

Thermodynamic description of phase transitions in crystals with degenerate localized levels

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A unified way of introducing the order parameter, based on atomic density matrices, is proposed for describing phase transitions associated with lifting of the degeneracy of localized levels.

Expressions describing the symmetry properties of the order parameter are obtained. For the examples of magnetic phase transitions and certain order-disorder phase transitions the relationships between this order parameter and the order parameters used earlier are analyzed. In the framework of the Landau theory the thermodynamics of the Jahn-Teller transition in KCuF_3 is analyzed and the possibility of Jahn-Teller ordering in the high-temperature superconductor $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is investigated.

At the present time it is possible to distinguish two levels of description of phase transitions in crystals. These differ in the choice of the order parameter (OP). As the latter one usually chooses either macroscopic quantities (such as the polarization, magnetization, or deformation tensor) or microscopic quantities (such as atomic displacements, spins, etc.).

The first level permits one to describe the macroscopic properties, e.g., the temperature behavior of the elastic moduli, the susceptibility, and the dielectric permittivity. The second level involves atomic characteristics and permits one to obtain more-detailed information about the temperature behavior of the low-symmetry phase.

In the present paper we have made the next step in the thermodynamic theory of phase transitions in crystals—a step involving the introduction of an OP determined from the density matrix of the crystal. Its use extends the possibilities of symmetry methods and thermodynamic methods of description of phase transitions, as we shall illustrate in the description of magnetic, Jahn-Teller, and ordering transitions.

THE ORDER PARAMETER AND ITS TRANSFORMATION PROPERTIES

Suppose that each atom (group of atoms) can be found in several states $|\psi_1\rangle, \dots, |\psi_n\rangle$, degenerate in energy in the high-temperature phase. Omitting for the moment the atomic index, we introduce for each atom the density matrix¹

$$\rho = \sum_{\alpha=1}^n |\psi_\alpha\rangle w_\alpha \langle \psi_\alpha|, \quad (1)$$

where w_α is the probability that the state $|\psi_\alpha\rangle$ is realized: $\sum_{\alpha=1}^n w_\alpha = 1$. In a basis $|\varphi_1\rangle, \dots, |\varphi_n\rangle$ such that

$$|\psi_\alpha\rangle = \sum_{\beta=1}^n U_{\alpha\beta} |\varphi_\beta\rangle, \quad (2)$$

we have

$$\rho_{\beta\gamma} = \sum_{\alpha=1}^n w_\alpha U_{\gamma\alpha}^* U_{\alpha\beta}. \quad (3)$$

For $n = 2$ the matrix has the form

$$U = \begin{pmatrix} p_{11} & p_{12} \\ -p_{12}^* & p_{11}^* \end{pmatrix} \equiv \begin{pmatrix} p_1 & p_2 \\ -p_2^* & p_1^* \end{pmatrix}, \quad (4)$$

where the polarizations $p_{\alpha\beta}$ are the coefficients of the expansion of the functions $|\psi_\alpha\rangle$ in the basis $|\varphi_\alpha\rangle$, and the following conditions on the normalization and phase should be fulfilled:

$$|p_1|^2 + |p_2|^2 = 1, \quad (p_1, p_2) = e^{i\omega} (p_2, p_1). \quad (5)$$

For systems with $n > 2$ it is more convenient to work with the coefficients p_{ij} , and in the case of two-level systems these conditions can be taken into account in explicit form.

From (1) and (4) it is easy to obtain

$$\begin{aligned} \rho &= \frac{1}{2} E + \frac{1}{2} \Delta\rho \\ &= \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{w_1 - w_2}{2} \begin{pmatrix} |p_1|^2 - |p_2|^2 & 2p_1^* p_2 \\ 2p_1 p_2^* & |p_2|^2 - |p_1|^2 \end{pmatrix}. \end{aligned} \quad (6)$$

We write the temperature-dependent part of ρ in terms of Pauli matrices:

$$\Delta\rho = \sum_{\alpha=x,y,z} \eta_\alpha \sigma_\alpha. \quad (7)$$

It is easy to show that $\sum_\alpha \eta_\alpha^2 = 0$ in the high-temperature phase and the sum tends to unity as $T \rightarrow 0$. In addition, from given values of η_α one can determine p_1, p_2 , and $w_1 - w_2$, i.e., indicate in what states and with what probability the given atom can be, and, consequently, also calculate the average for any operator specified at the given atom. All this makes it natural to identify $\boldsymbol{\eta}$ as the order parameter. We note that the components η_x, η_y , and η_z must not be interpreted as projections of the vector $\boldsymbol{\eta}$ on cartesian axes of real space; the vector $\boldsymbol{\eta}$ is specified in its own "energy" space.

