

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.

<sup>1</sup>We emphasize that to obtain self-consistent results it is necessary to introduce at least two parameters,  $n$  and  $n_0$ . By introducing only one parameter it is impossible to satisfy all the self-consistency conditions. The quantities  $n$  and  $n_0$  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.

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## 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 entropies are calculated. The results of the calculation are compared with the experimental data for the crystals KCN, NaCN, CsCN, and RbCN.

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### 1. INTRODUCTION

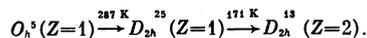
Structural phase transitions (PT) in crystals of the type MeCN (Me = K, Na, Rb, Cs) have been the subject of many studies. It has been experimentally established that the transitions in these crystals are connected with the ordering of the cyanide groups. Potassium cyanide (KCN) has at room temperature 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,<sup>1</sup> but move in a potential with a large number of minima. The published opinions concerning the form of this potential vary,<sup>1-6</sup> since it is impossible to dis-

tinguish 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  $D_{2h}^{25}$  ( $Z = 1$ ), 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,<sup>7,10,11</sup> Finally, at  $T = 83$  the CN undergoes one more second-order PT into a fully ordered state with space group  $D_{2h}^{13}$  and two molecules per unit cell.<sup>2,8-10</sup>

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



Cesium cyanide has at room temperature a structure of the CsCl type [space group  $O_h^1(Z=1)$ ].<sup>3</sup> In this phase, the cyanide groups move in an eight-minimum potential. At  $T \approx 193$  K CsCN undergoes a first-order phase transition without a change in the unit cell into a rhombohedral phase ( $D_{3d}^5(Z=1)$ ). In this phase the CN molecules are oriented along the [111] body diagonal of the cube, but the "head-tail" motion remains.<sup>3</sup> 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  $T \approx 110$  K a first-order phase transition into a monoclinic phase with space group  $C_2^4(Z=4)$ . 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.<sup>4,13</sup> Sugisaki *et al.*<sup>3</sup> suggest that the cyanide groups in the  $C_2^4$  phase are ordered 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.<sup>14</sup> 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,<sup>5,8,9</sup> specific heat,<sup>1-3</sup> NMR,<sup>4</sup> and others. Soft acoustic modes were observed in the investigations of the elastic properties.<sup>10,13</sup>

There are not many theoretical descriptions of the PT in alkali-metal cyanides.<sup>2,10,13,15,16</sup> Some of them<sup>2,10,13,15</sup> 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  $C_{44}$  and  $C_{11} - C_{12}$  depend linearly on  $(T - T_c)$ , 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.*,<sup>16</sup> 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  $D_{2h}^{25}$  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.*<sup>16</sup> use the value  $\Delta = 7.4 \times 10^{-3}$  eV measured<sup>17</sup> at  $T \sim 85$  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  $D_{2h}^{25}$  and  $D_{2h}^{13}$  phases are oriented along a planar diagonal of the cubic cell, it can be proposed that the intermediate states in the  $D_{2h}^{25}$  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  $D_{2h}^{25}$  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.<sup>1-3</sup> 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  $O_h^3$  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<sup>18</sup>

$$H = -\frac{1}{2} \sum_{ij} V_{ij}(\mathbf{R}-\mathbf{R}') n_i(\mathbf{R}) n_j(\mathbf{R}') - \sum_{ij} V_{ij}(\mathbf{R}-\mathbf{R}') n_i(\mathbf{R}) C_j(\mathbf{R}'), \quad (1)$$

where  $C_i(\mathbf{R}) = 1$  if the CN group on the site  $\mathbf{R}$  is in the

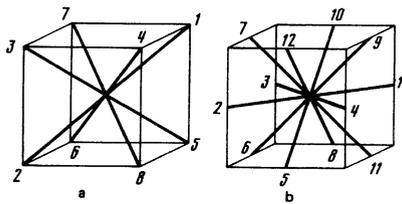


FIG. 1. a) Eight equally probable positions of a CN group in the high-symmetry phase  $O_h^1$  in a structure of the CsCl type. b) Twelve equally probable positions of the CN group in the high symmetry phase  $O_h^5$  in a structure of the NaCl type.

