connected with the transfer of dislocation electrons into the conduction band are also possible.

In conclusion, the authors thank É. I. Rashba for a helpful discussion of the work.

1 We emphasize that to obtain self-consistent results it is necessary to introduce at least two parameters, \( \alpha \) and \( \beta \). By introducing only one parameter it is impossible to satisfy all the self-consistency conditions. The quantities \( \alpha \) and \( \beta \) have different physical meanings (a similar situation was encountered in Ref. 18). Failure to understand this difference is apparently the cause of the principal error of Ref. 19, in which the first attempt was made to study the influence of mixing on the DS.

### Theory of structural phase transitions in cyanides of alkali metals

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The thermodynamic properties of a structural phase transition model for alkali-metal cyanides are discussed in the molecular-field approximation. The temperature dependences of the transition parameters and of the specific heat are obtained. The jumps and changes of the transition entropy are calculated. The results of the calculation are compared with the experimental data for the crystals KCN, NaCN, CaCN, and RbCN.

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### 1. INTRODUCTION

Structural phase transitions (PT) in crystals of the type MeCN (Me = K, Na, Rb, Cs) have been the subject of many studies. It has been experimentally established that the transitions in these crystals are connected with the ordering of the cyanide groups. Potassium cyanide (KCN) has at room temperature an NaCl structure, and in this phase the cyanide groups CN are disordered relative to the orientations of their longitudinal axes. It was found that the CN groups do not rotate freely, but move in a potential with a large number of minima. The published opinions concerning the form of this potential vary.\(^1\) Since it is impossible to distinguish in experiment with sufficient reliability the motion of the CN groups in an eight-minimum potential (equally probable orientation of the group axis relative to the body diagonals of the cube plus equally probable dispositions of the C and N atoms on the ends of the molecule) from that in a twelve-minimum potential (equally probable orientation of the group axis relative to the diagonals of the faces of the cube plus interchange of the positions of the C and N atoms in the molecule).

At atmospheric pressure KCN undergoes at 168 K, a first-order PT into a partially ordered phase with space group \( D_{3d} \) (\( Z = 1 \)), in which the CN groups are oriented...
along one diagonal of the (110) face, but the "head-tail" motion of the C and N atoms is preserved. Finally, at \( T = 83 \) K the CN undergoes one more second-order PT into a fully ordered state with space group \( D_{2h} \) and two molecules per unit cell.\(^{1,10}\)

NaCN has also the structure of NaCl and with decreasing temperature it undergoes the same sequence of two PT

\[
G(C(Z=1)) \rightarrow D_{2h}(Z=1) \rightarrow D_{2h}(Z=2).
\]

Cesium cyanide has at room temperature a structure of the CsCl type (space group \( C2 \langle Z = 1 \rangle \)). In this phase, the cyanide groups move in an eight-minimum potential. At \( T = 193 \) K CsCN undergoes a first-order phase transition without a change in the unit cell into a rhombohedral phase \( D_3(\langle Z = 1 \rangle) \). In this phase the CN molecules are oriented along the \([111]\) body diagonal of the cube, but the "head-tail" motion remains.\(^{7}\) No transition to the fully ordered state was observed in the CsCN crystal down to \( T = 15 \) K.

RbCN has at room temperature a structure of the NaCl type. It undergoes at \( T = 110 \) K a first-order phase transition into a monoclinic phase with space group \( C2\langle Z = 4 \rangle \). The orientation of the cyanide groups in the monoclinic phase has not been determined experimentally with sufficient degree of reliability, and it is not even clear whether this phase is fully ordered.\(^{18}\) Sugita et al.\(^1\) suggest that the cyanide groups in the \( C2\langle Z = 4 \rangle \) phase are oriented along the diagonals of the cube faces in such a way that the volume of the unit cell is four times the cell volume in the cubic phase.

When subjected to hydrostatic pressure, the cyanides of the alkali metals undergo polymorphic transformations. For example, at \( 20 \) kbar and at room temperature KCN undergoes a polymorphic transformation into a CsCl structure.\(^{14}\) Above \( 20 \) kbar, KCN undergoes with decreasing temperature a PT similar to the transition in CsCN.