We shall give a geometrical interpretation¹⁾ of the expressions obtained for two-level systems. For $T = 0$ the state of the system is uniquely specified by the polarization $(p_1 p_2)$ of the function $|\psi\rangle$. By virtue of the conditions (5) the polarization can be rewritten in the form

$$\mathbf{p} = \frac{1}{2} (C_1, C_2 e^{i\varphi}), \quad C_1^2 + C_2^2 = 4, \quad (8)$$

where $C_\alpha = 2|p_\alpha|$. Obviously, $0 \leq C_1 \leq 2$, and for each value in the interval $[0, 2]$ there exist 2π independent values of the angle φ (see Fig. 1). For the boundary points all the values of

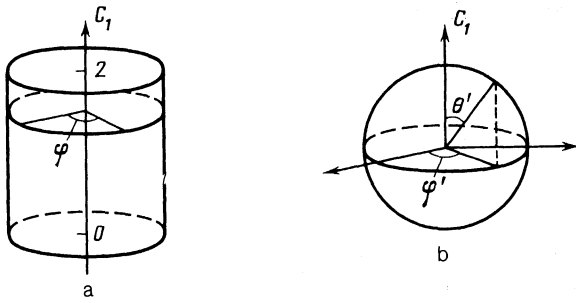


FIG. 1. Illustration of the equivalence of the complex projective space CP^1 (a) and the sphere S^2 (b).

φ correspond to the same polarization (the boundaries of the cylinder at $C_1 = 2$ and $C_1 = 0$ are "glued" to the same point), and we obtain a sphere of possible values of the polarization.

The one-to-one correspondence between \mathbf{p} and the points of such a sphere can be specified, e.g., by the expressions

$$\varphi' = \varphi, \quad \cos \theta' = 1/2(C_1^2 - 2). \quad (9)$$

Then the polarizations (10) and (01) correspond to the "poles" of the sphere, and polarizations of the form $2^{-1/2}(1, e^{i\varphi})$ correspond to the "equator."

It is easy to show that the points inside this sphere correspond to all possible values of the OP η ; the center of the sphere corresponds to the high-temperature phase ($|\eta| = 0$), and the phase transition is depicted as the onset of a nonzero η that increases with decrease of T to values $|\eta| = 1$ at $T = 0$.

We return to the case of arbitrary n . Entirely analogously, we can represent ρ in the form

$$\rho = \frac{1}{n}E + \frac{\Delta\rho}{n}. \quad (10)$$

As the components of the order parameter we can use the components of the matrix

$$\eta_{\alpha\beta} = (\Delta\rho)_{\alpha\beta}(n^2 - n)^{-1/2} \quad (11)$$

with the condition $\sum_{\alpha} \eta_{\alpha\alpha} = 0$ or introduce the analogs of the Pauli matrices for n -dimensional space and rewrite the expression (7). Here the equality $|\eta|^2 = 1$ at $T = 0$ follows from the condition $\rho^2 = \rho$ for a pure state. The dimensionality of the OP for the case of N -fold degeneracy is $\dim \eta = n^2 - 1$.

We have shown how the space of possible values of the OP at one atom is constructed from the density matrix. The procedure for extending this space to all the atoms of the crystal and studying its symmetry properties is described in detail in Ref. 3. Adhering to this procedure, we introduce matrices $D_R(g)$ so that

$$g\eta = D_R(g)\eta, \quad (12)$$

where g are elements of the symmetry group G of the crystal. The subscript R denotes the type of the basis functions (electronic $R = J - T$, spin $R = S$, etc.). The matrix $D_R(g)$ is easily determined from the transformation properties of the basis $|\varphi_1\rangle, \dots, |\varphi_n\rangle$ and the expressions (6), (7) or (10), (11). Below we give its form for different systems.

