CALCULATED STRUCTURES OF ASYMMETRIC MODIFICATIONS OF CYANOSPINELS

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Structural mechanisms of formation of low-symmetry phases of cyanospinels are described in terms of the phenomenological theory of phase transitions. These are examined for transitions from a spinel structure to two cubic F\(\overline{4}3c\) and four rhombohedral R\(\overline{3}c\) phases, induced by automorphic irreducible representations 9--2 and 9--3. Atomic coordinates and the symmetry types of occupied positions in asymmetric phases are determined. Criteria for discrimination between the two F\(\overline{4}3c\) as well as between the four R\(\overline{3}c\) phases are formulated. The structures of complex cyanides \(\text{Tl}_2\text{Zn(CN)}_4\) (F\(\overline{4}3c\), K\(_2\text{Zn(CN)}_4\), K\(_2\text{Hg(CN)}_4\), and Rb\(_2\text{Hg(CN)}_4\) (R\(\overline{3}c\)) are calculated. The displacements and irreducible representations inducing transitions from spinel structures to these phases are determined.

INTRODUCTION

In complex cyanides AB\(_2\)(CN)_4 (A = Zn, Cd, Hg; B = K, Rb, Tl), ferroelectric and other physical properties can spontaneously arise from structural transitions [1-6].

The crystal structure of these compounds at room temperature was first studied in [7]. The space group of the high-symmetry F\(d\overline{3}m\) phase was established by X-ray analysis; its structure was found to be close to the spinel structural type. More recently, details of cyanospinel structures were obtained by various physical methods of structure analysis [8-13]. Thus in [10], the structures of high- and low-symmetry modifications of K\(_2\)Hg(CN)_4 were determined by powder neutron diffraction analysis. At 298 K the crystals have a spinel structure, where Hg atoms occupy tetrahedral, and K atoms octahedral positions. Below the phase transition temperature the trigonally distorted modification with space group R\(\overline{3}c\) is formed. Upon transition to the low-temperature phase, tetrahedral complexes Hg(CN)_4 (adjacent along [111]) make \(\sim 7^\circ\) antiphase turns around the threefold axis; potassium ions are shifted by 0.01 nm. It was also found that the phase transition is characterized by the wave vector \(K = \{1/2, 1/2, 1/2\}\). The regular Hg(CN)_4 tetrahedra are trigonally distorted, leading to two types of cyanide anions in the ratio of 1:3 [8, 13].

The low-temperature form of Rb\(_2\)Hg(CN)_4 has space group R\(\overline{3}c\); this is also a slightly distorted spinel structure [6].

The structure of \(\text{Tl}_2\text{Zn(CN)}_4\), crystallizing from an aqueous solution at 300-310 K, was investigated by X-ray diffractometry in [12]. This compound has space group F\(\overline{4}3c\) and is a superstructure of the spinel structural type. Zinc atoms have a tetrahedral surrounding of cyano carbon atoms; thallium atoms have an octahedral environment of nitrogen atoms.

The aim of this work is to describe structural mechanisms underlying formation of all low-symmetry phases of cyanospinels using the phenomenological theory of second-order phase transitions and to give theoretical models of their structures.

Group-theoretical analysis of all available experimental data allows us to reveal critical irreducible representations (IR) inducing phase transformations in the analyzed compounds. These are four-dimensional IR 9--2 and 9--3 of the F\(d\overline{3}m\) group. The indices of IR and wave vector stars are given as in the reference book [14]. Irreducible representations 9--2 and 9--3 are linked by external automorphism. In this pair of IR, low-symmetry modifications have...
the same symmetry [15], and the structures of the corresponding phases differ. IR matrices are given in [15, 16]. Irreducible representations 9-2 and 9-3 do not enter the permutation representation of the crystal [16]. Therefore it is not the ordering of tetrahedral and octahedral cations or anions that is responsible for phase transitions in cyanospinels. The ordering of anions found experimentally [10, 12, 17, 18] is a secondary effect caused by the shifts of cations and anions (IR 9-2) or anions alone (IR 9-3). Indeed, the symmetrized second powers of IR 9-2 and 9-3 contain IR 11-7, which is responsible for the ordering of octahedral cations and anions. Detailed procedures for calculation of low-symmetry phase structures are given in [19, 20].

Figure 1 shows the diagram of all possible symmetrically diverse phases in the vicinity of a special multicritical point. Here we have a unique situation necessitating detailed theoretical investigations of structural mechanisms of low-symmetry phase formation: IR 9-2 and 9-3 induce four rhombohedral phases with the same space group R~c and two cubic phases with space group F43c. However, we do not know which of these correspond to the structures found experimentally. It is also of interest to reveal structural differences between these isosymmetric phases.

### STRUCTURAL MECHANISMS OF THE Fd3m → F43c PHASE TRANSITION

The Fd3m → F43c phase transition is induced by two four-dimensional IR 9-2 and 9-3 of the Fd3m group [14]. In both cases, the volume of the primitive cell of the Ed3m phase increases eightfold. The basis vectors of the F43c Bravais cell (A~i) (i = 1, 2, 3) are related to those of the Fd3m Bravais cell (A_i) as follows: A~i = 2A_i. Atomic coordinates in low-symmetry phases are (x, y, z)F~3c = 1/2(x, y, z)Fd3m + (1/4, 1/4, 1/4); unit cell parameters are aF43c = 2aFd3m; 64 AB2X4 units, i.e., A, B, and X atoms should occupy 64, 128, and 256 positions, respectively, in F43c phases.

The critical IR of the Fd3m phase enter the mechanical representation and hence Fd3m → F43c transitions are due to atomic displacements from positions 16(d) and 32(e) for IR 9-2 and from 32(e) for IR 9-3. These displacements lead to distortions of coordination polyhedra and changes in position symmetry of tetra- and octahedral cations. After transition to the F43c phase, positions 8(a) of A atoms (position symmetry T4(32m); coordinates 0, 0, 0) are split into three crystallographically nonequivalent types: 8(b) (T(23); 1/4, 1/4, 1/4), 24(d) (S4(4); 1/4, 0, 0), and 32(e') (C3(3); x1, x2, x3, x1, where x1 = 3/8). Positions 16(d) (D3d(32m); 5/8, 5/8, 5/8) of B cations are split into two nonequivalent types: 32(e'') (C3(3); x2, x2, x2, x2, where x2 = 1/16) and 96(h) (C1(1); x1, y1, z1, where x1 = 1/16, y1 = z1 = 3/16). In the Fd3m phase, X anions occupy positions 32(e) (C3(3m); x, x, x, where x = 3/8 + δ); in the F43c phase they are split to 32(e'') (C3(3); x3, x3, x3, x3, where x3 = 3/16 - δ/2), 32(e''') (C3(3); x4, x4, x4, x4, where x4 = 7/16 + δ/2), 96(h') (C1(1); x2, y2, z2, where x2 = 3/16 - δ/2, y2 = z2 = 1/16 + δ/2), and 96(h'') (C1(1); x3, y3, z3, where x3 = 7/16 + δ/2, y3 = z3 = 5/16 - δ/2).

The structure of the Fd3m phase may be represented as a close packing of polyhedral layers parallel to (001)