

Group-theoretical approach to orbital ordering in crystals with E_g and T_{2g} ions

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Orbital ordering in crystals with degenerate localized levels E_g and T_{2g} is investigated on the basis of the symmetry of atomic density matrices and their transformation properties. During ordering processes, several kinds of local state can be stabilized, among which those with asymmetrical distribution of electron density are of practical importance. They are related to the $E_g \otimes e_g$, $T_{2g} \otimes e_g$, and $T_{2g} \otimes t_{2g}$ Jahn-Teller effects. In crystals with E_g ions, the group-theoretical analysis leads to a large variety of possible ordered arrangements, whereas in those with T_{2g} ions there are only a few symmetry-allowed configurations.

I. INTRODUCTION

The orbital ordering in crystals with octahedrally coordinated, doubly degenerate E_g ions and triply degenerate T_{2g} ions is most evidently manifested by the cooperative Jahn-Teller effect. For an isolated center, the Jahn-Teller effect is associated with the stabilization of a single state of an orbitally degenerate ion by a spontaneous distortion of its neighborhood. The local distortions present in a crystal interact strongly and, if the concentration of active ions exceeds a certain limit, they order below a critical temperature. Along with that cooperative ordering, a certain configuration of local orbital states is stabilized.

Our aim is to investigate, by using only symmetry arguments, all such orbital configurations compatible with the crystal structure. For this purpose we reformulate and generalize a group-theoretical method which was applied earlier for orbital order of E_g ions.¹ This method was based on a semi-classical approach which treated the Jahn-Teller effect as the result of an interaction of partial electron densities of E_g symmetry with local distortions of the same symmetry. The two components of the E_g density formed a $2N$ -dimensional vector space (where N is the number of Jahn-Teller ions in the crystal) in which any Jahn-Teller configuration has been defined. On the basis of transformation properties of the configurations and assumptions equivalent to the conception of the soft mode, all symmetry-allowed arrangements were found and characterized by irreducible representations of the space group relevant to the disordered phase. These allowed configurations (orbital modes) define the correlations between local orbital states. The state in the reference position determines the energy of the configuration and represents, if unspecified by the symmetry analysis, a variable in the search for the crystal ground state.

Recently, a general theory of electronic ordering in crystals was outlined by Gurin, Budrina, and Syromyatnikov.² It is based on transformation properties of the density matrices under operations of the space-group symmetry of the crystal. Their approach gives better insight into the nature of the ordered states and more importantly, in contradistinction to the above-mentioned method,¹

it defines the order parameters in a natural way, thus allowing a thermodynamical description of ordering phenomena. In this paper, we shall first illustrate the basic ideas of Ref. 2 in greater detail. A symmetry analysis of local states of the E_g and T_{2g} ions, given in Secs. III and IV, shows the existence of different kinds of orbital ordering for these two kinds of ion. It is demonstrated that for E_g levels coupled with e_g distortions (the $E_g \otimes e_g$ Jahn-Teller effect), the approach of Gurin, Budrina, and Syromyatnikov is formally equivalent to the semiclassical method suggested in Ref. 1. Additional results on T_{2g} ions are also given. It is shown that the ordered states derived previously as stationary points of the potential surface of the vibronic Hamiltonian³ are, in fact, a general consequence of the symmetry properties of atomic density matrices. Finally, all symmetry-allowed crystal configurations of the T_{1g} orbitals are found.

II. ORDERING IN CRYSTALS WITH DEGENERATE LOCALIZED LEVELS

Gurin, Budrina, and Syromyatnikov² consider the general case in which each equivalent atom in the crystal can exist in several eigenstates $|\psi_1\rangle, |\psi_2\rangle, \dots, |\psi_n\rangle$ which are n -fold degenerate in the high-temperature (disordered) phase. These states occur with equal probability $w_\alpha = 1/n$ ($\alpha = 1, 2, \dots, n$). During the ordering process, such a mixed quantum state which is continuously transformed into a pure quantum state, is described generally by a linear combination of ψ_α 's. For simplicity, let us consider the ordering results for just one of the states, say $|\psi_i\rangle$. Consequently, upon ordering, the probability w_i tends to 1 while all others tend to 0. The local state on each site is completely described at all times by the density matrix, which is defined as

$$\rho = \sum_{\alpha=1}^n |\psi_\alpha\rangle w_\alpha \langle \psi_\alpha| = \text{diag}(w_1, w_2, \dots, w_n).$$

In another basis $\{|\phi_1\rangle, |\phi_2\rangle, \dots, |\phi_n\rangle\}$, related to the ψ_α 's by a unitary transformation represented by matrix U ,

$$|\psi_\gamma\rangle = \sum_{\alpha=1}^n U_{\gamma\alpha} |\phi_\alpha\rangle,$$

the density matrix acquires its general (nondiagonal) form with matrix elements

$$\rho_{\alpha\beta} = \sum_{\gamma=1}^n w_\gamma U_{\beta\gamma}^\dagger U_{\gamma\alpha}.$$