position  $i$  (with  $i=1, 2, \dots, 12$  in case  $a$  and  $i=1, 2, \dots, 8$  in case  $b$ ) and  $C_i(\mathbf{R})=0$  in the other cases. Next,  $n_i(\mathbf{R})=\langle C_i(\mathbf{R}) \rangle$  is the probability of finding the CN group on the site  $\mathbf{R}$  in the state  $i$ , and  $V_{ij}(\mathbf{R}-\mathbf{R}')$  is the matrix of the paired interaction between CN groups in the states  $i$  and  $j$  and on the sites  $\mathbf{R}$  and  $\mathbf{R}'$ .

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

$$F = \sum_{\mathbf{R}} \left\{ \frac{1}{2} \sum_{ij} V_{ij}(\mathbf{R}-\mathbf{R}') n_i(\mathbf{R}) n_j(\mathbf{R}') - T \ln \sum_j \exp \left( -\beta \sum_i V_{ij}(\mathbf{R}-\mathbf{R}') n_i(\mathbf{R}) \right) \right\}, \quad (2)$$

where  $\beta=1/T$ .

The average occupation numbers  $n_i(\mathbf{R})$  are expressed in terms of the parameters  $\eta_{\alpha,s}$  of the transition as follows<sup>18</sup>:

$$n_i(\mathbf{R}) = \sum_{\alpha,s} \eta_{\alpha,s} \sum_{\mathbf{k}_{i,s}} \psi_{\alpha}(\mathbf{k}_{i,s}) U_{\alpha}^i(\mathbf{k}_{i,s}) \exp(i\mathbf{k}_{i,s}\mathbf{R}), \quad (3)$$

where  $U_{\alpha}^i(\mathbf{k}_{i,s})$  are the eigenvectors of the interaction matrix

$$V_{ij}(\mathbf{k}_{i,s}) U_{\alpha}^i(\mathbf{k}_{i,s}) = \lambda_{\alpha}(\mathbf{k}_{i,s}) U_{\alpha}^j(\mathbf{k}_{i,s}), \quad (4)$$

$$V_{ij}(\mathbf{k}_{i,s}) = \sum_{\mathbf{R}, \mathbf{R}'} V_{ij}(\mathbf{R}-\mathbf{R}') \exp(i\mathbf{k}_{i,s}\mathbf{R}),$$

$\mathbf{k}_{i,s}$  is the wave vector in the first Brillouin zone.

The numbers  $\psi_{\alpha}(\mathbf{k}_{i,s})$  are determined from the condition that in the fully ordered state, when all  $\eta_{\alpha,s}=1$ , the average occupation numbers  $n_i(\mathbf{R})$  take on one of the two values, 0 or 1. The transition parameters are obtained from the consistency equations, which coincide with the condition  $\partial F/\partial \eta_{\alpha,s}=0$  for the minimum of the free energy.

Since the second PT (in order of decreasing temperature) in KCN and NaCN crystals involves a doubling of the unit-cell volume, we confine ourselves hereafter for the case  $a$ , to an investigation of the PT that are connected with the vectors  $\mathbf{k}_0=0$  and  $\mathbf{k}_1=(1/2)(\mathbf{b}_1+\mathbf{b}_2)$ . In case  $b$  we confine ourselves to the PT connected only with  $\mathbf{k}_0=0$ , since in CsCN (and in KCN under pressure) there is known from experiment only one transition  $O_h^1 \rightarrow D_{3d}^5$  without change of the unit-cell volume.

