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Stacking Order and Disorder in Layered $K_3Me(CN)_6$ Compounds Studied by Diffuse X-Ray Scattering: A Realization of the ANNNI Model?

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Layered crystalline materials like $K_3Me(CN)_6$ with Me = Cr, Mn, Fe, Co may often exist in various polytypic forms, due to a variety of choices of layer stacking modes. For cases where the interlayer constellations can be limited to only two energetically almost equivalent ways, the buildup of the crystal may be described by a spin-1/2 Ising-like model. For the system presently being studied one can rationalize the layer stacking to a four-valued choice (i.e., a 1D 4-state Potts case), or use an Ising-like two-sublattice model. Previous diffraction studies of $K_3Me(CN)_6$ indicated that two long-range ordered structures prevailed, an orthohombic one named MDO_1, with one double layer per repetition unit, and a monoclinic one, MDO_2, with two double-layer units. Our studies reveal a more complex situation: The Fe material is for the most part of the MDO_2 type. But in addition, in some crystal samples, a hitherto unobserved phase also appears, with six double-layer repetition units, in fact a hybrid of MDO_1 and MDO_2. The Co material is for the most part of the MDO_2 type, but contains in addition a considerable contribution of stacking disorder, as evidenced by the presence of diffuse X-ray scattering lines. The lines do, however, contain distinct maxima, indicating the presence of several layer stacking modes with preference of two, three, four, five, and seven double-layer correlations. The findings can be qualitatively discussed in terms of the ANNNI model.

KEY WORDS: Polytypism; Ising model; Order–disorder; X-ray scattering.

1. INTRODUCTION

Many layered materials are known to exhibit what is known as *polytypism*. SiC is often taken as a prototype, of which about 50 different varieties have

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been identified, but several other groups of materials, such as CdI_2, TiS_2, clays, micas, and other minerals, exhibit polytypism.(1)

The basic origin of polytypism is simple. Polytypic materials may be viewed as built up of *rigid* (molecular) *layers* stacked on top of each other, with possibilities of *at least two energetically similar* interlayer *constellations*. An infinite number of stacking sequences is thus possible, giving rise to what may be termed natural superlattices when longrange ordered. For SiC, structural variants with more than 100 layers per repetition unit have been reported (one claim of a structure with 594 layer units).

In most cases the energetic differences among various superstructure types are small, and their formation is very sensitive to the small details of the crystal growth conditions (temperature gradients, reactor vessel walls, presence of impurity ions, etc.). Often one finds several polytypes in the same crystal batch. Since the stacking sequences are formed during the growth process, it is in most cases not possible to alter a given crystal, for instance, by heat treatment.

Crystal polytypism has attracted both experimentalists and theorists. From the theory point of view the field appears appealing because modeling of growth mechanism by Ising-like models seems natural. In particular Price, Yeomans, and coworkers(2-4) have devoted considerable effort to this end, by application of the axial next-nearest-neighbor Ising (ANNNI) model. It was realized at an early stage that interaction to nearest neighbors alone could not account for the great variety of types. On the contrary, the main result of the studies of the ANNNI model is that the addition of a second, competing interaction opens up a great wealth of possible stacking sequences.

In the present work we shall show from X-ray diffraction that the system $K_3Me(CN)_6$ in fact shows such richness of polytypism.

It is a pleasure for us to dedicate this work to the commemoration of Lars Onsager, whose famous solution of the 2D Ising model we were able to give the first experimental realization of 20 years ago.(5)

2. LAYER STRUCTURE OF $K_3Me(CN)_6$

The crystal structure of the series with Me = Cr, Mn, Fe, Co was studied in Göteborg by Vannerberg and coworkers.(6-8) The main feature is that the $Me(CN)_6^{3-}$ octahedra are bound via fairly strong K^+ bridges in the crystallographic **a** and **b** directions to form quite rigid (001) planes. Each plane is electrically approximately neutral, so that interlayer forces are mostly of van der Waals type [(001) is a cleavage plane].