It is now advantageous to decompose the atomic density matrix into a constant part (preserved from the disordered phase) and a temperature-dependent part relevant to the ordering,

$$\rho = \frac{1}{n} E + \frac{1}{n} \Delta\rho,$$

where

$$\Delta\rho_{\alpha\beta} = \sum_{\gamma=1}^n (nw_\gamma - \delta_{\alpha\beta}) U_{\beta\gamma}^\dagger U_{\gamma\alpha} \Delta\rho. \quad (1)$$

As shown in Appendix A, the matrix $\Delta\rho$ may be expressed as a linear combination of $n^2 - 1$ n -dimensional analogs of Pauli matrices with real-valued coefficients $\eta_1, \eta_2, \dots, \eta_{n^2-1}$, which are interpreted as the order parameters. Namely, they are all 0 in the high-temperature phase and

$$\sum_{i=1}^{n^2-1} \eta_i^2 = 1$$

in the ordered low-temperature phase (see Appendix B).

Vectors $(\eta_1, \eta_2, \dots, \eta_{n^2-1})_1$ ($l = 1, 2, \dots, N$, where N is the number of ions in the system) which are defined in the space of $n \times n$ Hermitian matrices (the n^2 -th component corresponding to the unit matrix E is omitted) describe the actual state for each atom. In analogy to the soft mode in displacive phase transitions, this symmetry analysis of the electronic ordering is based on the assumption that the allowed configurations are those for which the corresponding vectors transform according to a single irreducible representation of the space group for the disordered phase.

The search for such crystal configurations or modes may be cumbersome, especially for higher degeneracies. Fortunately, it can be simplified after different kinds of ordering, realizable within the same system of degenerate levels, have been separated. This is illustrated below for the case of E_g and T_{2g} ions in local O_h point-group symmetry.

III. E_g IONS IN OCTAHEDRON COORDINATION

The electronic ordering may result in local states of different character which are specified by two classical quantities: the density $\psi\psi^*$ and the current-flow distribution of the electron cloud $(i\hbar/2m)(\psi\nabla\psi^* - \psi^*\nabla\psi)$. In the following, it will be shown that two distinct cases are possible with an E_g ion in octahedron coordination. One is the stabilization of the electronic states of noncubic (E_g) symmetry; the second is the stabilization of a state with cubic distribution of density but quadrupole ar-

rangements of electron currents.

Let us consider a doubly degenerate E_g ion with basis functions ϕ_1 and ϕ_2 specified by their orbital parts:

$$\phi_1 = \epsilon x^2 + \epsilon^2 y^2 + z^2 = \phi_2^* \quad (\epsilon = e^{2\pi i/3}).$$

The density matrix can be expressed with the help of Pauli matrices $\sigma_x, \sigma_y, \sigma_z$ as

$$\begin{aligned} \rho = \frac{1}{2} E + \frac{1}{2} \Delta\rho = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{1}{2} \eta_x \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ + \frac{1}{2} \eta_y \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} + \frac{1}{2} \eta_z \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \end{aligned} \quad (2)$$

where the actual values of η_x , η_y , and η_z determine both the eigenstates and their occupancies. If the eigenstates finally realized are related to the chosen basis by the unitary matrix

$$U = \begin{pmatrix} p_1 & p_2 \\ p_2^* & p_1^* \end{pmatrix}, \quad \text{with } |p_1|^2 + |p_2|^2 = 1,$$

then one gets, by comparing expressions (1) and (2), the relations²

$$\eta_x = (w_1 - w_2)(p_1 p_2^* + p_1^* p_2),$$

$$\eta_y = i(w_1 - w_2)(p_1 p_2^* - p_1^* p_2),$$

$$\eta_z = (w_1 - w_2)(|p_1|^2 - |p_2|^2).$$

Under symmetry operations of the O_h point group, the density matrix is transformed in the same way as the products $\phi_\beta^* \phi_\alpha$, i.e., according to the representation

$$E_g^2 = A_{1g} \oplus E_g \oplus A_{2g}.$$

The reduction of E_g^2 expresses a separation of the density matrix to a constant (irrelevant) part $\frac{1}{2} E$ associated with the one-dimensional unit representation A_{1g} and two temperature-dependent parts, namely, $(\eta_x, \eta_y, 0)$ and $(0, 0, \eta_z)$ for our choice of wave functions, which are associated with the two-dimensional irreducible representation E_g and the one-dimensional representation A_{2g} , respectively. [For a more common choice of wave functions, $\phi_{x^2} = (1/\sqrt{2})(2z^2 - x^2 - y^2)$ and $\phi_{x^2-y^2} = \sqrt{3/2}(x^2 - y^2)$, the basis of the E_g subspace is formed by Pauli matrices σ_x and σ_z instead of σ_x and σ_y in our case.] The space-group operations transpose the local states but do not mix the E_g and A_{2g} parts. This means that the crystal configurations (bases of the irreducible representations of the space group) combine only the E_g or A_{2g} parts of local density matrices, which leads to two distinct types of ordering.

Local states characterized by the vectors $(\eta_x, \eta_y, 0)$ and $(0, 0, \eta_z)$ are for special values of η_x, η_y, η_z given in Table I. It appears that the ordering of the \mathcal{E}_g type is associated with an onset of noncubic electron distribution and the vectors $(1, 0, 0)$ and $(0, 1, 0)$ may be formally considered as two E_g components of the electron density. This type of orbital ordering is thus related to the common

TABLE I. Ordered local states based on the e_g electron orbitals.