To find the explicit forms of (2) and (3) we must know the eigenvalues and eigenvectors of the interaction matrices, whose form is determined by the symmetry

of the twelve (eight) equilibrium positions of the CN group (see Fig. 1) and by the crystallographic symmetry  $O_h^1$  ( $O_h^5$ ) of the system. Standard calculations yield an expression for the free energy. In case  $a$

$$f_1 = \eta_1^2 + \alpha \eta_2^2 + \gamma \eta_3^2 + \delta \eta_4^2 - t \ln \{ 8 \exp(-\beta \delta \eta_4) \text{ch } \beta(\alpha \eta_2 - \gamma \eta_3) + 2 \exp(2\beta \delta \eta_4) [\exp(2\beta \eta_1) \text{ch } 2\beta(\alpha \eta_2 + \gamma \eta_3) + \exp(-2\beta \eta_1)] \}, \quad (5)$$

where

$$\begin{aligned} \alpha &= \lambda_1^{-1} [V_{11}(\mathbf{k}_1) - V_{12}(\mathbf{k}_1) + 2(V_{1,10}(\mathbf{k}_1) - V_{19}(\mathbf{k}_1))], \\ \gamma &= \lambda_1^{-1} [V_{11}(\mathbf{k}_1) - V_{12}(\mathbf{k}_1) - 2(V_{1,10}(\mathbf{k}_1) - V_{19}(\mathbf{k}_1))], \\ \delta &= 2^{1/2} \lambda_1^{-1} [V_{11}(0) + V_{12}(0) + 2(V_{1,10}(0) - V_{1,10}(0) - V_{1,9}(0))], \\ \lambda_1 &= V_{11}(0) + V_{12}(0) - 2V_{1,9}(0), \quad t=8T/\lambda_1 \end{aligned}$$

and  $V_{ij}(\mathbf{k}_1)$  and  $V_{ij}(\mathbf{k}_0)$  are the components of the twelve-dimensional matrices of the interaction between the CN groups in a structure of the NaCl type. The average occupation numbers are expressed in terms of the transition parameters as follows:

$$\begin{aligned} n_1 &= 1/12 + 1/4 \eta_1 + 1/6 \eta_4 + 1/4 (\eta_2 + \eta_3) \varphi_1, \\ n_2 &= 1/12 + 1/4 \eta_1 + 1/6 \eta_4 - 1/4 (\eta_2 + \eta_3) \varphi_1, \\ n_3 &= n_4 = 1/12 - 1/4 \eta_1 + 1/6 \eta_4, \\ n_5 &= n_6 = n_9 = n_{11} = 1/12 - 1/12 \eta_1 + 1/6 (\eta_2 - \eta_3) \varphi_1, \\ n_8 &= n_7 = n_{10} = n_{12} = 1/12 - 1/12 \eta_1 - 1/6 (\eta_2 - \eta_3) \varphi_1. \end{aligned} \quad (6)$$

In case  $b$

$$f_2 = \xi_1^2 + 3\mu \xi_2^2 + 3\lambda \xi_3^2 - t \ln 2 [\exp(6\beta \mu \xi_2) \times \text{ch } 2\beta(\xi_1 + 3\lambda \xi_3) + 3 \exp(-2\beta \mu \xi_2) \text{ch } 2\beta(\xi_1 - \lambda \xi_3)], \quad (7)$$

where

$$\begin{aligned} \mu &= (V_{11} + V_{12} - V_{17} - V_{13})/\alpha_1, \\ \lambda &= (V_{11} - V_{12} - V_{13} + V_{17})/\alpha_1, \\ \alpha_1 &= V_{11} + 3(V_{13} - V_{17}) - V_{12}, \\ t &= 16T/\alpha_1, \end{aligned}$$

$V_{ij} \equiv V_{ij}(\mathbf{k}_0=0)$  are the components of the eight-dimensional matrix of the paired interaction between the CN groups in a structure of the CsCl type. In this case the average occupation numbers are given by

$$\begin{aligned} n_1 &= 1/8 + 1/8 \xi_1 + 3/8 \xi_2 + 3/8 \xi_3, \quad n_2 = 1/8 - 1/8 \xi_1 + 3/8 \xi_2 - 3/8 \xi_3, \\ n_3 &= n_6 = n_9 = 1/8 + 1/8 \xi_1 - 1/8 \xi_2 - 1/8 \xi_3, \quad n_4 = n_5 = n_7 = 1/8 - 1/8 \xi_1 - 1/8 \xi_2 + 1/8 \xi_3. \end{aligned} \quad (8)$$

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 interaction matrix has three threefold 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  $T_0$  and remain equal at all temperatures below  $T_0$ . This situation, however, cannot take place if account 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. 19).