From the X-ray diffraction pattern the Göteborg group found that the materials could be classified into two basic long-range structure types

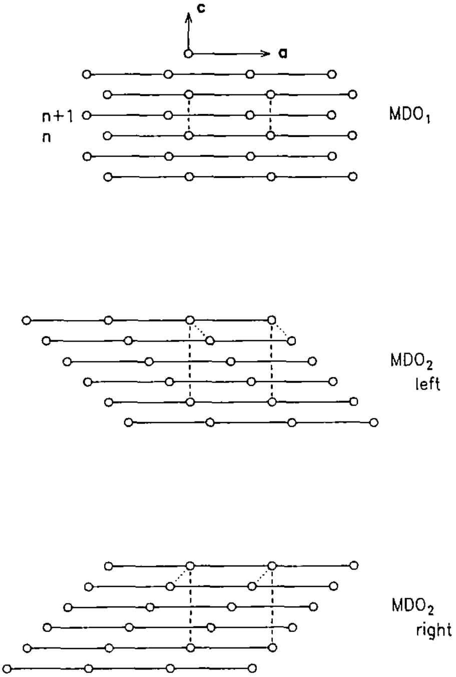

Fig. 1. Illustration of layer stacking modes MDO_1 and MDO_2. Orthorhombic unit cells are indicated by dashed lines, the primitive cell for MDO_2 is indicated by dots.

called MDO_1 and MDO_2 (MDO = "maximum degree of order"(9)). In MDO_1 the third layer is placed just at the same lateral position as the first layer (orthohombic structure), whereas in MDO_2 the third layer is shifted along **a** by half a lattice vector (monoclinic lattice), leading to a unit cell doubling along the layer stacking direction in this case (Fig. 1).

The presence of a diffuse scattering component in certain regions of *hkl* (for $h = \text{odd}$) was interpreted as due to the presence of a third phase, which would be stacking disordered.

The structure is such that nearest neighbor layers always are shifted $\pm\mathbf{a}/4$ relative to each other, the two ways being energetically equivalent. This fact would invite an Ising model treatment.

One must, however, take into account two separate sublattices, one for even-numbered layers, say, with $(1/4 \pm 1/4)\mathbf{a}$ (sublattice 1) and one for odd-numbered layers at $\pm 1/4\mathbf{a}$ (sublattice 2). This leads to *four* states per double layer, a situation which could be approached by a 1D four-state Potts model.(10) In Section 3 we describe the diffraction pattern in terms of a "two-sublattice Ising-type" picture.

3. THE ANNNI MODEL

The ANNNI model was introduced in 1981 by Elliott(10) to describe incommensurate magnetic phases in rare earths. It is characterized by the competition between nearest-neighbor and next-nearest-neighbor interactions, which may lead to complicated phase diagrams.

The model is also applied frequently to nonmagnetic statistical mechanical problems, like absorbed monolayers, intercalation compounds, and charge density waves (see Bak(11) for a review), and to polytypism in minerals.(2–4) For the latter case one identifies structural units, like layers, whose position or orientation may take one of two choices, denoted by a pseudo spin variable $S_n = \pm 1$. The Hamiltonian is very simple,

$$H = H_0 + H_{\mathrm{nn}} + H_{\mathrm{nnn}} \tag{1}$$

where H_0 is the noninteracting units contribution, and

$$H_{\mathrm{nn}} = -J_1 \sum_{nn'} S_n S_{n'} \tag{2}$$

runs over the nearest-neighboring layers, and

$$H_{\mathrm{nnn}} = -J_2 \sum_{nn''} S_n S_{n''} \tag{3}$$

runs over next-nearest neighbors.

For our case the pseudospin is taken to denote the lateral position x_n along one of the crystallographic directions (orthorhombic **a** axis). Layers are denoted by n, and are stacked along the **c** axis. Nearest-neighbor layers are always shifted by $\pm 1/4\mathbf{a}$ relative to each other,(6–8) so that there are *four* possible sites per layer. Although that might invite a description by a four-state Potts model,(12) one may remain in the simpler Ising model regime by introducing a two-sublattice description: We denote even-numbered layers ($n = 2p$) by sublattice 1, and assign the pseudospin variable $S_n = \pm 1$ to it, corresponding to $x_n = 0$ and $1/2$, respectively, and odd-numbered layers ($n = 2p + 1$) by sublattice 2, with pseudospin variables $T_n = \pm 1$, corresponding to $x_n = -1/4$ and $+1/4$, respectively.