Knowing (12), and using the algorithm and notation given in Ref. 3, we can write the composition of the representation d_R corresponding to the wave vector \mathbf{k} :

$$d_R^{\mathbf{k}} = \sum_{\nu}^{\otimes} n^{\nu} \tau^{\nu}, \quad (13)$$

$$n^{\nu} = \|H_{\mathbf{k}}^{\nu}\|^{-1} \sum_{h \in H_{\mathbf{k}}^{\nu}} \text{Sp } d^{\mathbf{k}\nu}(h) \gamma_{11}(h) \text{Sp } D_R(h); \quad (14)$$

the basis functions (modes) of the ν th irreducible representation (IR) at the first atom of the orbit are

$$\psi_1^{\mathbf{k}\nu} = \sum_{h \in H} (d^{\mathbf{k}\nu}(h) \otimes D_R(h)) \gamma_{11}(h), \quad (15)$$

and those at the i th atom are

$$\psi_i^{\mathbf{k}\nu} = \gamma_{11}(g_i) [d^{\mathbf{k}\nu}(g_i) \otimes D_R(g_i)] \psi_1^{\mathbf{k}\nu}. \quad (16)$$

Expressions (13)–(16) constitute the basis of the symmetry description of a phase transition of any type. Such an analysis, on the one hand, makes it possible to obtain information about the electronic or magnetic structure of the low-symmetry phase, and, on the other hand, is a necessary stage preceding the thermodynamic description of a phase transition, since it permits one to determine the relevant OP, its symmetry, and the concrete form of the thermodynamic potential.

We turn to the consideration of specific examples. Here we use the nomenclature of Ref. 4 for the wave vectors and irreducible representations.

MAGNETIC PHASE TRANSITIONS IN MAGNETS WITH LOCALIZED SPINS

The symmetry-and-thermodynamic description of such transitions has been the subject of a large number of papers (see, e.g., Ref. 5). Here, as the OP one uses the classical magnetization vector (specified at each stage), which transforms under rotations as an axial vector. At the same time, the results of group-theoretical analysis are applied in the case of very different values of the spin, including for $S = \frac{1}{2}$, the components of which transform according to the double-valued representation $D^{1/2}$ of the group $O(3)$.

We shall investigate this question using the above-described introduction of the order parameter in terms of the density matrix. For $S = \frac{1}{2}$ the spin functions $|\varphi_1\rangle$ and $|\varphi_2\rangle$ with z -components equal to $\pm \frac{1}{2}$ transform under rotations according to the representation $D^{1/2}$, the matrices of which, for Euler angles φ_1 , θ , and φ_2 , have the form (see Ref. 6)

$$D^{1/2}(\varphi_1, \theta, \varphi_2) = \begin{pmatrix} \cos \frac{\theta}{2} \exp\left(i \frac{\varphi_1 + \varphi_2}{2}\right) & i \sin \frac{\theta}{2} \exp\left(-i \frac{\varphi_1 - \varphi_2}{2}\right) \\ i \sin \frac{\theta}{2} \exp\left(i \frac{\varphi_1 - \varphi_2}{2}\right) & \cos \frac{\theta}{2} \exp\left(-i \frac{\varphi_1 + \varphi_2}{2}\right) \end{pmatrix} \quad (17)$$

In the terminology proposed above this matrix describes the transformation of the components p_1 and p_2 of the polarization vector. From (7) we can now also determine the matrices $D_{S=\frac{1}{2}}$ appearing in (12) for the elements g of interest, namely, those belonging to the subgroup G of $O(3)$. First of all, however, we note that η_x , η_y , and η_z , together with $\eta_0 = |p_1|^2 + |p_2|^2 = 1$, form a space of pair products of

the functions $|\varphi_1\rangle$ and $|\varphi_2\rangle$. It is known that such a composition of the basis functions of the IR $D^{1/2}$ of the group $O(3)$ can be decomposed into the direct sum of the subspaces L^0 and L^1 , which transform according to the IR D^0 and D^1 of the group $O(3)$. It is straightforward to show that D^0 is formed by the vector η_0 , and D^1 is formed by the vectors η_x, η_y, η_z . The latter transform as components of an axial vector, and, since they coincide with averages of Pauli matrices, we can interpret η as the average value of the spin at the given atom. We shall not give particular examples of ordering in magnets with $S = \frac{1}{2}$; they can be found in Ref. 5. It is necessary only to perform the corresponding replacement of the classical spin vector by the order parameter η .