### 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)

$$\partial f_i / \partial \eta_i = 0, \quad \partial f_i / \partial \xi_i = 0.$$

The consistency equations always have a trivial solution: all  $\eta_i$  (or  $\xi_i$ ) are equal to zero. This solution describes the high-symmetry phase ( $O_h^5$  and  $O_h^4$  in cases *a* and *b*, respectively). Starting with certain temperatures, 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

$$\begin{aligned} \Delta f_i = & (1 - 2/3\beta) \eta_i^2 + \alpha(1 - 2/3\alpha\beta) \eta_i^2 + \gamma(1 - 2/3\gamma\beta) \eta_i^2 \\ & + \delta(1 - \delta\beta) \eta_i^2 - 1/3\beta^2 \delta^2 \eta_i^2 - 1/3\beta^2 \delta \eta_i^2 \eta_i \\ & - 2/3\beta^2 (\alpha\eta_i + \gamma\eta_i)^2 \eta_i - 1/3\beta^2 \delta (\alpha^2 \eta_i^2 + \gamma^2 \eta_i^2) \eta_i \\ & - 2\beta^2 \delta \alpha \gamma \eta_i \eta_i \eta_i + 1/3\delta^3 \eta_i^3 + \dots \end{aligned} \quad (9)$$

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.  $\delta > 1 > \alpha, \gamma$ . The Curie-Weiss temperature is defined as  $t_{c1} = \delta$ . Since, however, (6) and (7) contain the third-degree invariant  $\eta_4^3$ , it follows that a first-order transition arises at  $t_{01} = 3\delta/4 \ln 2$  with a jump  $\Delta\eta_4 = 0.5$ . The corresponding entropy jump is  $\Delta S = \ln 3 - (1/3) \ln 2$ . Below  $t_{01}$ , the parameters  $\eta_1, \eta_2$ , and  $\eta_3$  become equal to zero. The average occupation numbers (6) describe in this case a partially ordered phase with space group  $D_{4h}^{17}(Z=1)$ , in which the cyanide groups occupy predominantly and with equal probability the positions

$$\begin{aligned} n_1 = n_2 = n_3 = n_4 = 1/12 + 1/6\eta_4, \\ n_5 = n_6 = n_7 = n_8 = n_9 = n_{10} = n_{11} = n_{12} = 1/12 - 1/12\eta_4. \end{aligned}$$

With further decrease of temperature, at  $t_{c2}$  determined from the equation

$$\ln \frac{2}{2\beta_{c2} - 1} = 3\beta_{c2}\delta, \quad \beta_{c2} = \frac{1}{T_{c2}}, \quad \eta_i = 1,$$

a second PT of second order occurs and is due to the appearance of the parameter  $\eta_1$ . The parameters  $\eta_2$  and  $\eta_3$  remain equal to zero below  $T_{c2}$ . Below  $t_{c2}$ , the functions describe a partially ordered phase  $D_{2h}^{25}(Z=1)$ , in which the CN groups occupy the positions

$$\begin{aligned} n_1 = n_2 = 1/12 + 1/6\eta_1 + 1/6\eta_i, \quad n_3 = n_4 = 1/12 - 1/6\eta_1 + 1/6\eta_i, \\ n_i = 1/12 - 1/12\eta_i, \quad (i=5, 6, 7, 8, 9, 10, 11, 12). \end{aligned}$$

Finally, with further decrease of temperature, now already independently of the relation between constants  $\alpha$  and  $\gamma$ , 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  $\eta_1\eta_2\eta_3$  and  $\eta_2\eta_3\eta_4$ ). The functions (6) describe in this case a fully ordered phase  $D_{2h}^{13}(Z=2)$ ,

in which the CN groups occupy the positions

$$\begin{aligned} n_i(0) = 1, \quad n_i(\tau) = 0 \quad (i=2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12), \\ n_2(\tau) = 1, \quad n_i(\tau) = 0 \quad (i=1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12) \end{aligned}$$

( $\tau$  is the parameter of the cell of the cubic phase  $O_h^5$ ).