Various experimental investigations were made of PT in alkali-metal cyanides: elastic and inelastic neutron scattering,\(^{3,5}\) specific heat,\(^{12,13}\) NMR,\(^*\) and others. Soft acoustic modes were observed in the investigations of the elastic properties.\(^{10,13}\)

There are not many theoretical descriptions of the PT in alkali-metal cyanides.\(^{7,10,12,13,14}\) Some of them,\(^5,10,11,14\) deal with a qualitative description of only the first PT encountered in potassium cyanide when the temperature is lowered, and it is shown in essence in Refs. 10 and 15 that in this PT the elastic constants \( C_{22} \) and \( C_{33} - C_{11} \) depend linearly on \((T - T_d)\), owing to the linear connections between the transition parameter and the elastic degrees of freedom.

The antiferroelectric PT in KCN at \( 83 \) K was theoretically investigated by dos Santos et al.,\(^{14}\) who calculated constants of the dipole-dipole interaction between the CN groups. The model Hamiltonian with these constants was solved in the molecular field (MF) approximation. In addition, they took into account the fact that the "head-tail" motion of the cyanide groups in the \( D_{2h} \) phase goes through eight intermediate states, whose energy is larger by \( \Delta E \) than the energy of the "head-tail" state.

In the investigation of the thermodynamics of the transition, dos Santos et al.\(^{14}\) use the value \( \Delta = 7.4 \times 10^{-3} \) eV measured\(^*\) at \( T = 85 \) K. As noted in Ref. 17, it is impossible to distinguish in experiment with sufficient reliability between the orientations of the CN groups along the planar and body diagonals of the cubic cell, since the CN groups in the \( D_3^{14} \) and \( D_3^{15} \) phases are oriented along a planar diagonal of the cubic cell, it can be proposed that the intermediate states in the \( D_3^{14} \) phase also lie on planar diagonals. In the cubic phase, the ground and intermediate states become equally probable. If, however, it is assumed that the intermediate states in the \( D_3^{14} \) phase lie on body diagonals, then one must propose free rotation of the cyanide groups in the cubic phase, which apparently contradicts the experimental data.\(^{17}\) We shall thus assume below that in the cubic phase of the KCN crystal the CN groups have twelve equally probable states. Ten excited states have an energy higher than the energy of the "head-tail" states, and it is apparently the latter quantity which was measured in Ref. 17.

We propose in this paper a statistical model of the PT in cyanides of alkali metals. The thermodynamic properties of the model will be discussed in the molecular field (MF) approximation.

\(2. \) THE MODEL. THE HAMILTONIAN, THE EXPRESSION FOR THE FREE ENERGY

As already noted, the potential in which the CN group moves in KCN in the cubic phase has not been uniquely established. However, starting with the ordering scheme of the cyanide group in the partly ordered and fully ordered phases, we shall assume that in the cubic phase of KCN the CN group moves in a twelve-minimum potential. A schematic representation of the twelve equally probable positions of the CN group in a structure of the NaCl type is shown in Fig. 1. In the CsCN crystal (and in KCN at pressures higher than 20 kbar), however, the cyanide group moves in an eight-minimum potential. The eight positions of the CN group in a CsCl structure are also shown in Fig. 1. It appears that the number of possible states of the cyanide group is determined by the type of the structure (NaCl or CsCl). The polymorphic transition from the NaCl to the CsCl structure cannot be explained, within the framework of the model considered below, and we consider therefore separately the structural PT connected with the ordering of the CN groups moving in twelve- and eight-minimum potentials. These two cases will be labeled here and elsewhere by the letters \( a \) and \( b \), respectively.