Thus, the analyses of the possible magnetic structures for $S = \frac{1}{2}$ in the language of components of the density matrix and in the language of atomic magnetization vectors are identical. In the former case, however, it is possible to obtain information about the width of the gap, the population of the levels, and the wavefunctions corresponding to these levels.

In the case $S > \frac{1}{2}$ the analogous decomposition of $[D^S]^2$ contains $D^{2S}, D^{2S-1}, \dots, D^0$. As before, with the vectors from D^1 we can associate the magnetization vector, and invoke the previous arguments for it. The vectors from D^2 correspond to the quadrupolar ordering, and the other vectors correspond to n -polar ordering. A review of variants of such orderings is given in, e.g., Ref. 7.

PHASE TRANSITIONS IN AMMONIUM HALIDES

We shall use this example to investigate the application of the density matrix in the thermodynamic description of order-disorder (O-D) phase transitions. Usually one uses as the OP the probabilities of finding the atoms or molecules in one particular position or another.⁸

In neighboring NH_4X the NH_4 tetrahedron can occupy two positions (Fig. 2). We assign the function $|\varphi_1\rangle$ to the first orientation, and the function $|\varphi_2\rangle$ to the second. It is easy to show that the elements $h_{13}, h_{14}, \dots, h_{36}$ of the group O_h (Ref. 4) interchange these functions, while the other elements act trivially ($p_1 \rightarrow p_1, p_2 \rightarrow p_2$). This makes it possible to determine the transformation of η :

$$D_{\text{O-D}}(h_i) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} \text{ for } 13 \leq i \leq 36 \quad (18)$$

and is the unit matrix for the other values of i .

In the case of an order-disorder phase transition it is usually necessary to take account of the blocking principle—a consequence of the small quantum penetrability of the barrier between $|\varphi_1\rangle$ and $|\varphi_2\rangle$. Therefore, we have no need to work with all the η_α , and it is sufficient to confine ourselves to the component η_z . This immediately makes it possible to indicate the labels of the irreducible representations responsible for the ordering. Thus, the δ -phase, in which the tetra-

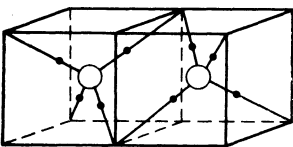


FIG. 2. Possible positions of the NH_4 tetrahedron in the compound NH_4X .

hedra are oriented "ferromagnetically," is described by the IR τ_2' for the star $\mathbf{k}_{12} = 0$, while the γ -phase, with "antiferromagnetic" orientation, is described by the IR τ_6 for the star \mathbf{k}_{11} .

It is easy to show that, by considering only the component η_z (or, for arbitrary degeneracy, only the diagonal part of the density matrix), we obtain a description identical to the description in the language of probabilities. At the same time, in a number of order-disorder phase transitions the barrier between the states can be small (e.g., in crystals with hydrogen bonds), and this makes it interesting to study such phase transitions in the proposed scheme.

JAHN-TELLER ORDERING IN KCuF_3

For the description of Jahn-Teller transitions it has been suggested that one use as the OP the magnitude of the gap at $T < T_c$ (Ref. 8) or the specific form of the electron function in the low-symmetry phase.¹⁰ In the former case the scalar nature of the OP means that we cannot describe the full diversity of the phases that arise, while in the latter case it is impossible to find the temperature dependence of the order parameter. Therefore, we shall describe in detail the use of the expressions (1)–(16) in the case of a Jahn-Teller phase transition for the example of KCuF_3 .

