Ginzburg–Landau Theory of Jahn–Teller Phase Transitions

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Jahn–Teller structural phase transitions are examined using a simple Ginzburg–Landau approach. The order parameter representing orbital order is complex for the case of doubly degenerate d-orbital states. We find tricritical behavior in ferromagnet-like orbital order under applied uniaxial stress and in antiferromagnet-like orbital order with varying strength of the interaction between the two sublattices.

KEYWORDS: Jahn–Teller effect, Ginzburg–Landau theory, structural phase transition, orbital order

A representative microscopic origin of structural phase transitions occurring without large-scale composition changes is a coupling between electronic orbital states and lattice distortions, called the Jahn–Teller coupling.\(^1\)\(^-\)\(^6\) For example, one electron occupies an electronic state spanned by doubly degenerate d-orbital states around Cu\(^{2+}\) or Mn\(^{3+}\) in the undistorted crystal structure. Such orbital states can order cooperatively at low temperatures, leading to a cubic-to-tetragonal transformation. \(^1\) Kanamori introduced pseudo-Pauli spin matrices \(\hat{\sigma}_{\alpha\beta}\) and \(\hat{\sigma}_{\alpha\gamma}\) operating on electronic states at site \(n\) and expressed the orbit–lattice interaction energy in the form\(^3\)

\[ H_JT = g_0 \sum_n \left( \hat{\sigma}_{\alpha\beta} Q_{\alpha\beta} + \hat{\sigma}_{\alpha\gamma} Q_{\alpha\gamma} \right). \]  

where \(Q_{\alpha\beta}\) and \(Q_{\alpha\gamma}\) represent appropriate linear combinations of atomic displacements at site \(n\). Their acoustic parts may be equated to \(e_2\) and \(e_3\), to be defined in (2) below. Then, an orbital order represented by \(\langle \hat{\sigma}_{\alpha\beta} \rangle \propto \cos \varphi\) and \(\langle \hat{\sigma}_{\alpha\gamma} \rangle \propto \sin \varphi\) at low temperatures gives rise to a cubic-to-tetragonal structural change represented by \(\langle Q_{\alpha\beta} \rangle = \eta_x \cos \varphi\) and \(\langle Q_{\alpha\gamma} \rangle = \eta_y \sin \varphi\). The tetragonal distortion is along the \(x\), \(y\), and \(z\) axes for \(\varphi = 2\pi/3\), \(-2\pi/3\), and 0, respectively. Hence, the orbital order is the order parameter of the phase transition in this problem.

We also note that the conventional continuum theory of proper martensitic transition\(^7\)-\(^10\) involves the strains only, including anharmonic displacements. However, it is unclear under what conditions this approach is justified. The aim of this letter is hence to set up a Ginzburg–Landau theory for the orbital order parameter coupled to the elastic strains in the Jahn–Teller systems. This is analogous to a similar Ginzburg–Landau theory for binary alloys by the present author.\(^1\)\(^1\)\(^-\)\(^1\)\(^3\) Such a coarse-grained theory can have a higher predicting power for complex phase transition behavior than microscopic theories and is indispensable for the study of phase ordering kinetics.\(^1\)\(^0\)\(^-\)\(^1\)\(^4\)

We define the diagonal strains as

\[ e_1 = \nabla_x u_x + \nabla_y u_y + \nabla_z u_z, \]
\[ e_2 = \nabla_x u_x - \nabla_y u_y, \]

\[ e_3 = \frac{1}{\sqrt{3}} (2 \nabla_z u_z - \nabla_x u_x - \nabla_y u_y), \]  

where \(\nabla_j\) \((j = x, y, z)\) are the space derivatives. The off-diagonal components are written as

\[ e_4 = \nabla_x u_y + \nabla_y u_x, \]
\[ e_5 = \nabla_y u_z + \nabla_z u_y, \]
\[ e_6 = \nabla_z u_x + \nabla_x u_z. \]  

In the bilinear order, the elastic energy density is expressed as

\[ f_a = \frac{K}{2} e_1^2 + \frac{C_0}{2} (e_2^2 + e_3^2) + \frac{C_{44}}{2} (e_4^2 + e_5^2 + e_6^2), \]  

where \(K\) is the bulk modulus, \(C_{44}\) is the shear modulus, and \(C_0\) is the background value of the modulus \(C'\) for the tetragonal strains. We shall see that \(C'\) is an effective modulus smaller than \(C_0\).