Type of ordering	Order parameters (η_x, η_y, η_z)	Eigenstates ^a ψ_1, ψ_2	Graphic representation	
			+	-
\mathcal{E}_g	$(\pm 1, 0, 0)$	$\phi_{z^2}, \phi_{x^2-y^2}$		
	$(0, \pm 1, 0)$	$\frac{1}{\sqrt{2}}(\phi_{z^2} \pm \phi_{x^2-y^2})$		
\mathcal{A}_{2g}	$(0, 0, \pm 1)$	ϕ_1, ϕ_2		

$$^a \phi_1 = \epsilon x^2 + \epsilon^3 y^2 + z^2 = \phi_2^* \quad (\epsilon = e^{2\pi i/3}),$$

$$\phi_{z^2} = (1/\sqrt{2})(\phi_1 + \phi_2) = (1/\sqrt{2})(2z^2 - x^2 - y^2),$$

$$\phi_{x^2-y^2} = (1/\sqrt{2})(\phi_1 - \phi_2) = \sqrt{3}/2(x^2 - y^2).$$

($E_g \otimes e_g$) Jahn-Teller effect in the interpretation of Ref. 1.

The second ordering of the \mathcal{A}_{2g} type is characterized by a cubic electron distribution with a quadrupole magnetic moment due to currents arranged as depicted in Table I. As the magnetic interactions are generally weak, one may anticipate merely subtle manifestations of an $E_g \otimes a_{2g}$ effect.

IV. T_{2g} IONS IN OCTAHEDRAL COORDINATION

The behavior of threefold-orbitally-degenerate T_{1g} or T_{2g} ions is complex. The orbital angular momentum is not quenched and even a moderate spin-orbit coupling may suppress Jahn-Teller distortions.⁴ This is probably one reason why indications of the cooperative Jahn-Teller ordering in the triply degenerate systems are rare. The following treatment shows that two cases of orbital ordering may be encountered. Both are characterized by a noncubic density distribution of local states.

Let us consider a T_{2g} ion with basis functions

$$\phi_{xy} = \sqrt{3}xy,$$

$$\phi_{yz} = \sqrt{3}yz,$$

$$\phi_{zx} = \sqrt{3}zx.$$

Under symmetry operations of the O_h point group, the density matrix is transformed according to the representation

$$T_{2g}^2 = A_{1g} \oplus E_g \oplus T_{2g} \oplus T_{1g}.$$

The reduction shows a decomposition into a constant part associated with the one-dimensional unit representa-

tion A_{1g} and three temperature-dependent parts which are associated with the irreducible representations E_g , T_{2g} , and T_{1g} , respectively. With our choice of wave functions, these three subspaces are as follows:

$$\mathcal{E}_g \quad \text{with } \Delta\rho = (\eta_1, \eta_2, 0, 0, 0, 0, 0)$$

$$= \eta_1 \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \eta_2 \sqrt{3} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix},$$

$$T_{2g} \quad \text{with } \Delta\rho = (0, 0, \eta_3, \eta_4, \eta_5, 0, 0, 0)$$

$$= \eta_3 \sqrt{3} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \eta_4 \sqrt{3} \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} + \eta_5 \sqrt{3} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix},$$

\mathcal{T}_{1g} with $\Delta\rho = (0,0,0,0,0,\eta_6,\eta_7,\eta_8)$

$$= \eta_6 \sqrt{3} \begin{bmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \\ + \eta_7 \sqrt{3} \begin{bmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{bmatrix} \\ + \eta_8 \sqrt{3} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{bmatrix}.$$

The \mathcal{E}_g case corresponds to the realization of a state stabilized by e_g distortions (the $T_{2g} \otimes e_g$ Jahn-Teller effect). In an important contradistinction to the $E_g \otimes e_g$ Jahn-Teller effect, which was discussed in the previous section, the order parameters η_1 and η_2 for T_{2g} ions cannot acquire arbitrary values. The requirement of a transition to a pure quantum state (see Appendix B) gives three solutions which are equivalent (i.e., related by the O_h symmetry operations):

$$\begin{aligned} \rho_1 &= (\eta, 0, 0, 0, 0, 0, 0, 0), \\ \rho_2 &= (-\eta/2, \eta\sqrt{3}/2, 0, 0, 0, 0, 0, 0), \\ \rho_3 &= (-\eta/2, -\eta\sqrt{3}/2, 0, 0, 0, 0, 0, 0). \end{aligned} \quad (3)$$

These states are coupled to the tetragonal e_g mode as shown in Table II.