The Hamiltonian of the model takes in the MF approximation the form\(^{16}\)

\[
H = \frac{1}{2} \sum_{< R, R' >} V_{1}(R-R')s_{a}(R)s_{a}(R') - \sum_{< R >} V_{2}(R-R')s_{b}(R)c_{b}(R),
\]

where \( c_{b}(R) = 1 \) if the CN group on the site \( R \) is in the...
In the fully ordered state, when all positions are occupied by CN groups in the states $i$ and $j$ and on the sites $R$ and $R'$, the free energy is given by

$$F = \sum_{R,R'} \{ \frac{1}{2} \sum_{k,k'} V_{ij}^{(R,R')} \sigma_i(R) \sigma_j(R') \}.$$

The expression for the free energy according to (1) is of the form

$$F = -T \sum_{R} \left\{ \sum_{k,k'} V_{ij}^{(R,R')} \sigma_i(R) \sigma_j(R') \right\},$$

where $\beta = 1/T$.

The average occupation numbers $n_i(R)$ are expressed in terms of the parameters $u_{a} \sigma_{a}$ of the transition as follows:

$$n_i(R) = \sum_{k,k'} \sigma_i \sigma_j \exp(\beta u_{a} \sigma_{a}) \exp(\beta u_{a} \sigma_{a}),$$

where $\sigma_i \sigma_j$ are the eigenvectors of the interaction matrix $V_{ij}^{(R,R')}$. The average occupation numbers are expressed in terms of the eigenvalues and eigenvectors of the interaction matrices are equal. (In case a the interaction matrices are equal.)

In case b the high-symmetry phase is connected only without change of the unit-cell volume. In this case the average occupation numbers are given by

$$n_i = \sum_{k,k'} \sigma_i \sigma_j \exp(\beta u_{a} \sigma_{a}) \exp(\beta u_{a} \sigma_{a}).$$

The following remark is in order here. In Eqs. (5)–(8) we have assumed for simplicity that the transition matrices corresponding to degenerate eigenvalues of the interaction matrices are equal. (In case a the transition matrices have three-state degenerate and one twofold degenerate eigenvalues.) In the approximation considered here this does not lead to any errors, since the transition parameters corresponding to one eigenvalue occur at one point of the transition $T_{P}$ and remain equal at all temperatures below $T_{P}$. This situation, however, cannot take place if accounts is taken, either in the Hamiltonian (1) or in the free energy (5) or (7), of some additional (e.g., multiparticle), interaction (see, e.g., Ref. 11).

3. INVESTIGATION OF THE FREE ENERGIES AND OF THE CONSISTENCY EQUATIONS

The consistency equations for the parameters of the transitions can be obtained in standard fashion; they coincide with the conditions for the minima of the free energies (5) and (7).
The consistency equations always have a trivial solution: all \( \eta_i \) (or \( L_j \)) are equal to zero. This solution describes the high-symmetry phase (OJ and O) in cases \( a \) and \( b \), respectively. Starting with certain temperature, nontrivial solutions of the consistency equations appear, where one or several of the transition parameters differ from zero. Which of the transition sequence is realized depends on the relation between the interaction constants of the Hamiltonian (1). We shall discuss cases \( a \) and \( b \) separately.

1. Transitions connected with the ordering of CN groups moving in a twelve-minimum potential (case \( a \)). It can be shown from the consistency equations that only four PT sequences are possible. This can be seen more clearly from the expansion of the free energy (5) in terms of the transition parameters. Part of this expansion is of the form

\[
\Delta f = \left( -\frac{1}{2} \sum_{i} \eta_i \eta_i^* + \sum_{i} \eta_i \eta_i^* \right) + \left( -\frac{1}{2} \sum_{i} \eta_i \eta_i^* + \sum_{i} \eta_i \eta_i^* \right) + 
\]

We emphasize that we have investigated expressions (5) and (7) and the consistency equations, and not the expansion (9) and the expansion (10) given below for case \( b \).