The symmetry of its cubic phase is O_h , and the coordinates of the atoms are $\text{K}-(0,0,0)$, $\text{Cu}-(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $\text{F}_1-(\frac{1}{2}, \frac{1}{2}, 0)$, $\text{F}_2-(0, \frac{1}{2}, \frac{1}{2})$, $\text{F}_3-(\frac{1}{2}, 0, \frac{1}{2})$. As a result of the phase transition, structures are formed that can be described by the wave vector $\mathbf{k}_{11} = (\frac{1}{2}, \frac{1}{2}, 0)$ or $\mathbf{k}_{13} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and the degeneracy of the E_g level is lifted.¹¹ In the symmetry description we find it convenient to use a complex basis in the space of the electron functions of the E_g level:

$$|\varphi_1\rangle = \varepsilon x^2 + \varepsilon^2 y^2 + z^2 = |\varphi_2\rangle^*, \quad (19)$$

where $\varepsilon = e^{2i\pi/3}$. The basis $|\varphi_1\rangle, |\varphi_2\rangle$ transforms according to the two-dimensional IR of the point group O_h , and, consequently, p_1 and p_2 transform according to this same IR. From the expressions (6) and (7) it is easy to write out the matrices $D_{\text{J-T}}(g)$. They are given in the Table.

Using the matrices obtained, we determine from the formulas (13) and (14) the composition of the J-T representation:

$$d_{\text{J-T}}^{\mathbf{k}_{12}} = \tau_3 + \tau_5, \quad d_{\text{J-T}}^{\mathbf{k}_{11}} = 2\tau_3 + \tau_7, \quad d_{\text{J-T}}^{\mathbf{k}_{13}} = \tau_2 + \tau_6. \quad (20)$$

The cause of the J-T phase transition is an interaction linear in the J-T and structural order parameters, which is possible only when the irreducible representations describing the J-T OP and the structural OP coincide. Therefore, in the given example it is necessary to know the composition of the mechanical representation, which is found using the same formulas (13) and (14):

$$d_{\text{M}}^{\mathbf{k}_{11}} = (\tau_{10} + \tau_{11})_{F_1} + (\tau_1 + \tau_3 + \tau_5 + \tau_7 + \tau_9)_{F_2, F_3}, \\ d_{\text{M}}^{\mathbf{k}_{13}} = (\tau_4 + \tau_6 + \tau_8 + \tau_{10})_{F_1, F_2, F_3}. \quad (21)$$

Here we have written out only that part of the complete mechanical representation whose composition overlaps with (20). Comparing (20) and (21), we see that J-T transitions in the perovskites ABX_3 can be described by the IR τ_3 and τ_7 for the star $\{\mathbf{k}_{11}\}$, and also by the IR τ_6 for the star $\{\mathbf{k}_{13}\}$. Just the modes of these representations are sufficient to describe the electron density in the low-symmetry phases.

TABLE I. Matrices of the J-T representation $D_{J-T}(g)$ for the elements g of the group O_h .

Symmetry elements						
h_1-h_4	h_5-h_8	h_9-h_{12}	$h_{13}-h_{16}$	$h_{17}-h_{20}$	$h_{21}-h_{24}$	$h_{25}-h_{48}$
1 0 0	$-\frac{1}{2} \frac{3^{1/2}}{2} 0$	$-\frac{1}{2} \frac{3^{1/2}}{2} 0$	1 0 0	$-\frac{1}{2} \frac{3^{1/2}}{2} 0$	$-\frac{1}{2} -\frac{3^{1/2}}{2} 0$	$D(h_{24+i}) = D(h_i)$
0 1 0	$\frac{3^{1/2}}{2} -\frac{1}{2} 0$	$\frac{3^{1/2}}{2} -\frac{1}{2} 0$	0 1 0	$\frac{3^{1/2}}{2} \frac{1}{2} 0$	$-\frac{3^{1/2}}{2} \frac{1}{2} 0$	
0 0 1	0 0 1	0 0 1	0 0 1	0 0 1	0 0 1	

We note also the following fact. The basis functions (19) themselves correspond to the OP values $\eta = (0,0, \pm 1)$. It is straightforward to verify that the electron density $|\psi_1|^2$ or $|\psi_2|^2$ in this case is invariant under the group O_h . Therefore, in the given case there can be no ordering associated with a change of the electron densities, and henceforth we shall confine ourselves entirely to considering the components η_x and η_y . It can be shown that the component η_z describes current ordering; the interaction associated with it is much weaker than in the case of a change of the electron density.