For the \mathcal{T}_{2g} case (the $T_{2g} \otimes t_{2g}$ Jahn-Teller effect), there are four equivalent solutions which lead to the stabilization of pure quantum states:

$$\begin{aligned} \rho_1 &= (0, 0, \eta/\sqrt{3}, \eta/\sqrt{3}, \eta/\sqrt{3}, 0, 0, 0), \\ \rho_2 &= (0, 0, \eta/\sqrt{3}, -\eta/\sqrt{3}, -\eta/\sqrt{3}, 0, 0, 0), \\ \rho_3 &= (0, 0, -\eta/\sqrt{3}, \eta/\sqrt{3}, -\eta/\sqrt{3}, 0, 0, 0), \\ \rho_4 &= (0, 0, -\eta/\sqrt{3}, -\eta/\sqrt{3}, \eta/\sqrt{3}, 0, 0, 0). \end{aligned} \quad (4)$$

These four states are coupled with shear t_{2g} deformations along the four body diagonals $[111]$, $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, and $[\bar{1}\bar{1}1]$, respectively (see Table II).

Finally, in the \mathcal{T}_{2g} subspace, there is no density matrix $\Delta\rho$ which could be transformed to the required diagonal form of

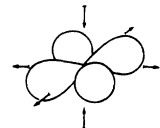
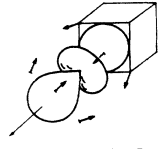
$$\Delta\rho = \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Consequently, any ordering according to the representation \mathcal{T}_{1g} is forbidden.

V. ORBITAL CONFIGURATIONS IN CONCENTRATED SYSTEMS WITH T_{2g} IONS

Electronic states are generally not related to the macroscopic crystal axes but rather to the local reference systems of atomic sites (coordination octahedra in our case). As shown in Ref. 1, the local axes may be defined uniquely even for irregular octahedra, except for an arbitrary labeling. With the axes labeled, any orbital configuration of T_{2g} ions is specified by a set of N local states which are characterized by two components of the density matrix (η_1, η_2) or three components (η_3, η_4, η_5) for the \mathcal{E}_g and \mathcal{T}_{2g} types of ordering, respectively. The orbital configuration thus represents a vector in a $2N$ - or $3N$ -dimensional space. Under the symmetry operations of

TABLE II. Ordered local states based on the t_{2g} electron orbitals.

Type of ordering	Order parameters ($\eta_1, \eta_2, \dots, \eta_8$)	Eigenstates	Graphic representation
\mathcal{E}_g	$\eta(1, 0, 0, 0, 0, 0, 0, 0)$ $\eta(-1/2, \sqrt{3}/2, 0, 0, 0, 0, 0, 0)$ $\eta(-1/2, \sqrt{3}/2, 0, 0, 0, 0, 0, 0)$	ϕ_{xy} ϕ_{yz} ϕ_{zx}	 $[001] \text{ or } [100] \text{ or } [010]$
\mathcal{T}_{2g}	$\eta(0, 0, 1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3}, 0, 0, 0)$ $\eta[0, 0, 1/\sqrt{3}, -1/\sqrt{3}, -1/\sqrt{3}, 0, 0, 0]$ $\eta(0, 0, -1/\sqrt{3}, 1/\sqrt{3}, -1/\sqrt{3}, 0, 0, 0)$ $\eta(0, 0, -1/\sqrt{3}, -1/\sqrt{3}, 1/\sqrt{3}, 0, 0, 0)$	$\frac{1}{\sqrt{3}}(\phi_{xy} + \phi_{yz} + \phi_{zx})$ $\frac{1}{\sqrt{3}}(\phi_{xy} - \phi_{yz} - \phi_{zx})$ $\frac{1}{\sqrt{3}}(\phi_{xy} - \phi_{yz} + \phi_{zx})$ $\frac{1}{\sqrt{3}}(\phi_{xy} + \phi_{yz} - \phi_{zx})$	 $[111] \text{ or } [1\bar{1}\bar{1}] \text{ or } [\bar{1}1\bar{1}] \text{ or } [\bar{1}\bar{1}1]$

the disordered phase, each vector is transformed to another vector of the same space. The transformation matrices generate a Jahn-Teller representation Γ_{JT} ($2N$ or $3N$ dimensional) which is reducible. Vectors transforming according to a single irreducible representation contained in Γ_{JT} are the allowed orbital configurations.

The reduction of Γ_{JT} is more readily performed if the local axes of octahedra are labeled in a symmetrical way. How best to proceed depends on the actual point symmetry of the octahedral site in the crystal. Let us first consider the \mathcal{E}_g type of ordering irrespective of whether it occurs for the E_g or T_{2g} ions. If the octahedral site is of orthorhombic point symmetry D_{2h} or its subgroups, it is possible to label the axes with respect to the space-group symmetry so that each operation transposes one site to another together with its labeled reference system. If there are rotations which permute axes of octahedra, the labeling is performed within a maximal subgroup of the full space group, in which such operations are left out. In crystals with ionic sites of cubic or trigonal point symmetry, this subgroup also has a physical meaning and we call it the relevant group.¹

Three cases should be distinguished. The above-mentioned case of D_{2h} or lower symmetry is characterized by the reduction of the E_g representation associated with the local density matrix into two unit representations of the actual site symmetry. As a consequence, the Jahn-Teller representation Γ_{JT} acquires the form of a sum of two permutation representations Γ_p of the crystal space group.¹

The second limiting case occurs for sites of cubic or trigonal point symmetry for which the E_g representation is not reduced. In that case it is advantageous to perform the representation analysis within the relevant group instead of the full space group of the disordered phase. It means that one takes into account only the symmetry operations which merely transport local states whereas those which include, in addition, some rotation of local states are omitted. These latter operations just transform each orbital mode to its symmetrical equivalent. It is obvious that these equivalent modes fall into one irreducible representation of the full space group. Apart from a considerable simplification of the analysis (the Jahn-Teller representation is reduced to two permutation representations as in the first case), the concept of the relevant group helps us avoid physically unreasonable modes. Namely, the use of the full space group would lead to an arbitrary mixing of the equivalent modes and, in particular, a mixing of local states. This is, however, not possible for T_{2g} ions, as they can occur only in states given in (3) or (4). For the $E_g \otimes e_g$ Jahn-Teller effect discussed in Ref. 1, this argument against mixing is not so strict. Nevertheless, even in that case there are several advantages which support the use of the relevant group.