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

$$O_h^5 \rightarrow D_{4h}^{17} \rightarrow D_{2h}^{25} \rightarrow D_{2h}^{13}(Z=2).$$

B.  $\delta > \alpha, \gamma > 1$ . The relations between  $\alpha$  and  $\gamma$  are arbitrary. Moreover, it suffices to have only one of the coefficients,  $\alpha$  or  $\gamma$ , larger than unity. Just as in case A, a parameter  $\eta_4$  arises at  $t_{01} = 3\delta/4 \ln 2$ , with a jump  $\Delta\eta_4 = 0.5$ . With further lowering of the temperature, at  $t_{c2}$ , there appear simultaneously the remaining three parameters  $\eta_1, \eta_2$  and  $\eta_3$ , i. e., a PT into a fully ordered  $D_{2h}^{13}$  phase takes place. The sequence of the PT is thus

$$O_h^5(Z=1) \rightarrow D_{2h}^{17}(Z=1) \rightarrow D_{2h}^{13}(Z=2).$$

C.  $\alpha > \delta, \gamma, 1$  or  $\gamma > \delta, \alpha, 1$ . In this case there occurs one first-order PT directly into an ordered phase  $D_{2h}^{13}(Z=2)$ . All the parameters arise simultaneously. This can be easily seen from the expansion (9), since it contains terms of the form  $\eta_2^2\eta_1, \eta_2^2\eta_4, \eta_3^2\eta_1, \eta_3^2\eta_4, \eta_1\eta_2\eta_3, \eta_2\eta_3\eta_4$ .

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.  $1 > \alpha, \delta, \gamma$ . At this relation between the interaction constants, there are two PT in the model. The first in order of decreasing temperature is of first order and is connected with the simultaneous appearance of the parameters  $\eta_1$  and  $\eta_4$ . The parameters  $\eta_2$  and  $\eta_3$  are equal to zero in this case. The functions (6) describe a partially ordered phase with space group  $D_{2h}^{25}(Z=1)$ , in which the CN molecules occupy predominantly and with equal probability the positions

$$\begin{aligned} n_1 = n_2 = 1/12 + 1/6\eta_1 + 1/6\eta_4, \quad n_3 = n_4 = 1/12 - 1/6\eta_1 + 1/6\eta_4, \\ n_i = 1/12 - 1/12\eta_i, \quad (i=5, 6, 7, 8, 9, 10, 11, 12). \end{aligned}$$

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  $\eta_1^2\eta_4$ , which lead in this case to a first-order transition, since the effective coefficient of  $\eta_1^4$  turns out to be less than zero. It must be noted that above-noted vanishing of the coefficient of  $\eta_1^4$  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  $\eta_1^4$ .

When the temperature is lowered further, a second-order PT takes place, simultaneously with the appear-

ance of the parameters  $\eta_2$  and  $\eta_3$ , into an ordered phase  $D_{2h}^{15}(Z=2)$ . This case corresponds to the experimentally observed situation in KCN and NaCN crystals at atmospheric pressure.

The temperature dependences of the transition parameters and of the specific heat, calculated from (5) and from the consistency equations, are shown in Fig. 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.

2. Transitions connected with the ordering of cyanide groups moving in an eight-minimum potential (case b). We investigate now the free energy (7) and the consistency equations. For the sake of clarity we again represent (7) by an expansion in the transition parameters:

$$\begin{aligned} \Delta f_2 = & (1-2\beta)\xi_1^2 + (1-2\beta\mu)\mu\xi_2^2 + (1-2\beta\lambda)\lambda\xi_3^2 \\ & - 8\beta^2[3\mu\lambda\xi_1\xi_2\xi_3 + 3\mu\lambda^2\xi_2\xi_3^2 + \mu^3\xi_2^2\xi_3^2] \\ & + 16\beta^3[3\mu^2\lambda\xi_1\xi_2\xi_3 + \lambda^3\xi_1\xi_3^3 + 3\mu^2\lambda^2\xi_2^2\xi_3^2] \\ & + 4\beta^3[\frac{1}{3}\xi_1^4 + \lambda^4\xi_3^4 + \mu^4\xi_2^4]. \end{aligned} \quad (10)$$

Depending on the relation between the interaction constants, three PT sequences are possible.