We shall consider the ordering associated with the star $\{k11\}$. Calculating the J-T modes (15) and (16), we can convince ourselves that the vector $\eta = (1,0,0)$ transforms according to the IR τ_7 , while $\eta = (0,1,0)$ and $\eta = (0,0,1)$ correspond to the two IR τ_3 and τ'_3 . From comparison with the experimental data¹¹ it is easy to see that the atomic displacements are also described by the IR τ_3 . Omitting the J-T mode associated with the current ordering (τ'_3), we assume that the mode $\eta = (0,1,0)$ participates in the phase transition with weight η . Then from the expressions (6) and (7) we obtain the relationship between $w_1 - w_2$, $p_1 = |p_1|e^{i\varphi}$, $p_2 = |p_2|$, and the order parameter η :

$$\begin{aligned} (w_1-w_2) |p_1| |p_2| \cos \varphi &= 0, \\ (w_1-w_2) |p_1| |p_2| \sin \varphi &= \eta, \\ (w_1-w_2) (|p_1|^2 - |p_2|^2) &= 0. \end{aligned} \quad (22)$$

Solving (22), we find

$$w_{1,2} = \frac{1}{2} \pm \frac{1}{2} \eta, \quad |p_1|^2 - |p_2|^2 = \frac{1}{2}, \quad \varphi = (2n+1) \frac{\pi}{2}. \quad (23)$$

The information about the populations w_i is fundamentally new in the grouptheoretical description of phase transitions. The possibility of obtaining it is due to the proposed choice of order parameter. By determining the dependence $\eta(T)$ subsequently from thermodynamics, we can also find the temperature dependence of the gap Δ , since

$$\Delta = kT \ln \frac{1-|\eta|}{1+|\eta|}. \quad (24)$$

It should be noted that the experimental study of $\Delta(T)$ is one of the ways of proving the J-T nature of the phase transition.

Above, we considered effects associated with the relevant order parameter (the IR τ_3 for the star $\{k11\}$). At the same time, from the theory of phase transitions it is well known¹³ that ordering with respect to the relevant OP can

occur together with pre-ordering with respect to accompanying order parameters, allowance for which does not change the symmetry already established. In the given case such an OP ξ transforms according to the IR τ_5 of the star $k_{12} = 0$. The vectors corresponding to this IR are $\eta = (1,0,0)$ at each atom. With allowance for the accompaniment, the expressions (23) take the form

$$w_{1,2} = \frac{1}{2} \pm \frac{1}{2} (\eta^2 + \xi^2)^{1/2}, \quad |p_1|^2 + |p_2|^2 = 1, \quad \text{tg } \varphi = \eta/\xi. \quad (25)$$

Thus, if a transition with respect to the relevant representation leads to a structure of the antiferromagnetic type with orientation along the y axis of the "energy" space, allowance for the accompaniment leads to tilting of the pseudospin vectors in the direction of the x axis. This is the analog of weak ferromagnetism. This conclusion agrees with the experimental data, which show¹⁴ that in $KCuF_3$ the electronic structure at $T < T_c$ is described by the vectors $\eta = \eta(\cos \varphi, \pm \sin \varphi, 0)$, where the angle φ decreases with temperature, reaching the value $\varphi = 71^\circ$ as $T \rightarrow 0$.

To find the temperature dependence of η and ξ we shall analyze the thermodynamic potential. Generally speaking, the relevant OP η has three components (from the number of rays of the star $\{k11\}$), but we shall take only one of these into account, in accordance with experiment. Then,

$$\Phi = r_1 \eta^2 + u_1 \eta^4 + r_2 \xi^2 - v \xi^3 + u_2 \xi^4 + \gamma_1 \eta^2 \xi - P \xi. \quad (26)$$

Here ξ is the accompanying OP and we have also taken the pressure P into account. As in the theory of weak ferromagnetism, if we are not investigating the complete phase diagram, but confining the analysis to the temperature and field dependences of η and ξ , we can consider the potential

$$\Phi = r_1 \eta^2 + u_1 \eta^4 + r_2 \xi^2 - P \xi - \gamma \eta^2 \xi. \quad (27)$$

From the equations for the minimization of Φ we obtain

$$\xi = \frac{1}{2r_2} (P + \gamma \eta^2), \quad \eta^2 = -\frac{2r_1 r_2 - \gamma P}{4u_1 r_2 - \gamma^2}. \quad (28)$$

From (28) we can find the dependence of the angle of tilt of the pseudospin:

$$\text{tg } \varphi = \text{tg } \eta/\xi \sim (T_c - T)^{1/2}, \quad (29)$$

i.e., its decrease with decreasing temperature.