The third case, not discussed in our previous paper,¹ concerns octahedral sites of tetragonal point symmetry or orthorhombic and monoclinic point symmetry with elements along the diagonals. The E_g representation is reduced to a sum of two different one-dimensional representations, one of which is the unit representation. The

choice of the subgroup which labels the local axes is generally not unique. The representation analysis itself should be performed in any case within the full space group of the disordered phase. This represents a more complicated procedure than in the first two cases. Furthermore, the orbital modes obtained are not always physically acceptable. An example concerning the cooperative Jahn-Teller effect in the magnetoplumbite structure [space group $P6_3/mmc$ (D_{6h}^4)] is given in Appendix C.

It is of special importance for the $T_{2g} \otimes e_g$ effect that there is always a local state, namely, the tetragonal state given in (3), which transforms according to the unit representation of the point symmetry of a given site in the crystal. (This also holds for the cubic and trigonal sites if one accepts the concept of the relevant group.) Such invariant states imply the existence of the one-colored crystal configurations which will be discussed in the next section.

A somewhat different situation occurs for the T_{2g} ordering. If the point symmetry of the octahedral site is cubic, the T_{2g} representation is not reduced. The symmetry analysis can be then performed within the relevant group where all symmetry elements which permute allowed local states (4) are excluded. The symmetry of this relevant group is, therefore, lower than for the \mathcal{E}_g ordering. In other cases, the T_{2g} representation is reduced to a sum of two or three irreducible representations of the actual point-group symmetry. Invariant local states (4) and, consequently, one-colored configurations in the $T_{2g} \otimes t_{2g}$ effect exist (apart from the above-mentioned cubic sites under the use of the relevant group) for sites of trigonal point-group symmetry D_{3d} and its subgroups.

A. $T_{2g} \otimes e_g$ Jahn-Teller effect

Reduction of the Jahn-Teller representation of order $2N$ leads to a large number of modes, $2m$ for each wave vector \mathbf{k} (where m is the number of equivalent positions in the unit cell). As shown for the analogous $E_g \otimes e_g$ case,¹ most modes combine local states (η_1, η_2) with their inversion $(-\eta_1, -\eta_2)$. Since the inversion of local states is not possible in T_{2g} ions [the modes can combine only states given in (3) or, for the $T_{2g} \otimes t_{2g}$ case, in (4)], the number of allowed orbital modes is severely reduced. It appears that, in a system with local axes labeled in a symmetrical way as suggested above, all allowed configurations in the $T_{2g} \otimes e_g$ case can be related to colored space groups. There is always a one-colored configuration which combines only one of three states in (3). It corresponds to the unit representation of the space group (or the relevant group for octahedral sites of the cubic or trigonal point-group symmetry). Depending on the choice of orbital states (3) in the reference position, one may get, however, up to three quite distinct arrangements. The second possibility is the three-colored configurations in which each color represents a different state of (3). They correspond to two-dimensional irreducible representations and exist for space groups (relevant groups) with subgroups of order 3. A comprehensive list

of three-colored space groups has been published.⁵ As the colors can be interchanged, one always gets two arrangements for each group.

B. $T_{2g} \otimes t_{2g}$ Jahn-Teller effect

In the $T_{2g} \otimes t_{2g}$ case, one may consider configurations which combine one, two, or four states of (4). The first possibility is primitive and corresponds to the unit representation of the space group (or the relevant group for sites of cubic point symmetry). These one-colored configurations exist for T_{2g} ions located in cubic sites or sites of symmetry D_{3d} and its subgroups. The other two cases suggest the use of two- and four-colored space groups. The configurations constructed in this way, however, need not represent bases of irreducible representations, and so the colored analogy is misleading. In fact, modes which would combine two states do not exist at all. The four-colored configurations associated with three-dimensional irreducible representations are theoretically possible for cubic space groups only, provided that the ions occupy the general positions. Such configurations are of little practical importance since, even in very complicated cubic structures (BaCuO₂, some zeolites), the octahedrally coordinated sites occur in special positions on the trigonal axis.

VI. CONCLUSION

The actual state of atoms with degenerate orbital levels is represented by the density matrix. For the E_g and T_{2g} ions in local O_h symmetry under study, the atomic density matrix transforms according to representations $E_g^2 = A_{1g} \oplus E_g \oplus A_{2g}$ and $T_{2g}^2 = A_{1g} \oplus E_g \oplus T_{2g} \oplus T_{1g}$, respectively. This expresses a reduction of ordering pro-

cesses into several distinct kinds in which orbital states can be regarded as classical entities of different symmetries. The arrangements of these entities in crystals have been investigated with use of group-theoretical methods, in analogy to the analysis of crystal modes of vector character (displacements, spins, etc.).