A.  $1 > \lambda, \mu$ . At  $t_{c1} = 2$  a parameter  $\xi_1$  appears with a second-order transition. The parameters  $\xi_2$  and  $\xi_3$  remain equal to zero below  $t_{c1}$ . The functions (8) describe a partially ordered phase  $T_d(Z=1)$  in which the CN molecules occupy with equal probability the positions  $n_1 = n_3 = n_6 = n_8 > n_i$  ( $i = 2, 4, 5, 7$ ). With further decrease of temperature, a first order transition into a fully ordered phase  $C_{3v}^5(Z=1)$  takes place simultaneously with appearance of the parameters  $\eta_2$  and  $\eta_3$ . It must be noted that the phase  $C_{3v}^5$  is polar and the crystal should have ferroelectric properties in this case.

B.  $\lambda > 1, \mu$ . At this relation between the interaction constants there is only one PT into the fully ordered

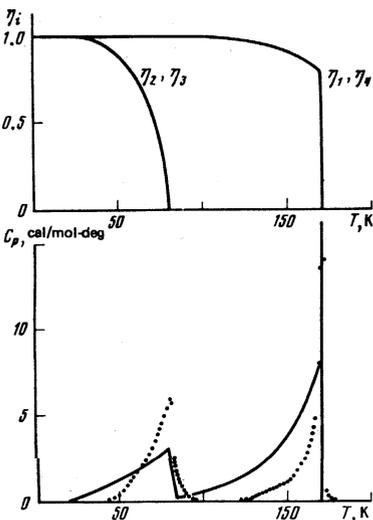


FIG. 2. Temperature dependences of the order parameters and of the specific heat for the KCN crystal (solid-theory, points-experiment<sup>1</sup>).

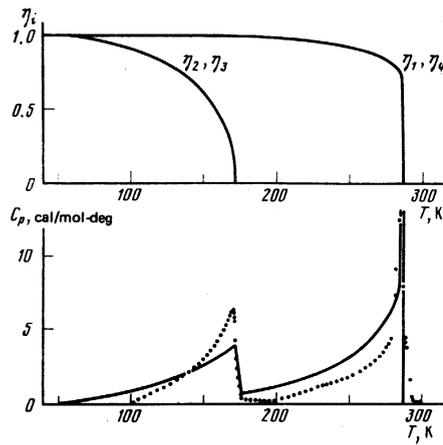


FIG. 3. Temperature dependences of the order parameters and of the specific heat for the NaCN crystal (solid-theory, points-experiment<sup>2</sup>).

phase  $C_{3v}^5(Z=1)$  with simultaneous appearance of all three parameters of the transition (see (10)).

We do not know of any experimental data to indicate that is observed a PT corresponding to cases A and B is observed in the considered family of crystals. Therefore, just as in cases A to C in Sec. 1 above, we do not present here the calculated thermodynamic characteristics of the transitions. They can be easily obtained from (7).

C.  $\mu > 1, \lambda$ . In this case a first-order phase transition takes place at  $t_{01} = 8\mu/3$  into a partially ordered phase  $D_{3d}^5(Z=1)$ , in which the CN groups occupy with equal probability positions  $n_1 = n_i$  ( $i = 3, 4, 5, 6, 7, 8$ ). The jump of the transition parameter is  $\Delta\xi_2 = 2/3$ . The difference between the transition temperature and the Curie-Weiss temperature is  $t_{01} - t_{c1} = 2\mu[4/3 \ln 3 - 1]$ . The jumps of the entropy and of the latent heat of the transition are

$$\Delta S = 3 \ln 2 - \frac{1}{2} \ln 3; \quad Q = 4 \ln 2 / \ln 3 - \frac{1}{3}.$$

With further decrease of the temperature, a second PT of second order takes place, with simultaneous appearance of the parameters  $\xi_1$  and  $\xi_2$  into a fully ordered phase  $C_{3v}^5(Z=1)$ .