Before defining the order parameter, we give some discussion on the Jahn–Teller interaction for doubly degenerate d-orbital states,\(^3\) whose wave functions are represented as linear combinations of the wave functions proportional to \(2x^2 - x^2 - y^2\) and \(x^2 - y^2\). The index \(n\) denoting the lattice site is dropped here for simplicity. The orbital states proportional to \(2x^2 - x^2 - y^2\), \(2y^2 - x^2 - x^2\), and \(2z^2 - x^2 - y^2\) are written as \(|x^2\rangle\), \(|y^2\rangle\), and \(|z^2\rangle\), respectively, while those with wave functions proportional to \(x^2 - y^2\), \(x^2 - z^2\), and \(z^2 - x^2\), are written as \(|x^2 - y^2\rangle\), \(|y^2 - z^2\rangle\), and \(|z^2 - x^2\rangle\), respectively. As orthogonal, complete bases, we define

\[ |1\rangle = |x^2 - y^2\rangle = \frac{1}{\sqrt{3}} (|x^2\rangle - |y^2\rangle), \]  

\[ |2\rangle = |z^2\rangle. \]  

Because the electronic orbit is stretched in the \(x\), \(y\), and \(z\) axes in the states \(|x^2\rangle\), \(|y^2\rangle\), and \(|z^2\rangle\), respectively, the orbit–lattice coupling energy at each site in cubic solids should be of the form,

\[ H_{JT} = -g_k [Q_x |x^2\rangle \langle x^2| + Q_y |y^2\rangle \langle y^2| + Q_z |z^2\rangle \langle z^2|], \]  

in the bra and ket representation of quantum mechanics, where \(g_k\) is a positive coupling constant and \(Q_j\) represents the atomic displacements whose acoustic parts are \(\nabla_j u_j\). The sum of \(H_{JT}\) over all the lattice sites becomes (1) with \(g_k = \sqrt{3} g_k / 4\), \(Q_2 = Q_y = Q_x \propto e_2\), and \(Q_3 = (2Q_z - Q_x - Q_y) / \sqrt{3} \propto e_3\), if we neglect a constant...
term proportional to $\sum Q_i$. The pseudo-Pauli matrices are defined at each lattice site and are expressed as $\sigma_z = |1\rangle \langle 1| - |2\rangle \langle 2|$ and $\sigma_x = |1\rangle \langle 2| + |2\rangle \langle 1|$.

First, we consider ferromagnet-like orbital order in spinel-type crystals such as CuFe$_2$O$_4$ and Mn$_2$O$_4$. We introduce a coarse-grained, two-component order parameter $(\psi_1, \psi_2)$ as

$$
\psi_1(r) = -\mathcal{E}^{-d} \sum_n (\sigma_{nz}), \quad \psi_2(r) = -\mathcal{E}^{-d} \sum_n (\sigma_{nx}),
$$

where the summation is over lattice points in an appropriately defined cell with a lattice constant $\ell$ longer than the original lattice constant $a$, and $r$ is a representative position within the new cell. The average $\langle \cdot \rangle$ is taken doubly over the quantum and thermal fluctuations. It is convenient to define the complex order parameter by $\psi = \psi_1 + i \psi_2 = |\psi| \exp(i\varphi)$. The free-energy density $f_{IT}$ representing the orbit-lattice coupling reads

$$
f_{IT} = -g(e_3 \psi_1 + e_2 \psi_2) = -g \Re[(e_3 + ie_2) \psi^*]. \tag{8}
$$

