \delta S_y \\ \delta S_z \\ \delta T_2 \\ \delta T_3 \end{bmatrix} = 0. \quad (20)$$

The first set has a double root  $\omega_1^{(e)} = 0$  corresponding to the two MFA constants of motion,  $H^{JT} - F^{\text{mol}}Q_3$  and  $E_1 - \sqrt{3}E_2 = -3^{-1/2}(3S_x^2 - 2)$ . In a more refined theory, these roots will correspond to a pair of relaxation- or diffusion-type modes, analogous to the parallel spin-deviation modes in uniaxial ferromagnets.<sup>6</sup> The remaining pair of roots is given by

$$(\omega_2^{(e)})^2 = \frac{1}{4} [(3F^{\text{mol}} + \Omega)^2 + 8\Omega^2 - (9/\sqrt{2})\Omega v_q \langle S_x \rangle]. \quad (21)$$

From the second set, we obtain for  $T > T_c$  another double root  $\omega_1^{(0)} = 0$ , corresponding to the additional MFA constants of motion in the disordered phase,  $\sqrt{2}S_y + T_3$  and  $S_z + \sqrt{3}T_2$ . The remaining pair  $\omega_2^{(0)}$  coincides with  $\omega_2^{(e)}$ . For  $T < T_c$ , we obtain in the limit  $\Omega \ll v_0$

$$(\omega_1^{(0)})^2 = \Omega^2 + (v_q/v_0)(2\Omega^2 + 3v_0 \langle H^{JT} \rangle), \quad (\omega_2^{(0)})^2 = \frac{1}{4} [(3F^{\text{mol}} - \Omega)^2 + 4\Omega^2 - 2\Omega^2 v_q/v_0]. \quad (22)$$

The mode frequencies are shown in Fig. 2 as functions of temperature. All the nonzero frequencies show a strong temperature dependence, but none of them is the soft mode connected with the stability limits at  $T_1$  and  $T_2$ . The soft mode will be one of the relaxation- or diffusion-type modes which are represented in the RPA by  $\omega_1^{(e)} = 0$ .

The present theory has to be improved by taking the coupling with the elastic displacement field

$$H_{\text{coupl}} = g[(2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy})Q_3 + \sqrt{3}(\epsilon_{xx} - \epsilon_{yy})Q_2] \quad (23)$$

into account.

A number of JT spinels show ferrodistorptive transitions and local distortions (i.e., large  $\langle Q_i^2 \rangle$ ) above  $T_c$  as revealed by Mössbauer spectroscopy and x-ray techniques.<sup>7,8</sup> However, the interaction energy in these systems may be so large that coupling to higher vibronic levels has to be taken into account.<sup>9</sup> The conditions of the theory may thus be better satisfied by the recently investigated double perovskites<sup>10</sup>  $A(\text{Cu}_x\text{Zn}_{1-x})$ -

$\text{WO}_6$  with  $A = \text{Ba}, \text{Sr}$ , which show ferrodistorptive JT transitions. In these crystals even for  $x=1$  the distance between nearest-neighbor Cu complexes is about twice that in the spinels. In the recently found Cu-hexanitro compounds<sup>11</sup> such as  $\text{K}_2(\text{Cu}, A)(\text{NO}_2)_6$  which are derived from the double perovskite structure, the distance between JT ions is still larger. Depending on the  $A$  ion, they show ferrodistorptive or antiferrodistorptive tran-

sitions. Phase transitions induced by crystalline field effects of rare-earth ions, on the other hand, have recently been investigated both experimentally and theoretically.<sup>12</sup>

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<sup>1</sup>See for instance M. C. M. O'Brien, Proc. Roy. Soc., Ser. A 281, 323 (1964).

<sup>2</sup>See H. Gränicher and K. A. Müller, Mater. Res. Bull. 6, 977 (1971).

<sup>3</sup>This corresponds closely to the representation given in Eqs. (27) of Ref. 1.

