A three-dimensional order parameter is proposed for Jahn–Teller phase transitions related to splitting of the ion $E_g$-level. A thermodynamic theory of these transitions is constructed on its basis. A selection rule of possible orderings is introduced that is based on the simultaneous entrance of the relevant order parameter into the composition of the mechanical and Jahn–Teller representations. Developed methods are approved for analysis of the structural transition in perovskites of the $\text{KCuF}_3$ type.

Significant progress in the area of the thermodynamic description of structural and magnetic phase transitions (PT) [1, 2] has been achieved recently, which is due to a considerable degree to the well developed symmetric methods of determining a relevant order parameter [1]. In the case of Jahn–Teller (JT) PT the order parameter (OP) is not so graphic, which constrains development of thermodynamic approaches to their description. Symmetrized combinations of pairwise products $\Phi_1 \Phi_2$ of the electron wave functions $\Phi_i$ are used for the JT transitions in a number of papers [3,4]. Such an approach permits indicating the change in the electron density distribution for a given change in symmetry, but only for $T = 0$. Another widespread method of describing a JT PT is based on analysis of possible distortions of the nearest neighborhood of JT ions. A change in the symmetry of the nearest neighborhood is identified with a change in the symmetry of the electron density distribution and the whole symmetric analysis reduces to enumeration of the possible kinds of distortion of isolated structural formations. Such an approach is based on a specific model that takes account of electron–phonon interaction in a linear approximation with the nearest neighbors. In this paper it is proposed to use components of the density matrix as OP, which will permit application of developed symmetric and thermodynamic methods of PT analysis in detail to JT PT.

Let us consider a JT ion in a cubic neighborhood with a double degenerate $E_g$ type level [5]

\[
|\Phi_1\rangle = \varepsilon x^2 + \varepsilon y^2 + z^2, \quad |\Phi_2\rangle = \varepsilon x^2 + \varepsilon y^2 + z^2.
\]  

where $\varepsilon = \exp(2\pi i/3)$. The JT PT consists in removal of the degeneration accompanying distortion of the crystal structure. The wave functions of the new levels can be represented in the form of superposition of the functions (1)

\[
|\Psi\rangle = \hat{U} |\Phi\rangle, \quad \hat{U} = \begin{bmatrix} p_1 p_2 \\ -p_2 p_1 \end{bmatrix},
\]

where $|\Phi\rangle$ is a column vector. Therefore, the states of the JT ion at $T = 0$ is described by a set of numbers $p = (p_1, p_2)$. We designate the quantity $p$ as the polarization. The numbers $p_1$ and $p_2$ are related by the conditions

\[
|p_1|^2 + |p_2|^2 = 1, \quad e^{i\alpha}(p_1, p_2) = (p_1, p_2).
\]

where the first condition yields normalization of the function $|\Phi\rangle$, while the second reflects the phase uncertainty in assigning the wave function. Consequently, the manifold of possible values of $p$ is two-dimensional.

For $T>0$ the ion state is not described by assigning just the wave functions. It is also necessary to give the probabilities $\omega_1$ and $\omega_2$ ($\omega_1 + \omega_2 = 1$) of finding an electron at each level. Together with the matrix $\hat{U}$ (taking account of the binding conditions these are three real quantities) these probabilities determine the ion state completely at any temperature and can be ordering parameters. But it is more convenient for us to go over to the mean of the Pauli operators. The static mean of an arbitrary operator $\hat{A}$ has the form

$$\langle \hat{A} \rangle = \omega_1 \langle \Psi_1 | \hat{A} | \Psi_1 \rangle + \langle \Psi_2 | \hat{A} | \Psi_2 \rangle.$$  

The operator $\hat{A}$ given in a space of two functions can always be represented in the form of a linear combination of Pauli operators

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \sigma_0 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix},$$

and, correspondingly, $\langle \hat{A} \rangle$ can be expressed in terms of the means of these operators $\eta_{\alpha} = \langle \sigma_{\alpha} \rangle$. These latter have the form

$$\eta_x = (\omega_1 - \omega_2) (p_x^* p_x + p_y^* p_y);$$
$$\eta_y = i (\omega_1 - \omega_2) (p_x^* p_y - p_y^* p_x);$$
$$\eta_z = (\omega_1 - \omega_2) (|p_x|^2 - |p_y|^2),$$

$\langle \sigma_0 \rangle = 1$ and will not be considered below.