A. \( 5 > 1 > a, \gamma \). The Curie-Weiss temperature is defined as \( T_a = b \). Since, however, (6) and (7) contain the third-degree invariant \( q_1^3 \), it follows that a first-order transition arises at \( T_a = 3/4 \pm 2 \) with a jump \( \Delta \eta = 0, 5 \). The corresponding entropy jump in \( \Delta T = \ln 3 - (1/3) \ln 2 \). Below \( T_a \), the parameters \( \eta_1, \eta_2, \eta_3 \) become equal to zero. The average occupation numbers (6) describe in this case a partially ordered phase with space group \( D_{2h}(Z = 1) \), in which the cysshite groups occupy predominantly and with equal probability the positions

\[ n_{11} = n_{21} = n_{31} = n_{41} = \frac{a}{2} \eta_1, \]

\[ n_{12} = n_{22} = n_{32} = n_{42} = \frac{a}{2} \eta_2, \]

\[ n_{13} = n_{23} = n_{33} = n_{43} = \frac{a}{2} \eta_3, \]

\[ n_{14} = n_{24} = n_{34} = n_{44} = \frac{a}{2} \eta_4. \]

With further decrease of temperature, at \( T_a \) determined from the equation

\[ \ln \frac{2}{3} = \frac{4}{3} a \Delta \eta, \quad \Delta \eta = \frac{1}{T_a} - 1, \]

a second PT of second order occurs and is due to the appearance of the parameter \( \eta_2 \). The parameters \( \eta_1, \eta_3, \eta_4 \) and \( \eta_2 \) remain equal to zero below \( T_a \). Below \( T_a \), the functions describe a partially ordered phase \( D_{2h}(Z = 1) \), in which the CN groups occupy the positions

\[ n_{11} = n_{21} = n_{31} = n_{41} = \frac{1}{2} q_1, \]

\[ n_{12} = n_{22} = n_{32} = n_{42} = \frac{1}{2} q_2, \]

\[ n_{13} = n_{23} = n_{33} = n_{43} = \frac{1}{2} q_3, \]

\[ n_{14} = n_{24} = n_{34} = n_{44} = \frac{1}{2} q_4. \]

Finally, with further decrease of temperature, now already independently of the relation between constants \( a \) and \( b \), a third (second-order) PT takes place with simultaneous appearance of the parameters \( \eta_2 \) and \( \eta_3 \) (these parameters appear together, since (9) contains terms of the form \( \eta_2 \eta_3 \)). The functions (6) describe in this face a fully ordered phase \( D_{2h}(Z = 2) \), in which the CN groups occupy the positions

\[ n_{11} = n_{21} = n_{31} = n_{41} = \frac{1}{2} q_2, \]

\[ n_{12} = n_{22} = n_{32} = n_{42} = \frac{1}{2} q_2, \]

\[ n_{13} = n_{23} = n_{33} = n_{43} = \frac{1}{2} q_3, \]

\[ n_{14} = n_{24} = n_{34} = n_{44} = \frac{1}{2} q_4. \]

Thus, the following sequence of transition occurs in the considered case:

\[ \Omega_a^{(Z = 1)} = D_{2h}^{(Z = 2)} = \Omega_a^{(Z = 2)}. \]

B. \( 5 > a, \gamma > 1 \). The relations between \( a \) and \( \gamma \) are arbitrary. Moreover, it suffices to have only one of the parameters, \( a \) or \( \gamma \), larger than unity. Just as in case \( A \), a parameter \( \eta_2 \) arises at \( T_a = 3/4 \pm 2 \), with a jump \( \Delta \eta = 0, 5 \). With further lowering of the temperature, at \( T_a \), there appear simultaneously the remaining three parameters \( \eta_1, \eta_2, \eta_3 \), i.e., a PT into a fully ordered \( D_{2h}(Z = 2) \) phase takes place. The sequence of the PT is thus

\[ \Omega_a^{(Z = 1)} = \Omega_a^{(Z = 2)} = D_{2h}^{(Z = 2)} = \Omega_a^{(Z = 2)}. \]