The superposition principle which holds for degenerate orbital eigenfunctions is generally not applicable to density matrices. Even if they are associated with a multidimensional irreducible representation, there may exist just some symmetry-equivalent states which are physically acceptable. These equivalent states do not represent a degeneracy in the usual sense. In particular, they are not allowed to mix.

The analysis of orbital configurations in systems with E_g ions has been described to a large extent in our earlier work.¹ Some additional aspects of the theory are emphasized in Secs. III and V of the present paper. Compared with the large variety of configurations allowed and those actually observed in systems with E_g ions, T_{2g} ions allow just a few ordered arrangements which can all be found without the tedious representation analysis. In nearly all crystals (with only a few exceptions in the $T_{2g} \otimes t_{2g}$ Jahn-Teller effect) primitive "one-colored" arrangements of high symmetry are possible. For the $T_{2g} \otimes e_g$ Jahn-Teller effect, there may occur, in addition, "three-colored" configurations of lower symmetry.

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APPENDIX A: THE VECTOR SPACE OF $n \times n$ HERMITEAN MATRICES

Any $n \times n$ Hermitean matrix can be expressed as a combination of n^2 linearly independent matrices. For our purposes we choose a set consisting of (1) the unit matrix E , (2) $n-1$ diagonal matrices,

$$A_1 = \text{diag}(n-1, -1, -1, \dots, -1), \quad A_2 = \left[\frac{n(n-1)}{(n-1)(n-2)} \right]^{1/2} \text{diag}(0, n-2, -1, -1, \dots, -1),$$

$$A_3 = \left[\frac{n(n-1)}{(n-2)(n-3)} \right]^{1/2} \text{diag}(0, 0, n-3, -1, -1, \dots, -1), \dots, A_{n-1} = \left[\frac{n(n-1)}{2} \right]^{1/2} \text{diag}(0, 0, \dots, 0, 1, -1),$$

(3) $(n^2-n)/2$ real symmetric matrices of the type

$$A_i = \left[\frac{n(n-1)}{2} \right]^{1/2} \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & & & & 1 \\ \cdot & & & & \cdot \\ \cdot & & & & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot \end{pmatrix}$$

with only two nonvanishing entries (1's), and (4) $(n^2-n)/2$ Hermitean matrices of the type

$$A_i = \left[\frac{n(n-1)}{2} \right]^{1/2} \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & & & & i \\ \cdot & & & & \cdot \\ \cdot & & & & \cdot \\ \cdot & -i & \cdot & \cdot & \cdot \end{pmatrix}$$

with only two nonvanishing entries ($-i$ and i). The matrices A fulfill the normalization condition

$$(A_i, A_j) = \text{Sp}(A_j^\dagger A_i) = n(n-1)\delta_{ij}. \quad (\text{A1})$$

For $n=2$, one gets a set of well-known Pauli matrices

$$A_1 = \sigma_z, \quad A_2 = \sigma_x, \quad A_3 = \sigma_y.$$

The temperature-dependent part of the density matrix $\Delta\rho$ then acquires the form

$$(\eta_1, \eta_2, \eta_3) = \begin{pmatrix} \eta_1 & \eta_2 + i\eta_3 \\ \eta_2 - i\eta_3 & -\eta_1 \end{pmatrix}.$$

For $n=3$, there is a system of eight basis matrices A , and $\Delta\rho$ in the general case becomes

$$(\eta_1, \eta_2, \dots, \eta_8) = \begin{pmatrix} 2\eta_1 & \sqrt{3}\eta_3 + i\sqrt{3}\eta_6 & \sqrt{3}\eta_4 + i\sqrt{3}\eta_7 \\ \sqrt{3}\eta_3 - i\sqrt{3}\eta_6 & -\eta_1 + \sqrt{3}\eta_2 & \sqrt{3}\eta_5 + i\sqrt{3}\eta_8 \\ \sqrt{3}\eta_4 - i\sqrt{3}\eta_7 & \sqrt{3}\eta_5 - i\sqrt{3}\eta_8 & -\eta_1 - \sqrt{3}\eta_2 \end{pmatrix}.$$

APPENDIX B: GENERAL REQUIREMENTS IMPOSED ON THE DENSITY MATRIX

Since the ideal ordering implies a realization of a pure quantum state, one may conclude that $\Delta\rho$ should be equivalent (up to a unitary transformation) to the diagonal matrix

$$A_1 = \text{diag}(n-1, -1, -1, \dots, -1).$$

From this requirement and the normalization conditions (A1), a necessary condition for the ordered state follows immediately:

$$\sum_{i=1}^{n^2-1} \eta_i^2 = 1.$$

For $n=2$, any density matrix $\Delta\rho$ can be transformed to the diagonal matrix $A_1 = \sigma_z$ and condition (B1) is sufficient for realization of a pure quantum state. It is not true, in general, for the case of higher degeneracies. This is illustrated in Sec. IV for the orbital ordering in triply degenerate T_{2g} ions which permits discrete states only, even if it is characterized by multidimensional order parameters.