It is evident from (6) that above the JT ($T>T_c$) transition point $\omega_1 = \omega_2$ and $\eta_\alpha = 0$. For $T<T_c$ $\omega_1 \neq \omega_2$ and $\eta_\alpha \neq 0$ where $|\eta|$ grows with the reduction in temperature so that as $T \to 0$ $|\eta| \to 1$. Moreover, assigning $\eta$ permits determination of the set of $\omega_i$ and $p_i$, by solving (6), that yield the ion state uniquely. Therefore, the vector $\eta$ can be considered as an order parameter associated with this ion. Its direction yields the atomic wave function with least energy.

Let us go over to the transformation properties of the OP $\eta$. The basis (1) is transformed, under rotations, into the irreducible representation (IR) $E_g$ of the group $O_h$, therefore, the $p_i$ are also transformed by the same IR. By using (6), the transformation properties of $\eta$ can be determined

$$g \eta = D_{\text{JT}}(g) \eta,$$  

where the matrix $D_{\text{JT}}(g)$ of the JT-representation is represented in Table 1 while $g$ are elements of crystal symmetry.

By knowing the order parameter transformation laws in an individual atom, it is easy to go over to order parameters being realized in the whole crystal. Such a procedure is described in [1]; we present just the final expressions.

The composition of the JT representations corresponding to the wave vector $K$ is

$$d_{\text{JT}} = \sum^{+}_v n_v K,$$  

TABLE 1

<table>
<thead>
<tr>
<th>$h_1$</th>
<th>$h_1-h_4$</th>
<th>$h_3-h_4$</th>
<th>$h_5-h_{12}$</th>
<th>$h_{13}-h_{16}$</th>
<th>$h_{17}-h_{20}$</th>
<th>$h_{21}-h_{24}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-1.2</td>
<td>-1.2 $\sqrt{3}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1.2 $\sqrt{3}$</td>
<td>0</td>
<td>0</td>
<td>-1.2 $\sqrt{3}$</td>
</tr>
</tbody>
</table>

For $T>0$ the ion state is not described by assigning just the wave functions. It is also necessary to give the probabilities $\omega_1$ and $\omega_2$ ($\omega_1 + \omega_2 = 1$) of finding an electron at each level. Together with the matrix $\hat{U}$ (taking account of the binding conditions these are three real quantities) these probabilities determine the ion state completely at any temperature and can be ordering parameters. But it is more convenient for us to go over to the mean of the Pauli operators. The static mean of an arbitrary operator $\hat{A}$ has the form

$$\langle \hat{A} \rangle = \omega_1 \langle \Psi_1 | \hat{A} | \Psi_1 \rangle + \langle \Psi_2 | \hat{A} | \Psi_2 \rangle.$$  

The operator $\hat{A}$ given in a space of two functions can always be represented in the form of a linear combination of Pauli operators

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \sigma_0 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix},$$

and, correspondingly, $\langle \hat{A} \rangle$ can be expressed in terms of the means of these operators $\eta_{\alpha} = \langle \sigma_{\alpha} \rangle$. These latter have the form

$$\eta_x = (\omega_1 - \omega_2) (p_x^* p_x + p_y^* p_y);$$
$$\eta_y = i (\omega_1 - \omega_2) (p_x^* p_y - p_y^* p_x);$$
$$\eta_z = (\omega_1 - \omega_2) (|p_x|^2 - |p_y|^2),$$

$\langle \sigma_0 \rangle = 1$ and will not be considered below.

It is evident from (6) that above the JT ($T>T_c$) transition point $\omega_1 = \omega_2$ and $\eta_\alpha = 0$. For $T<T_c$ $\omega_1 \neq \omega_2$ and $\eta_\alpha \neq 0$ where $|\eta|$ grows with the reduction in temperature so that as $T \to 0$ $|\eta| \to 1$. Moreover, assigning $\eta$ permits determination of the set of $\omega_i$ and $p_i$, by solving (6), that yield the ion state uniquely. Therefore, the vector $\eta$ can be considered as an order parameter associated with this ion. Its direction yields the atomic wave function with least energy.

Let us go over to the transformation properties of the OP $\eta$. The basis (1) is transformed, under rotations, into the irreducible representation (IR) $E_g$ of the group $O_h$, therefore, the $p_i$ are also transformed by the same IR. By using (6), the transformation properties of $\eta$ can be determined

$$g \eta = D_{\text{JT}}(g) \eta,$$  

where the matrix $D_{\text{JT}}(g)$ of the JT-representation is represented in Table 1 while $g$ are elements of crystal symmetry.

By knowing the order parameter transformation laws in an individual atom, it is easy to go over to order parameters being realized in the whole crystal. Such a procedure is described in [1]; we present just the final expressions.

The composition of the JT representations corresponding to the wave vector $K$ is

$$d_{\text{JT}} = \sum^{+}_v n_v K.$$