The nearest-neighboring Hamiltonian contribution may now be written

$$H_{\mathrm{nn}} = -J_1 \sum_{p} S_{2p} T_{2p+1} \tag{4}$$

whereas the next-nearest-neighbor term will read

$$H_{\mathrm{nnn}} = -J_2 \sum_p (S_{2p} S_{2p+2} + T_{2p-1} T_{2p+1}) \tag{5}$$

The coupling constants J_1 and J_2 are phenomenological parameters, originating from local elastic layer distortions.(2)

The solution of the ANNNI model Hamiltonian has been discussed in several contexts by various authors.(11) The most relevant solution for our purpose is that given by Price and Yeomans.(2–4) Explicit solution for our two-sublattice model has not been worked out. However, it is well known that for magnetic systems multiple-sublattice cases behave qualitatively similar to one-sublattice ones, so we expect that the qualitative picture of the Price–Yeoman model will apply also for our case.

In Section 4 the X-ray scattering is discussed in terms of the pseudospin model.

4. X-RAY SCATTERING

In the following we shall use the orthorhombic unit cell of the MDO_1 phase as our indexing reference. Let the structure factor of each individual layer be

$$F_L = F_L(hkl) \tag{6}$$

One should keep in mind that each layer is assumed to be fully ordered in the *ab* plane, so that $F_L(hkl)$ contains already a sharpness in the two indices h and k, such that only integer values of h and k are allowed.

The total scattering amplitude is obtained by a sum over all layers n (from 0 to $N-1$),

$$\begin{aligned} F_{\mathrm{tot}}(Q) &= F_L \sum_n e^{2\pi i x_n \cdot h} e^{2\pi i (l/2) \cdot n} \\ &= F_L \sum_n e^{2\pi i x_n \cdot h} e^{\pi i l \cdot n} \end{aligned} \tag{7}$$

where x_n varies from layer to layer according to the actual stacking sequence.

The pseudospin variables S_n and T_n of Section 3 may now be introduced, giving

$$\begin{aligned} F_{\mathrm{tot}}(\mathbf{Q}) = F_L \sum_p \{ & [\tfrac{1}{2}(1 + S_{2p}) + \tfrac{1}{2}(1 - S_{2p})\, e^{i\mathbf{Q}\cdot\mathbf{a}/2}]\, e^{i\mathbf{Q}\cdot\mathbf{c}p} \\ & + [\tfrac{1}{2}(1 + T_{2p+1}) + \tfrac{1}{2}(1 - T_{2p+1})\, e^{i\mathbf{Q}\cdot\mathbf{a}/2}]\, e^{-i\mathbf{Q}\cdot\mathbf{a}/4} e^{i\mathbf{Q}\cdot\mathbf{c}\cdot(p+1/2)} \} \end{aligned} \tag{8}$$

which can be developed into

$$F_{\text{tot}}(\mathbf{Q}) = F_L \Big[\cos(\mathbf{Q}\cdot\mathbf{a}/4)\cdot(e^{i\mathbf{Q}\cdot\mathbf{a}/4} + e^{i\mathbf{Q}\cdot\mathbf{c}/2}) \sum_p e^{i\mathbf{Q}\cdot\mathbf{c}p}$$

$$- i\sin(\mathbf{Q}\cdot\mathbf{a}/4) \sum_{\mathrm{p}} (e^{i\mathbf{Q}\mathbf{a}/4} S_{2p} + e^{i\mathbf{Q}\cdot\mathbf{c}/2} T_{2p+1})\, e^{i\mathbf{Q}\cdot\mathbf{c}p} \Big] \qquad (9)$$

Q is the scattering vector. In terms of reciprocal lattice vectors $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ one may write

$$\mathbf{Q} = 2\pi(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \qquad (10)$$

Since $\mathbf{Q}\cdot\mathbf{a}/4 = \frac{1}{2}\pi h$, the second term of (9) vanishes for even index $h (h = 2m)$, giving sharp "family reflections"$^{(6-8)}$ for that case, because the p-sum requires $l =$ integer. The prefactor requires $m + l =$ even for the family reflections.