APPENDIX C: $E_g \otimes e_g$ AND $T_{2g} \otimes e_g$ JAHN-TELLER EFFECT IN THE MAGNETOPLUMBITE-TYPE STRUCTURE

(B1) The magnetoplumbite structure [space group $P6_3/mmc$ (D_{6h}^4); $a \sim 5.9$ Å and $c \sim 23.2$ Å] comprises three octahedrally coordinated sites: the twelvefold site

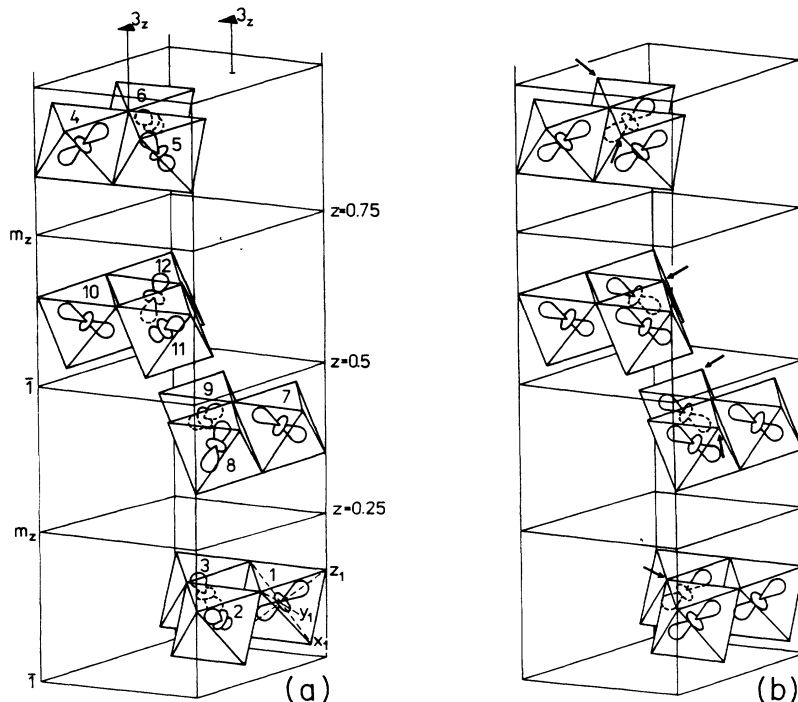


FIG. 1. Ordering of ϕ_{z^2} orbitals in octahedral sites 12k of the magnetoplumbite structure [$P6_3/mmc$ (D_{6h}^4)]— the modes associated with (a) the unit representation Γ_1^+ and (b) the two-dimensional representation Γ_6^+ . [If in (b) two-thirds of ϕ_{z^2} orbitals are turned to corners marked by the arrows, another configuration belonging to Γ_6^+ is obtained.]

TABLE III. One-dimensional orbital modes for the 12k positions in the magnetoplumbite structure [$P6_3/mmc (D_{6h}^4)$] structure.

No.	Orbital mode	Representation
1	$\eta_{x,1} + \eta_{x,2} + \eta_{x,3} + \eta_{x,4} + \eta_{x,5} + \eta_{x,6} + \eta_{x,7} + \eta_{x,8} + \eta_{x,9} + \eta_{x,10} + \eta_{x,11} + \eta_{x,12}$	Γ_1^+
2	$\eta_{y,1} + \eta_{y,2} + \eta_{y,3} + \eta_{y,4} + \eta_{y,5} + \eta_{y,6} + \eta_{y,7} + \eta_{y,8} + \eta_{y,9} + \eta_{y,10} + \eta_{y,11} + \eta_{y,12}$	Γ_1^-
3	$\eta_{y,1} + \eta_{y,2} + \eta_{y,3} - \eta_{y,4} - \eta_{y,5} - \eta_{y,6} - \eta_{y,7} - \eta_{y,8} - \eta_{y,9} + \eta_{y,10} + \eta_{y,11} + \eta_{y,12}$	Γ_2^+
4	$\eta_{x,1} + \eta_{x,2} + \eta_{x,3} - \eta_{x,4} - \eta_{x,5} - \eta_{x,6} - \eta_{x,7} - \eta_{x,8} - \eta_{x,9} + \eta_{x,10} + \eta_{x,11} + \eta_{x,12}$	Γ_2^-
5	$\eta_{x,1} + \eta_{x,2} + \eta_{x,3} + \eta_{x,4} + \eta_{x,5} + \eta_{x,6} - \eta_{x,7} - \eta_{x,8} - \eta_{x,9} - \eta_{x,10} - \eta_{x,11} - \eta_{x,12}$	Γ_3^+
6	$\eta_{y,1} + \eta_{y,2} + \eta_{y,3} + \eta_{y,4} + \eta_{y,5} + \eta_{y,6} - \eta_{y,7} - \eta_{y,8} - \eta_{y,9} - \eta_{y,10} - \eta_{y,11} - \eta_{y,12}$	Γ_3^-
7	$\eta_{y,1} + \eta_{y,2} + \eta_{y,3} - \eta_{y,4} - \eta_{y,5} - \eta_{y,6} + \eta_{y,7} + \eta_{y,8} + \eta_{y,9} - \eta_{y,10} - \eta_{y,11} - \eta_{y,12}$	Γ_4^+
8	$\eta_{x,1} + \eta_{x,2} + \eta_{x,3} - \eta_{x,4} - \eta_{x,5} - \eta_{x,6} + \eta_{x,7} + \eta_{x,8} + \eta_{x,9} - \eta_{x,10} - \eta_{x,11} - \eta_{x,12}$	Γ_4^-