C. \( a > 5, \gamma, y \). At this relation between the interaction constants, there are two PT in the model. The first one is of decreasing temperature is of first order and is connected with the simultaneous appearance of the parameters \( \eta_1, \eta_2, \eta_3 \). The parameters \( \eta_1, \eta_2 \) are equal to zero in this case. The functions (6) describe a partially ordered phase with space group \( D_{2h}(Z = 1) \), in which the CN molecules occupy predominantly and with equal probability the positions

\[ n_{11} = n_{21} = n_{31} = n_{41} = \frac{1}{2} q_1, \]

\[ n_{12} = n_{22} = n_{32} = n_{42} = \frac{1}{2} q_2, \]

\[ n_{13} = n_{23} = n_{33} = n_{43} = \frac{1}{2} q_3, \]

\[ n_{14} = n_{24} = n_{34} = n_{44} = \frac{1}{2} q_4. \]

This can be easily seen from the expansion (6), since it contains terms of the form \( \eta_1 \eta_2 \eta_3 \eta_4 \).

The aforementioned transition sequences have not been experimentally observed in the here-investigated family of crystals; we shall therefore not discuss their thermodynamic properties.

D. \( 1 > a, \delta, \gamma \). At this relation between the interaction constants, there are two PT in the model. The first one is of decreasing temperature is of first order and is connected with the simultaneous appearance of the parameters \( \eta_1, \eta_2, \eta_3, \eta_4 \). The relations between \( \beta, \gamma, \delta \) are different for each of the PTs. The functions (6) describe a partially ordered phase with space group \( D_{2h}(Z = 1) \), in which the CN molecules occupy predominantly and with equal probability the positions

\[ n_{11} = n_{21} = n_{31} = n_{41} = \frac{1}{2} q_1, \]

\[ n_{12} = n_{22} = n_{32} = n_{42} = \frac{1}{2} q_2, \]

\[ n_{13} = n_{23} = n_{33} = n_{43} = \frac{1}{2} q_3, \]

\[ n_{14} = n_{24} = n_{34} = n_{44} = \frac{1}{2} q_4. \]

This PT is of first order for the following reason: as already noted, we have assumed everywhere that the transition parameters corresponding to degenerate eigenvalues of the interaction matrices are equal. In this case this has led to identical vanishing of the coefficient of the fourth power of the expansion (5) in powers of \( \eta_1 \). Equations (5) and (9), however, contain terms of the type \( \eta_1^2 \eta_2 \), which lead in this case to a first-order transition, since the effective coefficient of \( \eta_1^2 \) turns out to be less than zero. It must be noted that above-noted vanishing of the coefficient of \( \eta_1^2 \) is a property of the model, and may not take place if the model is somehow modified. It seems to us however, that the model considered here takes full enough account of the real interactions in the cyanides of alkali metals, and that allowance for the additional interactions will not change the sign of the effective coefficient of \( \eta_1^2 \).

When the temperature is lowered further, a second-order PT takes place, simultaneously with the appea-
It must be noted that the phase transition at normal pressure \( Z = 1 \) was experimentally observed in the CrCN crystal at normal pressure and in the KCN and NaCN crystals at high pressure. It was established in experiment that the \( D_{1}^{a} \) phase is the axis of the cyanide group.

The first-order phase transition \( O_{d}^{a}(Z = 1) \rightarrow D_{1}^{a} \) (\( Z = 1 \)) was experimentally observed in the CrCN crystal at normal pressure and in the KCN and NaCN crystals at high pressure. It was established in experiment that the \( D_{1}^{a} \) phase is the axis of the cyanide group.

The temperature dependences of the transition parameters and of the specific heat, calculated from (5) and from the consistency equations, are shown in Figs. 2 and 3, which show for comparison the experimental temperature dependences of these quantities for the crystals KCN and NaCN. The interaction constants and the changes of the entropy calculated from them are given together with the experimental values in the table.