For odd index h ($h = 2m + 1$), only the second term survives. Information on the layer configuration (S and T) can be deduced from this type of scattering. We calculate the intensity, and take expectation values $\langle\cdot\rangle$ (ensemble averages) for pseudospin correlation functions, giving for the intensity

$$I(2m+1, k, l) = F_{\text{tot}}(\mathbf{Q})\, F^*_{\text{tot}}(\mathbf{Q})$$

$$= F_L F_L^* \cdot \sum_{p,\,p'=0}^{N-1} [\langle S_{2p} S_{2p'}\rangle + \langle T_{2p+1} T_{2p'+1}\rangle$$

$$+ (-1)^m\, i(\langle S_{2p} T_{2p'+1}\rangle\, e^{-i\pi l} - \langle S_{2p'} T_{2p+1}\rangle\, e^{\pi i l})]$$

$$\times\, e^{(2\pi i l(p-p'))} \qquad (11)$$

In this formula the index l is a continuous variable unless the layers are long-range ordered.

For MDO_1, $S_{2p} = 1$ and $T_{2p+1} = 1$, giving rise to Bragg scattering for all $l =$ integer.

For MDO_2, $S_{2p} = 1$, $S_{2p+2} = -1$ and $T_{2p+1} = 1$, $T_{2p+3} = -1$, giving rise to scattering only for $l =$ half-integer.

Other ordered stacking models may be introduced in a similar way.

For completely *statistical disorder*, on the other hand, only self-correlations survive: $p = p'$, for which $\langle S_{2p}\cdot S_{2p'}\rangle = 1$, giving

$$I_{\text{diffuse}} = N\cdot F_L F_L^*$$

which is continuous in l (diffuse line along l).

For correlations to nearest-neighboring planes $\langle S_{2p} T_{2p+1} \rangle$ survives also, giving a $\sin(\pi l)$-type modulation of the diffuse line.

More complicated correlation functions may be envisaged, such as a Markov chain growth model used in a previous study.(13)

5. OBSERVATIONS

We have previously studied the diffuse scattering from Di-aqua-bis-Salisylato-Copper(II) (DSC),(13) which showed no stacking long-range order, but very pronounced short-range correlation, as determined from modulated diffuse streaks. In that case the data were interpreted in terms of a Markov-chain growth mechanism to second neighbor, equivalent to a second-neighbor Ising model.(14)

Two compounds in the $K_3Me(CN)_6$ series were recently reinvestigated, namely the Fe and Co compounds.

5.1. $K_3Fe(CN)_6$

Two single-crystal species of the Fe compound were studied. In agreement with earlier work,(7) the MDO_2 structure dominates, showing sharp Bragg peaks for $h = 2m + 1$ with $l =$ half-integer, as shown in Fig. 2a. No diffuse scattering component was observed, indicating absence of disorder. However, whereas one specimen showed only $l =$ half-integer scattering, the second specimen showed additional Bragg peaks at $l = 1/6$ and $5/6$ as shown in Fig. 2b. In fact the reflections indicate not only a sixfold enlargement of the unit cell relative to MDO_1, but it is also of a single domain type ($l = 1/6$ and $5/6$, not $-1/6$ and $-5/6$). A long-range order as indicated in Fig. 3, would account for this observation. Interestingly, it is a hybrid of MDO_1 and MDO_2.

5.2. $K_3Co(CN)_6$

For this compound Vannerberg(7) reported MDO_2 structure with appreciable diffuse scattering in addition.

We have investigated one crystal specimen only of this material, and in fact Vannerberg's findings were confirmed. However, the "diffuse" lines, at first glance seemingly randomly fluctuating, turn out to be not all only diffuse, but also well structured.

In Fig. 4 we point out at least four different periods centered around $l = 1/2$, namely 1/3, 1/4, 2/5, and 2/7. Thus it seems that in the Co compound several phases are simultaneously present.