12k, the fourfold site $4f_{VI}$, and the twofold site $2a$.⁶ Let us consider that the orbitally degenerate ions occupy the 12k site with coordinates $x \sim \frac{1}{6}$, $y \sim -\frac{1}{6}$, $z \sim 0.11$ (see Fig. 1) and investigate possible orbital configurations with wave vector $\mathbf{k} = \mathbf{0}$.

The 12k site resides on the diagonal mirror plane which permutes local axes of the coordination octahedra. In order to label the axes in a systematic way, the first task is to find a subgroup of $P6_3/mmc$ in which this mirror plane is left out. There are four such subgroups of order 2, $P6_3/m$, $P6_322$, $P6_2c$, and $P31c$, of which the most convenient to use is the first one. The choice of local axes in position 1 is shown in Fig. 1(a). By selecting the $P6_3/m$, the reference systems in positions 2 and 3 are related to position 1 by the triad 3_z , in positions 4–6 by the inversion center $\bar{1}$, and in positions 7–9 and 10–11 by the mirror plane m_z at $z = 0.25$ and 0.75 , respectively.

The Jahn-Teller representation Γ_{JT} of order $2m = 24$ is reduced to a sum of one-dimensional representations $\Gamma_1^+ - \Gamma_4^+$ and two-dimensional irreducible representations $\Gamma_5^+ - \Gamma_8^+$ of the space group $P6_3/mmc$ for $\mathbf{k} = \mathbf{0}$:

$$\Gamma_{JT} = \Gamma_1^+ + \Gamma_1^- + \Gamma_2^+ + \Gamma_2^- + \Gamma_3^+ + \Gamma_3^- + \Gamma_4^+ + \Gamma_4^- + 2\Gamma_5^+ + 2\Gamma_5^- + 2\Gamma_6^+ + 2\Gamma_6^- + 2\Gamma_7^+ + 2\Gamma_7^- + 2\Gamma_8^+ + 2\Gamma_8^-.$$

The basis vectors of the one-dimensional representations are given in Table III. They correspond to configurations in which orbital states in the three positions at one z level retain the threefold symmetry. The simplest mode No. 1

associated with the unit representation Γ_1^+ is shown in Fig. 1(a). It combines the tetragonal states η_x and possesses the $P6_3/mmc$ symmetry. High symmetry is also retained for all configurations which combine the orthorhombic states η_y : $P6_3/m$ for No. 2, $P6_322$ for No. 3, $P31c$ for No. 6, and $P6_2c$ for No. 7.

For each two-dimensional irreducible representation in Γ_{JT} , there are two different bases of complicated form. Realistic configurations are obtained only by combining vectors of both bases. Among them, the special cases are the configurations in which orbital states in the three positions at one z level are arranged ferrodistoritively. A practical importance has, namely, the low-energy configuration associated with representation Γ_6^+ which is shown in Fig. 1(b). This configuration of $Cmcm$ symmetry was confirmed in recent structural refinement of the substituted hexaferrite $BaFe_{2.5}Mn_{9.5}O_{19}$ with orbitally doubly degenerate ions Mn^{3+} in the octahedral sites.⁷

In the case of triply degenerate T_{2g} ions, only the tetragonal local states given in Sec. IV by expression (3) are allowed. This reduces the number of possible configurations in the magnetoplumbite structure to three. The first one is the “one-colored” configuration in the sense of Sec. V A, which corresponds to the arrangement in Fig. 1(a) (the ϕ_{z^2} orbitals should be, of course, replaced by the ϕ_{xy} orbitals). Another possibility is related to the three-colored group $P6_3/mmc(E)Cmcm$ in the notation of Harker.⁵ It gives rise to two configurations, one of which corresponds to Fig. 1(b) and the second is its alternative mentioned therein.

¹Z. Jiráček, Phys. Rev. B **35**, 5437 (1987).

²O. V. Gurin, G. L. Budrina, and V. N. Syromyatnikov, Zh. Eksp. Teor. Fiz. **95**, 1335 (1989).

³U. Öpik and M. H. L. Pryce, R. Soc. London., Ser. A **238**, 425 (1957).

⁴M. D. Sturge, in *Solid State Physics*, edited by F. Seitz, D.

Turnbull, and H. Ehrenreich (Academic, New York, 1967), Vol. 20, p. 91.

⁵D. Harker, Acta Crystallogr. A **37**, 286 (1981).

⁶W. D. Townes, J. H. Fang, and A. J. Perrotta, Z. Kristallogr. **125**, 437 (1967).

⁷Z. Jiráček and E. Pollert (unpublished).