Here, it is informative to consider how $\psi$ is changed with respect to a rotation of the reference frame by $\pi/2$. The rotation about the $x$ axis is equivalent to the replacement, $y \rightarrow z$, $z \rightarrow -y$, with $x$ unchanged, which yields the transformation $\psi \rightarrow \exp(-2\pi/3)\psi$. The rotations about the $y$ and $z$ axes yield $\psi \rightarrow \exp(2\pi/3)\psi^*$ and $\psi \rightarrow \psi^*$, respectively. The complex strain defined by $e_3 + ie_2$ is also changed in the same manner and $f_{IT}$ is invariant for these rotations. Generally, in the presence of the cubic crystal symmetry in the disordered phase, the total free energy density $f = f(\psi, u)$ for $\psi$ and the elastic strains should be invariant with respect to these rotations. We propose the Landau expansion $f = f_0(\psi) + f_{IT} + f_3$ close to the transition with

$$
f_0(\psi) = \frac{r_0}{2} |\psi|^2 + \frac{u}{4} |\psi|^4 + \frac{C}{2} |\nabla \psi|^2 - B_0(\psi_3 - 3\psi_1 \psi_2^2), \tag{9}
$$

where $u$, $C$, and $B_0$ are positive constants. We also assume that $r_0$ depends on the temperature $T$ as $r_0 = A_0(T - T_0)$, where $A_0$ is a positive constant and $T_0$ is a constant temperature. Due to the last third-order term, the ordered states with $\varphi = 0, 2\pi/3$, and $-2\pi/3$ are favored, and correspond to the tetragonally distorted states with the symmetry axes along the $z$, $x$, and $y$ axes, respectively.

The real parts of $\psi^{3-k}(e_3 + ie_2)^k$ $(k = 0, 1, 2, 3)$ constitute four third-order invariants. More explicitly, they are written as $I_{30} = \psi_1^3 - 3\psi_1 \psi_2^2 = M^3 \cos 3\varphi$, $I_{31} = (\psi_1^2 - \psi_2^2)e_3 - 2\psi_1 \psi_2 e_2$, $I_{32} = \psi_1 (e_3^2 - e_2^2) - 2\psi_2 e_2 e_3$, and $I_{33} = e_3^3 - 3e_3 e_2^2$. We may assume a third-order term expressed as $\sum_{j=1}^3 B_j I_{3j}$ in the free energy density, where $B_j$ are the coefficients. In (9), for simplicity, we retain a third-order term proportional to $I_{30}$ only. The invariant $I_{30}$ has been of crucial importance in the conventional nonlinear strain theory.\textsuperscript{7-9}

If small $e_3$ is induced in the disordered phase, we have $\psi \approx g e_3/r_0$ in the static limit. Elimination of $\psi$ yields the effective elastic modulus $C'$ for the tetragonal strains,

$$
C' = C_0 - g^2/r_0. \tag{10}
$$

We next consider a tetragonal state stretched along the $z$ axis under the stress-free condition, where $\psi_1 = M > 0$ and $\psi_2 = 0$. By setting $e_3 = g M/C_0$, we obtain the equation of state, $r + uM^2 - 3B_0M = 0$, with

$$
r = M_0 - g^2/C_0 = A_0(T - T_0), \tag{11}
$$

where $T_0 = T_0 + g^2/A_0 C_0$. At $r = r_{tr}$, a first-order phase transition occurs, and $M$ and $e_3$ change from 0 to $M_{tr}$ and $e_{3tr}$, respectively, where

$$
r_{tr} = 2B_0^2/u, \quad M_{tr} = 2B_0/u, \quad e_{3tr} = 2gB_0/C_0 u. \tag{12}
$$

For $r < r_{tr}$, the ordered phase is stable and $M$ is expressed as

$$
M = \frac{3}{4} M_{tr} \left[1 + \sqrt{1 - 8r/9r_{tr}}\right]. \tag{13}
$$

The elastic modulus $C'$ in (10) immediately above the transition is expressed as $C_0 w/(1 + w)$ with

$$
w = 2C_0 B_0^2/g^2 u. \tag{14}
$$

In terms of the elastic properties, $w$ represents weakness of the first-order phase transition.