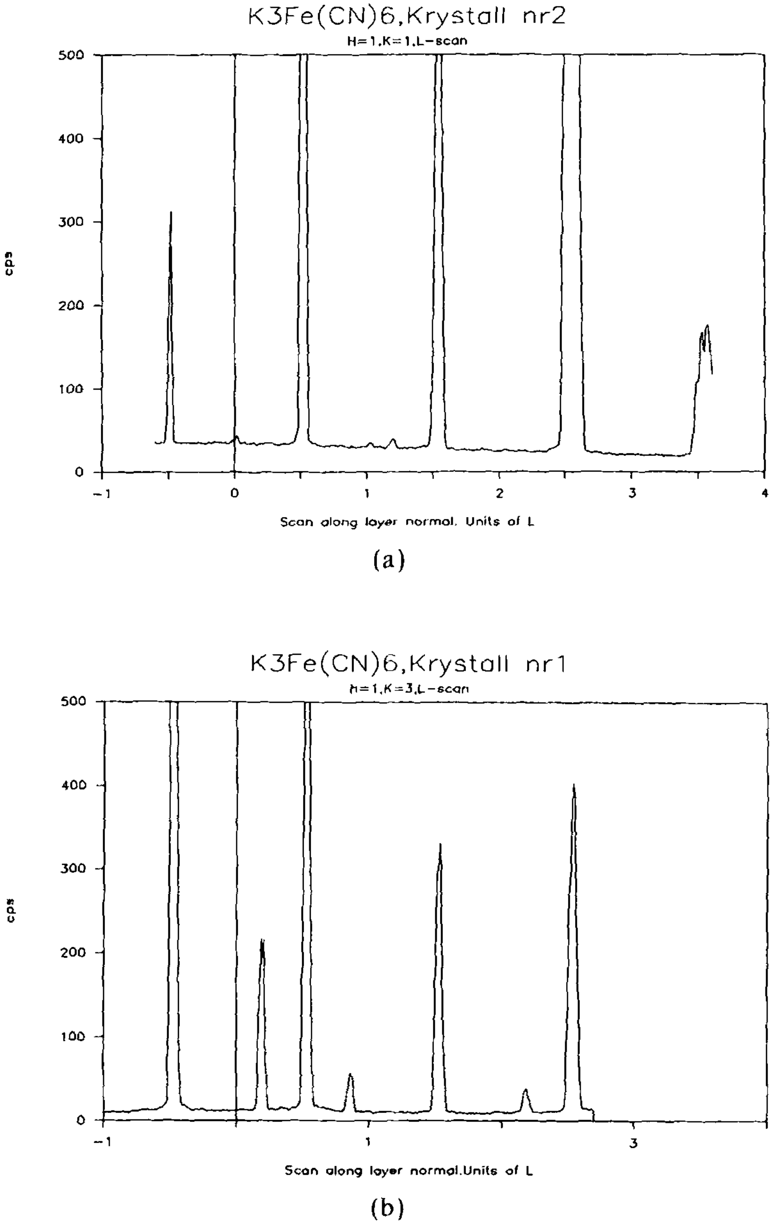

Fig. 2. Diffraction pattern for *l*-scans (along layer normal) for $h = 1$ (odd) for two samples of $K_3Fe(CN)_6$: (a) Crystal no. 2, showing half index *l*-peaks ($k = 1$), (b) crystal no. 1, showing additional peaks at $l = 1/6$ and $5/6$ ($k = 3$).

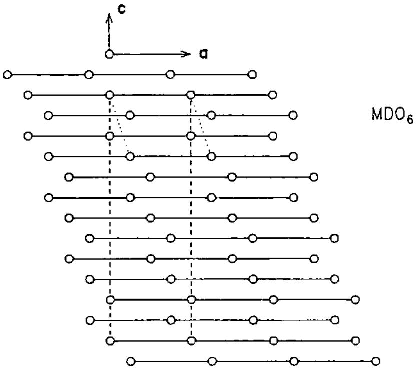

Fig. 3. A possible stacking sequence (MDO_6) to account for additional peaks in Fig. 2b. The sixfold enlarged unit cell is shown by dashed lines, the primitive cell by dots.

6. DISCUSSIONS

In Fig. 5 we show a phase diagram by Price and Yeoman for the ANNNI model,[2] valid at low temperatures within the mean field approximation.