The first-order phase transition  $O_h^1(Z=1) \rightarrow D_{3d}^5(Z=1)$  was experimentally observed in the CsCN crystal at normal pressure<sup>3</sup> and in the KCN and NaCN crystals at high pressure.<sup>14</sup> It was established in experiment that in the  $D_{3d}^5$  phase the axis of the cyanide group

TABLE I.

	NaCN		KCN		CsCN	
	Theory	Experiment	Theory	Experiment	Theory	Experiment
$T_{01}$ , K	287.7	287.7	168.3	168.3	193	193
$T_{c1}$ , K	172	172	82.9	82.9	13	-
$\Delta S$ , cal/mol-deg	2.02	2.73	2.02	2.01	3	2.04
$\Delta S_1$ , cal/mol-deg	3.5	2.8	3.5	2.01	2.8	2.6
$\Delta S_2$ , cal/mol-deg	1.38	1.21	1.38	1.32	1.38	-
Interaction constants in fractions of $T_{01}$	$\left\{ \begin{array}{l} 9.3 = \lambda_1 \\ 1.16 = \alpha\lambda_1 \\ 1.27 = \gamma\lambda_1 \\ 6.2 = \frac{3}{2}\delta\lambda_1 \end{array} \right.$		$\left\{ \begin{array}{l} 9.3 = \lambda_1 \\ 0.775 = \alpha\lambda_1 \\ 1.116 = \gamma\lambda_1 \\ 6.2 = \frac{3}{2}\delta\lambda_1 \end{array} \right.$		$\left\{ \begin{array}{l} 0.158 = \alpha_1\lambda \\ 6.6 = \alpha_1\mu \\ 0.145 = \alpha_1 \end{array} \right.$	

is oriented in these crystals along a body diagonal of the cube, but the CN group remains disordered relative to the "head-tail" motion.<sup>3</sup> However, no second PT into an ordered phase was observed in CsCN down to  $\approx 15$  K. It appears that this transition takes place at lower temperatures, although one cannot rule out the presence of quantum tunneling effects in these crystals, and that a disordered  $D_{3d}^5$  phase is preserved also at  $T=0$ . The temperature dependences of the transition parameters and of the specific heat for the transition sequence  $O_h^1(Z=1) \rightarrow D_{3d}^5(Z=1) \rightarrow C_{3v}^5(Z=1)$  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

$$\mathbf{k}_0=0, \mathbf{k}_1=\frac{1}{2}(\mathbf{b}_1+\mathbf{b}_2), \mathbf{k}_2=\frac{1}{2}\mathbf{b}_3, \mathbf{k}_3=\frac{1}{2}(\mathbf{b}_1+\mathbf{b}_2+\mathbf{b}_3).$$

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

$$\begin{aligned} f_3 = & \theta_1^2 + \frac{1}{2}a\theta_2^2 + \frac{1}{2}b\theta_3^2 + \frac{1}{2}c\theta_4^2 + \frac{1}{2}d\theta_5^2 + \frac{2}{3}e\eta_1^2 \\ - & T \ln \{ 4 \exp(-\frac{2}{3}\beta e\eta_1) [ \text{ch } \beta(a\theta_2 - d\theta_5) + \text{ch } \beta(b\theta_3 - c\theta_4) ] \\ & + 2 \exp(\frac{1}{3}\beta e\eta_1) [ \exp(2\beta\theta_1) \text{ch } \beta(a\theta_2 + b\theta_3) \\ & + \text{ch } \beta(a\theta_2 + d\theta_5) + \exp(-2\beta\theta_1) \text{ch } \beta(a\theta_2 - b\theta_3 - c\theta_4 + d\theta_5) ] \}, \end{aligned} \quad (11)$$