The corresponding OP ξ in the given case turns out to be responsible for the onset of the tetragonal deformation $e \sim \xi$. In fact, the quantities $e_1 = 3^{1/2}(e_{xx} - e_{yy})$ and $e_2 = 2e_{zz} - e_{xx} - e_{yy}$, like the components ξ_1 and ξ_2 , transform according to the representation τ_5 with $k = 0$, as a result of

which we can add invariants of the type $e_1^2 + e_2^2$ and $e_1\xi_1 + e_2\xi_2$ to the potential (26). It is the latter invariant which gives rise to the relation $c/a - 1 \sim \xi$.

We have considered in detail the picture of the ordering with respect to the IR τ_3 for the star $\{\mathbf{k}11\}$. The possible transition with respect to the IR τ_7 for the same star is not observed experimentally, and the symmetry-and-thermodynamic analysis of the J-T transition with respect to the IR τ_6 for the star $\{\mathbf{k}13\}$ is analogous to that performed above, so we shall omit it.

SYMMETRY ANALYSIS OF THE STRUCTURAL TRANSITION IN THE HIGH-TEMPERATURE SUPERCONDUCTOR $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

The structural transition observed in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ from the tetragonal to the orthorhombic phase is attracting particular attention in view of the fact that in the (T, x) plane the intersection of the structural-transition line $T_d(x)$ and the superconducting-transition line $T_c(x)$ coincides with the region of the maximum values of T_c . In addition, a similar transition has been noted in a Y-Ba-Cu-O superconductor. In the literature the hypothesis that this transition has a J-T character is often discussed. Therefore, we shall analyze first of all the possibility of the onset of J-T ordering.

At the present time, basically three variants of the change of structure are under discussion: 1) a transition with respect to $\mathbf{k} = 0$ (Ref. 15); 2) a transition with respect to $\mathbf{k}_{13} = (1, 1, 0)$, with rotation of the oxygen octahedra about the (110) axis, the space group of the new phase being D_{2h}^{18} (Ref. 16); 3) a transition with respect to the same star, but with rotation of the octahedra about the (100) and (010) axes, respectively, for the planes $z = 0$ and $z = \frac{1}{2}$, the symmetry group of the new phase being D_{2h}^{10} (Ref. 17). Therefore, we shall confine ourselves to considering the two stars $\mathbf{k}_{14} = 0$ and $\mathbf{k}_{13} = (1, 1, 0)$.

In the case of \mathbf{k}_{14} the compositions of the mechanical representation and J-T representation, calculated in accordance with (13) and (14), are equal to

$$\begin{aligned} d_{\text{mex}}(\text{Cu}) &= \tau_4 + \tau_{10}, & d_{\text{mex}}(\text{O}_{xy}) &= \tau_4 + \tau_8 + 2\tau_{10}, \\ d_{\text{mex}}(\text{La}) &= d_{\text{mex}}(\text{O}_z) = \tau_1 + \tau_4 + \tau_9 + \tau_{10}, & d_{\text{J-T}}(\text{Cu}) &= \tau_1 + 2\tau_5. \end{aligned} \quad (30)$$

In the brackets we have indicated the atoms at which the particular IR are realized, and O_α denotes the oxygen atoms lying in the α -direction from the nearest copper atom. From (30) it can be seen that a J-T transition for $\mathbf{k} = 0$ is possible only with respect to the IR τ_1 . The latter does not change the symmetry, and we have an isostructural phase transition, which contradicts experiment. There is no other possibility of J-T ordering with $\mathbf{k} = 0$.