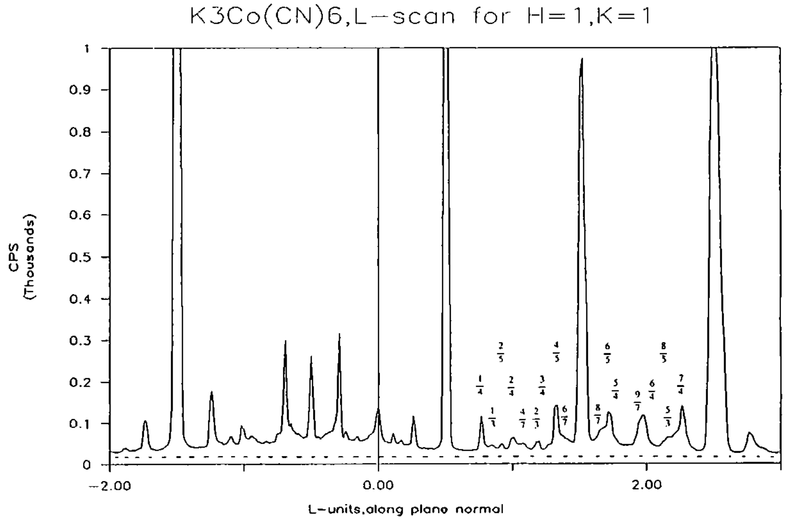

Fig. 4. Diffraction pattern for *l*-scan for $h = 1$ (odd) for a sample of $K_3Co(CN)_6$. Referred to the $l = 1/2$ peak, the "satelite" peaks may be indexed by $q = 1/4$, 1/3, 2/7, and 2/5. The background level is indicated by a dashed line, showing some diffuse scattering contribution at all *l*.

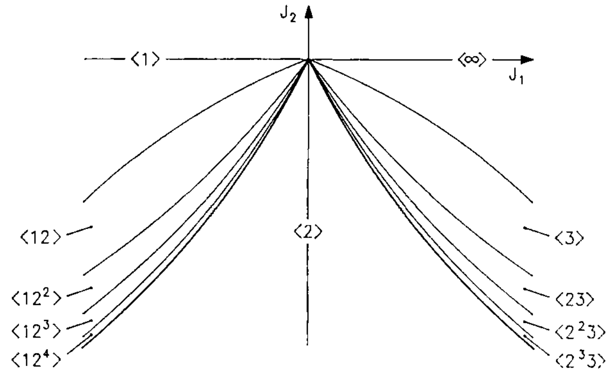

Fig. 5. Phases predicted for the ANNNI model in the parameter space of the two competing interactions J_1 and J_2 at low temperatures (figure reproduced from ref. 2).

Several phases are predicted in the coupling parameter space of J_1 (first neighbors) and J_2 (second neighbors). Of particular interest is the occurrence of an enless number for complicated phases ("devil's staircase"(11)) surrounding the "⟨2⟩" phase. (The notation ⟨*nm* ··· ⟩ means *n* up spins followed by *m* down spins, etc.; for instance, $\langle 12^2 \rangle$ means ↑↓↓↑↑↓↑↑↓↓).

For our case the interlayer coupling strengths J_1 and J_2 are phenomenological, effective parameters originating from local elastic layer distortions. Thus they may vary considerably with the metal atom Me, since the metal affects the lattice geometry.(6-8) This could explain the occurrence of MDO_1 (which corresponds to ⟨1⟩) for the Cr and Mn compounds and of MDO_2(⟨2⟩) for the Fe and Co compounds.

To understand the occurrence of several phases of the same material, one has to realize that the stacking sequence in the crystal is detemined by the layer-by-layer growth at the crystal-to-solution interface. The growth conditions, like local gradients, convection, and substrate walls, may vary sufficiently in the growth beaker to affect the effective J_1 and J_2. Thus even very small variations near the multiphase boundary may promote one or the other phase to grow. For the Fe compound we move from the ⟨2⟩ regime into one of the more complicated ones. For the Co compound we see the presence of several long-period phases in addition to the ⟨2⟩ phase. More detailed studies, also including the Mn compound, will be performed, and more detailed quantitiative analyses undertaken to fit the models to the observed diffraction diagrams.

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