where

$$\begin{aligned} a = & (V_{11}(\mathbf{k}_2) - V_{14}(\mathbf{k}_2) + 2(V_{12}(\mathbf{k}_2) - V_{13}(\mathbf{k}_2)))/\lambda_2(\mathbf{k}_2), \\ b = & (V_{11}(\mathbf{k}_1) - V_{14}(\mathbf{k}_1) + 2(V_{12}(\mathbf{k}_1) - V_{13}(\mathbf{k}_1)))/\lambda_2(\mathbf{k}_1), \\ c = & (V_{11}(\mathbf{k}_1) - V_{14}(\mathbf{k}_1) - 2(V_{12}(\mathbf{k}_1) - V_{13}(\mathbf{k}_1)))/\lambda_2(\mathbf{k}_1), \\ d = & (V_{11}(\mathbf{k}_2) - V_{14}(\mathbf{k}_2) - 2(V_{12}(\mathbf{k}_2) - V_{13}(\mathbf{k}_2)))/\lambda_2(\mathbf{k}_2), \\ e = & (V_{11}(\mathbf{k}_0) + V_{14}(\mathbf{k}_0) + 2V_{19}(\mathbf{k}_0) - 2(V_{12}(\mathbf{k}_0) + V_{13}(\mathbf{k}_0)))/\lambda_2(\mathbf{k}_0), \\ \lambda_2(\mathbf{k}_3) = & V_{11}(\mathbf{k}_3) + V_{14}(\mathbf{k}_3) - 2V_{19}(\mathbf{k}_3). \end{aligned}$$

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

$$\partial f_3 / \partial \theta_i = \partial f_3 / \partial \eta_i = 0.$$

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  $a=b>1, e, c, d; a=c>1, e, b, d; b=d>1, a, c, e; c=d>1, a, b, e$ , 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

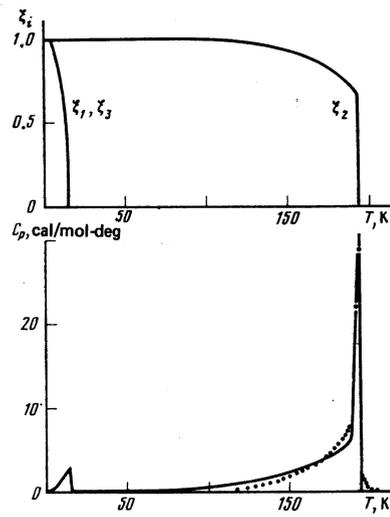


FIG. 4. Temperature dependences of the order parameters and of the specific heat for the crystal CsCN (solid-theory, points-experiment<sup>3</sup>).

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,<sup>10,15</sup> there is realized the first-order PT  $O_h^5(Z=1) \rightarrow D_{2h}^{25}(Z=1)$  (which was observed experimentally in KCN and NaCM) 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

volume of the unit cell is quadrupled in the low-symmetry ordered phase, then a phase transition directly into an ordered phase is impossible, and a sequence of two PT must take place. If, however, the space group  $C_w^4$  ( $Z=4$ ) established experimentally for RbCN below 110 K is correct, then the CN groups in this phase should be ordered relative to two equilibrium positions, and somewhere at low temperatures there should be a second PT into a fully ordered phase, in which the unit-cell volume should be least double the cell volume in the  $C_s^4$  ( $Z=4$ ) phase. It should be noted that an absence of a PT at low temperatures, by virtue of quantum tunneling effect, can likewise not be ruled out.

In our opinion, the PT in the RbCN crystal calls for a thorough experimental study. It is also of interest to obtain experimentally an answer to the question of the existence of a second PT in the CsCN crystal. If the CN groups in this crystal remain disorderd down to  $T=0$ , this may be evidence of strong tunneling of the C and N atoms relative to the "head-tail" states.

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## 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  $Cu^{2+}$ ,  $Mn^{3+}$ , and  $Cr^{2+}$  in an octahedral surrounding). According to the Jahn-Teller