<sup>4</sup>Corresponding to the limit  $\omega \rightarrow \infty$  of Ref. 1.

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## Critical Properties of Antiferromagnets

H. K. Charles, Jr., and R. I. Joseph

*Department of Electrical Engineering, The Johns Hopkins University, Baltimore, Maryland 21218*

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The first eight terms of the low-field, high-temperature staggered-susceptibility series are obtained for a two-sublattice exchange-interaction model of antiferromagnetism for arbitrary spin and loose-packed lattices. For the bcc lattice and  $S = \frac{1}{2}$  (Heisenberg model) the ratio of the antiferromagnetic critical (Néel) temperature  $T_N$  to the ferromagnetic critical (Curie) temperature  $T_c$  is  $1.09 \pm 0.01$ , and the antiferromagnetic susceptibility critical index  $\gamma_N$  is  $1.40_{-0.02}^{+0.03}$ .

In order to apply various inequalities associated with critical-point exponents<sup>1</sup> to antiferromagnetic material, e.g.,  $\text{RbMnF}_3$ ,<sup>2</sup> it is necessary to consider parameters which characterize the staggered susceptibility,<sup>3,4</sup>

$$\chi_{st} \sim (T - T_N)^{-\gamma_N}.$$

It is known for the  $S = \frac{1}{2}$  Ising model for loose-packed lattices, as well as for the classical ( $S = \infty$ ) Heisenberg model,<sup>5,6</sup> that these parameters are identical with those characterizing the divergence of the ferromagnetic susceptibility,

$$\chi \sim (T - T_c)^{-\gamma},$$

i.e.,  $T_N = T_c$ ,  $\gamma_N = \gamma$ . On the other hand, Rushbrooke and Wood<sup>6</sup> (RW) have found from a calculation of the first seven terms in the low-field, high-temperature staggered-susceptibility expansion for the Heisenberg antiferromagnet (loose-packed lattices and general spin) that  $T_N > T_c$ . To our knowledge no calculation of the quantity  $\gamma_N$  has been made for a quantum-mechanical model (the RW series are at least one term too short to

obtain reliable estimates of  $\gamma_N$ ). The purpose of the present Letter is to provide such an estimate.

For the bcc lattice and  $S = \frac{1}{2}$  we find that  $\gamma_N = 1.40_{-0.02}^{+0.03}$  ( $T_N/T_c = 1.09 \pm 0.01$ ). This value of  $\gamma_N$  is in agreement with all available estimates of  $\gamma$  ( $S = \frac{1}{2}$ :  $\gamma = 1.36 \pm 0.04$ ,<sup>7</sup>  $\gamma = 1.41 \pm 0.02$ ,<sup>8</sup>  $\gamma = 1.43 \pm 0.01$ <sup>9</sup>). It also compares favorably with the latest estimates for the  $S = \infty$  Heisenberg case,  $\gamma = 1.41 \pm 0.02$ ,<sup>10</sup> where  $\gamma_N = \gamma$ . The close agreement between  $\gamma_N$  for  $S = \frac{1}{2}$  and  $S = \infty$  suggests that  $\gamma_N$  has little, if any, spin dependence for the Heisenberg model. This is further supported by experimental evidence from  $\text{RbMnF}_3$  ( $S = \frac{5}{2}$ ), for which  $\gamma_N = 1.38 \pm 0.02$ .<sup>2</sup> Hence we feel that our results add considerable credence to the universality concept of critical exponents.<sup>11,12</sup>

Our system is a lattice of  $N$  sites containing atoms of spin  $S$ , gyromagnetic ratio  $g$ , each atom having  $z$  nearest neighbors, which may be decomposed into two distinct and interpenetrating sublattices. The antiferromagnetic staggered susceptibility arises from a consideration of the effect on an exchange Hamiltonian of a small change in the external magnetic field  $H$  ( $z$  directed) which reverses direction at alternate