For \mathbf{k}_{13} the compositions of the mechanical and J-T representations have the form

$$\begin{aligned} d_{\text{mex}}(\text{Cu}) &= \tau_4 + \tau_6 + \tau_8, & d_{\text{mex}}(\text{O}_{x,y}) &= 2\tau_1 + \tau_3 + \tau_5 + 2\tau_7, \\ d_{\text{mex}}(\text{O}_z) &= d_{\text{mex}}(\text{La}) \\ &= \tau_1 + \tau_3 + \tau_4 + \tau_5 + \tau_6 + \tau_8, & d_{\text{J-T}}(\text{Cu}) &= \tau_1 + 2\tau_7. \end{aligned} \quad (31)$$

Here, two types of J-T ordering are possible, with respect to the irreducible representations τ_1 and τ_7 . The IR τ_1 corresponds to $\boldsymbol{\eta} = (\pm 1, 0, 0)$. In this case the oxygen octahedra experience tetragonal deformations of alternating signs at

neighboring copper ions. The symmetry group of the new phase is D_{2h}^{19} .

The IR τ_7 corresponds to two modes: $\boldsymbol{\eta} = (0, \pm 1, 0)$, and $\boldsymbol{\eta} = (0, 0, \pm 1)$. Omitting the latter for the same reasons as in the preceding section, we find that the J-T ordering is described by the alternation of $|\psi_1\rangle = |\varphi_1\rangle + |\varphi_2\rangle$ and $|\psi_2\rangle = |\varphi_1\rangle - |\varphi_2\rangle$, where $|\varphi_1\rangle$ and $|\varphi_2\rangle$ are given in (19). This same IR appears twice in the composition of the mechanical representation, and the two variants of the corresponding motions of the oxygen atoms can be described as 1) the rotation of oxygen octahedra about the z axis, or 2) compression and stretching of the octahedra along the x and y axes. In both cases the symmetry group of the ordered phase is D_{2h}^{18} .

The latter variant is close to that proposed in Ref. 16 (the wave vector and symmetry group of the new phase are the same as in Ref. 16), but a different pattern of motion of the oxygen octahedra is observed. It is straightforward to determine that the oxygen-atom displacements proposed in Ref. 16 are described by a mode of the IR τ_3 (\mathbf{k}_{13}) with one ray participating. The variant¹⁷ with the symmetry group D_{2h}^{10} is also described by the IR τ_3 , but two rays of the star participate; this is a two-ray transition, in the terminology of Ref. 5. It is very complicated to distinguish these two variants experimentally because of the presence of domains in the sample, but it is possible to detect the difference in, e.g., an experiment with polarized neutrons.⁵

Thus, in none of the three variants proposed in Refs. 15–17 for the structural changes in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ can the pattern of the motion of the oxygen atoms be due to the Jahn-Teller effect. We note, however, that in comparison with the identification of the wave vector and the symmetry group of the new phase the determination of the displacements of the atoms is a considerably more complicated experimental problem, and, in the general case, requires precise knowledge of the intensities of the superstructure reflections.

CONCLUSION

The proposed way of choosing the order parameter makes it possible to describe phase transitions of different kinds in crystals (J-T phase transitions, magnetic phase transitions, transitions of the order-disorder type, etc.) in a unified manner. The possibility has appeared of describing ordering of any multipolarity for magnetic phase transitions, and, in the case of phase transitions of the order-disorder type, of investigating the case of arbitrary quantum penetrability of the barrier. The merits of the proposed OP are manifested most prominently in the analysis of J-T ordering, for which the requirement that the relevant IR appear in the composition of both the mechanical and the J-T representation sharply narrows the number of possible superstructures, as shown above for the examples of KCuF_3 and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

Another merit of the proposed scheme is the possibility of using a standard algorithm³ of group-theoretical analysis, and the fact that it can serve as a basis for the thermodynamic description of phase transitions (in the framework of the Landau expansion of the free energy), as has been demonstrated for J-T phase transitions. In this case it is possible to determine not only the temperature dependence of the gap but also the expectation values of all single-ion operators or of quantities containing them.

As the multiplicity n of the degeneracy increases, the dimensionality $n^2 - 1$ of the order parameter increases rapidly, and this makes the calculations tedious for large n .

¹⁾This interpretation is based on the topological equivalence of the sphere S^2 and the complex projective manifold CP^1 . By its construction, the latter (see Ref. 2) coincides with the set of all values of the polarization \mathbf{p} .

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