The fluctuation effect is much more complicated in ordered states than in disordered states due to the two-component nature of $\psi$. The second-order contributions to $f$ from the fluctuations of $\psi$ and the strains are written as

$$
\delta f = \frac{1}{2} r_L (\delta \psi_1)^2 + \frac{1}{2} r_T \psi_2^2 + \frac{C}{2} |\nabla \psi|^2 + \delta \delta f, \tag{15}
$$

where $\delta \psi_1 = \psi_1 - M$, and $\delta f$ is obtained from (4) if $e_3$ and $e_2$ are replaced by $e_3 - g \psi_1/C_0^*$ and $e_2 - g \psi_2/C_0^*$, respectively. The longitudinal and transverse inverse susceptibilities, $r_L$ and $r_T$, are given by

$$
r_L = 2uM^2 - 3B_0M, \quad r_T = 6B_0M. \tag{16}
$$

It is worth noting that $r_T$ is positive owing to the third-order term, while it vanishes in the (isotropic) many-component spin systems.\textsuperscript{14,15} Considering homogeneous deviations, we eliminate $\delta \psi_1$ and $\psi_2$ to obtain effective elastic moduli, $C'_L$ and $C'_T$, for the strains $e_3$ and $e_2$, respectively. In terms of $w$ in (14) and $m \equiv M/M_{tr}$, they are expressed as

$$
\frac{C'_L}{C_0' L} = \frac{w (4m^2 - 3m)}{1 + w (4m^2 - 3m)}, \quad \frac{C'_T}{C_0' T} = \frac{9wm}{1 + 9wm}. \tag{17}
$$

In Fig. 1, we display these elastic moduli near the transition for $w = 0.04$. The modulus $C'_L$ below the transition is continuously connected to $C'$ in (11) above the transition and is smaller (larger) than $C'_T$ for $r$ larger (smaller) than $-45/16 + 3\sqrt{45/32} r_{tr}$.

For inhomogeneous deviations, we express the strains in terms of the Fourier components assuming the mechanical equilibrium.\textsuperscript{5,11,14} Then, the space integral of $\delta f$ is expressed as

$$
\int d^3 r \delta f = \frac{1}{2} \sum_{\alpha, \beta = 1, 2} \sum_k A_{\alpha \beta} (k) \psi_{\alpha k} \psi_{\beta k}. \tag{18}
$$
where $A_{ij}(\mathbf{k})$ is a non-negative-definite matrix dependent on the direction of the wave vector, $\mathbf{k} \equiv k^{-1} \mathbf{k}$. Note that we include $\frac{\partial^2 \Phi}{\partial \psi^2} / 2 C_0''$ in the first two terms in (15). For $\mathbf{k}$ along [110], we obtain $A_{22} = A_{12} = 0$ and hence $\lim_{r \to 0} (\psi_2 / \psi_1)^2 = 1/r^2$. As a result, the velocity of the transverse sound propagating along [110] and polarized along [110] is given by $c_{110}(\rho) = (C_1' / \rho)^{1/2}$, $\rho$ being the mass density. In passing, let us consider the limit $B_0 \to 0$ with $r(0) < g$ fixed. Here, $C'_T \to 0$, while $C'_L / C''_0 \to 1 - 1/[1 + 2 C_0' r/g^2]$. In accordance with this result, Pytte found that $c_{110}$ vanishes for all temperatures below the transition in the absence of the third-order terms.