### Table I.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Theory</th>
<th>Experiment</th>
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<tbody>
<tr>
<td>KCN</td>
<td></td>
<td></td>
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<tr>
<td>NaCN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsCN</td>
<td></td>
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</tbody>
</table>

#### Parameters

- \( \Delta \) (theory) vs. \( \Delta \) (experiment)
- \( S_{n} \) (theory) vs. \( S_{n} \) (experiment)
- Interaction constants in function of \( T_{c} \)

The jumps of the entropy and of the latent heat of the transition are

\[ \Delta S = 3 \ln 2 - 1 \ln 2 \]

With further decrease of the temperature, a second PT of second order takes place, with simultaneous appearance of the parameters \( t_{1} \) and \( t_{2} \) into a fully ordered phase \( D_{1}^{a} \) (\( Z = 1 \)).

The jump of the transition parameter is \( \Delta t_{1} = 2 \). The difference between the transition temperature and the Curie-Weiss temperature is \( t_{1} - t_{2} = 2 \mu / 4 \ln 3 - 1 \).

The jumps of the entropy and of the latent heat of the transition are

\[ \Delta S = 3 \ln 2 - 1 \ln 2 \]

With further decrease of the temperature, a second PT of second order takes place, with simultaneous appearance of the parameters \( t_{1} \) and \( t_{2} \) into a fully ordered phase \( D_{1}^{a} \) (\( Z = 1 \)).

The first-order phase transition \( O_{d}^{a}(Z = 1) \rightarrow D_{1}^{a} \) (\( Z = 1 \)) was experimentally observed in the CrCN crystal at normal pressure and in the KCN and NaCN crystals at high pressure. It was established in experiment that the \( D_{1}^{a} \) phase is the axis of the cyanide group.

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With further decrease of the temperature, a second PT of second order takes place, with simultaneous appearance of the parameters \( t_{1} \) and \( t_{2} \) into a fully ordered phase \( D_{1}^{a} \) (\( Z = 1 \)).

The first-order phase transition \( O_{d}^{a}(Z = 1) \rightarrow D_{1}^{a} \) (\( Z = 1 \)) was experimentally observed in the CrCN crystal at normal pressure and in the KCN and NaCN crystals at high pressure. It was established in experiment that the \( D_{1}^{a} \) phase is the axis of the cyanide group.

\[ \Delta S = 3 \ln 2 - 1 \ln 2 \]
is oriented in these crystals along a body diagonal of the cube, but the CN group remains disordered relative to the "head-tail" motion. However, no second PT into an ordered phase was observed in CsCN down to lower temperatures, although one cannot rule out the presence of quantum tunneling effects in these crystals, and that a disordered D_{4h} phase is preserved also at $T=0$. The temperature dependences of the transition parameters and of the specific heat for the transition sequence $O_3^+(Z=1) \rightarrow D_{4h}^+(Z=1) \rightarrow C_{1v} (Z=1)$ are shown in Fig. 4, which shows also for comparison the known experimental data. The other thermodynamic characteristics of the transitions, together with the experimental data for the CsCN crystal, are listed in the table.

3. Phase transitions in RbCN. As noted in the Introduction, the PT in RbCN is accompanied by quadrupling of the unit-cell volume. To allow for this in the investigation of PT in our model, we must take into account the wave vectors

$$k = 0, k = a/(a + b + c), k = a/(a + b), k = a/(a + b + c).$$

The expressions for the average occupation numbers in terms of the transition parameter are analogous in this case to (6), and are omitted because of their complexity.

The free energy is of the form

$$F = \frac{1}{2} \sum_{ijkl} \left[ a_{ijkl} \psi_{i}(k) \psi_{j}(k) + b_{ijkl} \psi_{i}^{*}(k) \psi_{j}^{*}(k) \right] + \sum_{i} \left[ c_{i} \psi_{i}(k) \psi_{i}^{*}(k) + d_{i} \psi_{i}(k) + e_{i} \psi_{i}^{*}(k) + f_{i} \right],$$

where

$$\psi_{i}(k) = \frac{1}{Z} \int \exp \left[ \frac{1}{k} \left( a_{i} \psi_{i}(k) + b_{i} \psi_{i}(k) + c_{i} \psi_{i}^{*}(k) + d_{i} \psi_{i}(k) + e_{i} \psi_{i}^{*}(k) + f_{i} \right) \right].$$