Furthermore, some new effects can be predicted if a uniaxial stress $\sigma_a$ is applied along the $z$ axis. The tetragonal variant with $\psi_1 > 0$ and $\psi_2 = 0$ is favored below the transition. However, the phase behavior becomes more interesting in the case of compression $\sigma_a < 0$, so we limit ourselves to this case. As shown in Fig. 2, the temperature-stress plane is divided into two regions by a line of first-phase transition (line F) and a critical line (line C). These two lines meet at a tricritical point, where $r = r_{tr}$ and $\sigma_a = 0$, and meets the critical line (solid line) at the tricritical point, where $r = r_{tr}$ and $\sigma_a = -\sigma_c$. Above the curves, we have a tetragonal phase ($\varphi = \pm \pi$), while below them, we have two stable orthorhombic variants ($2\pi/3 < |\varphi| < \pi$) as expressed by (21).

$$\psi_1 = -M \cos \varphi_a, \quad \psi_2 = \pm M \sin \varphi_a,$$

(21)

where the angle $\varphi_a = \pi - \varphi$ is in the range $0 < \varphi_a < \pi/3$ and satisfies $\sin^2 \varphi_a = (3/4)[1 - |\sigma_a/\sigma_c|/(8 M^2 3 M_{tr})]$. Here, $\varphi_a \to \pi/3$ as $\sigma_a \to 0$ for $r < r_{tr}$, $\varphi_a \to 0$ as line C is approached, and $\varphi_a$ remains nonvanishing as line F is approached from below. The moduli $C''_0$ for the strain $e_2$ tends to zero as line C is approached both from above and below. Near the critical line, $\psi_1$ is less singular than $\psi_2$ and we may set $\psi_1 = -M + c_2 \psi_2^2 + c_4 \psi_2^4 + \cdots$ from $\partial^2 \Phi / \partial \psi_1^2 = 0$. The Landau expansion for the primary order parameter $\psi_2$ then becomes $\tilde{f} = c_2 \psi_2^2 + c_4 \psi_4^4 + \cdots$, where elimination of $\psi_1$ yields the sixth-order term with $a_0 > 0$. We have $a_2 = 0$ and $a_4 > 0$ on line C, while $a_2$ and $a_4$ are written as linear combinations of $r - r_{tr}$ and $|\sigma_a| - \sigma_c$ near the tricritical point.16) The maximum point on line C is given by $r = r_{max} = 9 r_{tr}/2$ and $|\sigma_a| = \sigma_{max} = 16 \sigma_c$. If $r$ is fixed in the region $r_{tr} < r < r_{max}$, the orthorhombic phase is realized in a window region of $|\sigma_a|$. This region is expressed as $a_2 \approx r \to r_{max} + (9/8) r_{tr} |\sigma_a| / \sigma_{max} - 1 < 2$ slightly below the maximum point.

In MnF$_3$, the orbital order occurs alternatively in two sublattices with a symmetry axis along one of the cubic axes (say, the $z$ axis). In such cases, it is convenient to introduce the two complex variables, $\psi_A = \psi_{A1} + i \psi_{A2}$ and $\psi_B = \psi_{B1} + i \psi_{B2}$, for sublattices A and B.3) Then, we have the antiferromagnet-like order parameter $\zeta = \psi_A - \psi_B$ in addition to the ferromagnet-like order parameter $\psi = \psi_A + \psi_B$. The orbital order in MnF$_3$ is represented by $\psi = -2 M \sin \phi$ and $\zeta = \pm 2 i M \cos \phi$, where $\phi$ is the canting angle of the sublattice order. The solid is uniaxially deformed along the $z$ axis.

In the linear order with respect to the strains, the orbit-lattice coupling may be written as
\[ f_{\text{JT}} = -g \Re[e_3 - ie_2 |\psi| - g' \Re[e_3 + ie_2 |\psi|^2]. \] (22)

The free energy density \( f \) for \( \psi, \zeta \), and the strains is even with respect to the cubic terms with respect to those of \( f \).

\[ \begin{align*}
    f &= f_0(\psi_\alpha) + f_0(\psi_\beta) + f_{\text{JT}} + f_{\text{el}} + \frac{1}{4} r'(|\psi|^2 - |\zeta|^2) \\
    &= B' \Re[\psi_\alpha \psi_\beta |\psi| + u'(|\psi|^2 - |\zeta|^2)^2, \]
\] (23)

where \( f_0 \) is given by (9) and the last three terms arise from the interaction between the two sublattices since \( |\psi|^2 - |\zeta|^2 = 4 \Re[\psi_\alpha \psi_\beta] \). In the bilinear order, we have \( \delta f = (r + r_1)|\psi|^2/4 + (r - r_1)|\zeta|^2/4 \) after elimination of the tetragonal strains, where

\[ r = r_0 - g^2/C_0, \quad r_1 = r' - g^2/C_0'. \] (24)

Thus, the disordered phase is linearly unstable for \( r < -r_1 \) with respect to the fluctuations of \( \psi \) and for \( r < r_1 \) with respect to those of \( \zeta \). However, first-order phase transitions are induced by the cubic terms \(( \propto B_0, B' \)

and the phase behavior becomes very complicated for general \( r', B', u', g' \), and applied stress.

Here, we consider the effect of \( r' \) assuming \( B' = u' = g' = 0 \) under the stress-free condition.\(^b\) Let the phase angles of \( \psi_\alpha \) and \( \psi_\beta \) be \( \varphi_\alpha \) and \( \varphi_\beta \), respectively. Then the angle-dependent part in \( f \) is written as

\[ -B_0[|\psi_\alpha|^3 \cos(3\varphi_\alpha) + |\psi_\beta|^3 \cos(3\varphi_\beta)] + r_1|\psi_\alpha \psi_\beta| \cos(\varphi_\alpha - \varphi_\beta). \]

For \( r_1 < 0 \), we find \( \varphi_\alpha = \varphi_\beta \), leading to ferromagnet-like order \(( \zeta = 0) \). While for \( r_1 > 0 \), the skewed state with \( \varphi_\alpha = -\varphi_\beta \) and \( \cos 2\varphi_\alpha < 0 \) minimizes the free energy. For this antiferromagnet-like order, we set \( \psi_\alpha = \psi_\beta^* = iM \exp(i\phi) \) in (23) to obtain

\[ f = r M^2 + \frac{u}{2} M^4 - 2B_0 M^3 \sin 3\phi - r_1 M^2 \cos 2\phi. \] (25)

In Fig. 3, we show the phase diagram in the plane of \( r \) and \( r_1 \). A line of first-order phase transition starts from the point where \( r = r_l \) and \( r_1 = 0 \), and ends at a tricritical point where \( r = r_{l1} = 9r_{l2}/2 \). On this line we have \( 2r/r_{l1} = 1 + (2r_{l1}/3r_{l2} + 1)^{1/3} \), \( 4 \sin^2 \phi = 2 - (2r_{l1}/3r_{l2} + 1)^{1/3} \), and \( M = 2 \sin 3\phi \). For \( r_1 > 9r_{l2}/2 \), however, the phase transition becomes second-order with a critical line given by \( r = r_1 \) and the primary order parameter is \( \Im \psi_\alpha = \Im \zeta/2 \). The system is in the disordered phase \(( M = 0) \) above the two lines. For small \( r_1 \) or far below the critical line, the effect of \( r_1 \) becomes weak and \( \phi \approx \pi/6 \).

We have presented a Ginzburg–Landau theory for relatively simple Jahn–Teller models to find rich phase transition behavior. The relationship between the non-linear strain theory\(^7\)-\(^10\) and the present theory (with the true order parameter retained) is not still clear. However, when the discontinuity of the first-order phase transition is weak \(( w \ll 1) \), the linear relation \( \psi \approx g(e_3 + ie_2)/r_0 \) holds and the two schemes yield essentially the same results near the transition \(( |r| \ll g^2/C_0) \). It is also of great interest how the phase ordering kinetics proceeds under the influence of the nonlocal interaction (18) and the cubic terms in the free energy.\(^10\),\(^12\),\(^13\)

\footnotesize

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\[ \text{Figure 3. Phase diagram of a Jahn–Teller system modelled using (25) with positive } r_1 \text{ favoring canted antiferromagnet-like orbital order. The system is in the disordered phase } (M = 0) \text{ above the line of first-order phase transition (dashed line) and the critical line (solid line).} \]