The consistency equations for the transition parameters $\lambda$ and $\gamma$, can be determined from (11) in accord with the condition

$$\delta_{i} \partial_{k} a_{i} \Delta_{i} = 0.$$

We do not report here the investigations of the possible PT sequences as functions of the relations between the interaction constants in (11). We note only that an analysis of (11) and of the self-consistency equations shows that in our model there is no direct PT into an ordered phase with quadrupling of the unit-cell volume. An exception is the case of equality of the constants $a = b > 1, c, d; a = c > 1, b, d, h = d > 1, a, c, e; c = d > 1, a, b, e,$ which seems unlikely to us for the real situation in RbCN.

We have investigated possible PT with observable unit-cell volume quadrupling in RbCN for the cases of an eight-minimum potential, in structures of both the CsCl and NaCl type. Just as in the case of the twelve-minimum potential, no immediate PT with quadrupling of the unit-cell volume is observed, with the exception of the particular case when certain interaction constant are equal. Thus, the PT experimentally observed in RbCN cannot be explained within the framework of our model.

4. CONCLUSION

From a comparison of the theoretical and experimental thermodynamic characteristics of the PT in KCN, CsCN, and NaCN (see Figs. 2-4 and the table) it can apparently be assumed that the statistical model proposed in this paper describes sufficiently accurately the features of the PT in these crystals and can serve as a basis for more detailed research.

As noted in the Introduction, the first transitions in cyanides of alkali metals, in decreasing order in temperature, are ferroelastic, i.e., the shear elastic constant softens in these transitions. In the initial Hamiltonian of our model we have described only the orientational degrees of freedom, and took no account of their interaction with the acoustic phonons. This connection with the elastic strains can be phenomenologically taken into account in standard fashion, by adding appropriate terms to (5) and (7). We wish to call attention to the fact that in this model, in contrast to those discussed by others, there is realized the first-order PT $O_3^+(Z=1) \rightarrow D_{4h}^+(Z=1)$ (which was observed experimentally in KCN and NaCN) even if no account is taken of the interaction of the transition parameters with the acoustic phonons. As for an explanation of the phase transition in RbCN our model must apparently be refined. At the present time, however, there are in our opinion no experimental data for this refinement. In particular, it has not been established in experiment with sufficient reliability whether the CN groups in RbCN are fully or partly ordered below 110 K.

As already noted in Sec. 3, if the PT in RbCN is connected with ordering of the CN groups, and if the

FIG. 4. Temperature dependences of the order parameters and of the specific heat for the crystal CsCN (solid-theory, points-experiment).
Polaron effects and exchange interaction in magnetic dielectrics with Jahn-Teller ions

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We consider the influence of electron-phonon interaction on the band width and on the values of the exchange integrals in magnets containing ions with orbital degeneracy (Jahn-Teller ions). The case of electrons on a doubly degenerate level, which interact with a nondegenerate phonon mode, is investigated in detail. The analysis is based on the Hubbard model with phonons taken into account. It is shown that a polaron narrowing of the bands takes place and depends, generally speaking, on the manner of occupation of the orbitals. Those terms of the effective exchange Hamiltonian which correspond to virtual transitions without a change in the orbital state are not significantly renormalized, while terms that include transitions between different orbitals acquire, on account of the phonons, exponential suppression factors that depend on the temperature. This leads to a strong decrease of the effective exchange integrals with temperature, as observed experimentally in a number of magnetic dielectrics with Cu$^{2+}$. 

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1. INTRODUCTION

An interesting special class of magnetic substances comprises compounds in which the state of the magnetic ions is characterized by orbital as well as spin degeneracy. The ions whose ground state turns out to be degenerate in a crystal field of sufficiently high symmetry are called Jahn-Teller (JT) ions (these include, e.g., the ions Cu$^{2+}$, Mn$^{2+}$, and Cr$^{3+}$ in an octahedral surrounding). According to the Jahn-Teller