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Intrinsic Chaotization Model for a Perovskite $KMnF_3$ Crystal

BY ALICJA RATUSZNA AND ADAM KACHEL

Institute of Physics, Silesian University, 4 Uniwersytecka Str., 40-007 Katowice, Poland

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Abstract

The intrinsic chaotization model proposed by Kassan-Ogly & Naish [*Acta Cryst.* (1986), B42, 297–335] is used to describe the temperature evolution of the $KMnF_3$ crystal structure. This is an example of a crystal in which there are two structural phase transitions: cubic→tetragonal ($T_1 = 186$ K) and tetragonal →orthorhombic (with monoclinic distortion of the pseudocubic cell, $T_2 = 91$ K). For each phase the parameters defined in the model were calculated, *i.e.* 'order parameter' η_α, mean energy E, tilting angle of the octahedra ψ_α and lattice parameters a_α. These last values were compared with experimentally determined parameters a_p, b_p, c_p with a relative deviation of about 5×10^{-5} in the high-temperature region, 5×10^{-4} for a and b and 1.7×10^{-3} for c at 140 K, and 2.5×10^{-3} at 10 K.

Introduction

Kassan-Ogly & Naish (1986) proposed a phenomenological model to describe and elucidate the mechanism and occurrence of structural deformations in ionic crystals of the perovskite type. Geometric conditions such as the dimensions of ions forming the crystal determine the formation of one of two crystal types called shifting and tilting types. These types are determined by the loose packing of ions in the lattice at high temperatures, a state called 'immanent chaotization' by the authors. Interactions between the ions, which shift them from the equilibrium positions by a value Δ_α ($\alpha = x, y, z$) are described by a Hamiltonian of the Ising type (Ising, 1925; Landau & Lifshitz, 1964; Reiff, 1965; Stanley, 1971). Kassan-Ogly & Naish (1986) postulated an 'order parameter', η_α, which describes the evolution of the crystals with temperature.

With decreasing temperature the 'chaotic' interactions between ions are replaced by correlated interactions due to the ions approaching each other more closely. In systems of the shifting type, which allow displacement of cations within the anionic octahedra, a correlated displacement of anion–cation–anion chains takes place. In tilting types of crystals the strongest correlation is found in the planes between anions forming MnF_6 octahedra. A detailed description of the structure of both types of crystals together with considerations of the degrees of freedom and correlated interactions may be found in the paper by Kassan-Ogly & Naish (1986).

In the following section the most important assumptions are given together with definitions of the parameters of the model. It is followed by an attempt to apply this model to the temperature evolution of the perovskite structure of a $KMnF_3$ crystal. $KMnF_3$ is one of the most investigated crystals (Beckman & Knox, 1961; Knox, 1961; Okazaki & Suemune, 1961; Bernard & Walker, 1976; Hidaka, 1975; Shirane, Minkiewicz & Linz, 1970; Hidaka, Fujii & Maeda, 1986; Lockwood & Torri, 1974; Hidaka, Ohama, Okazaki, Sakashita & Yamakawa, 1975; Minkiewicz & Shirane, 1969; Minkiewicz, Fujii & Yamada, 1970; Reshchikova, Zinienko & Aleksandrov, 1969; Sakashita & Ohama, 1982; Gibaud, Cowley & Nouet, 1989; Cox, 1989) and was chosen as an example for this reason. It belongs to the tilting-ion type forming MnF_6 octahedra which can be freely displaced in the plane (of the face) in which they lie. They are closely bonded to Mn^{2+} forming rigid octahedra. Displacements of fluoride ions in the plane perpendicular to the axis of rotation of the octahedra with which these displacements are correlated, are responsible for distortion of the elementary cells with decreasing temperature.

In $KMnF_3$ two structural phase transitions may be observed: to the tetragonal system at $T_1 = 186.5$ K and to the orthorhombic system at $T_2 = 91$ K, which are the result of freezing of the ion displacements.

Based on the Kassan-Ogly & Naish formalism, calculations were made of such quantities as the order parameter η_α and energy E of the system as a function of temperature. The temperature dependences of lattice parameters a_α, displacements of fluoride ions from the equilibrium position Δ_α, and angles of tilting of the octahedra ψ_α can be calculated from the order parameters. These values were calculated for $KMnF_3$ from the experimentally determined phase-transition temperatures T_1 and T_2. Temperature variations of lattice parameters (and types of structural distortion) were also determined

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experimentally and compared with the a_α value calculated from the model.

Principal assumptions of the Kassan-Ogly & Naish model

A detailed description of this model was given in the paper by Kassan-Ogly & Naish (1986). Only the principal assumptions and definitions of model parameters for perovskite crystals of the tilting type are given here. It is assumed that:

(*a*) The Mn^{2+} ions are immobile inside the octahedra, the fluoride ions which form the octahedra have two degrees of freedom in the plane perpendicular to the Mn^{2+}—F^- bonds, while the potassium cations located in the vacancies between the octahedra have three degrees of freedom and their noncorrelated displacements do not play any significant part in the context of this model. Thus, the influence of their motion on the changes of the phase-transition temperature is not considered here.

(*b*) A potential V is defined, which describes only the interactions between neighbouring planes formed by the fluoride ions. Use is also frequently made of the interaction parameter J_α defined as $J_\alpha = V(\Delta_\alpha)^2/kT$.

(*c*) It is postulated that a system of this kind may be described by an Ising-type Hamiltonian

$$H_\alpha = -\tfrac{1}{2}V(\Delta_\alpha)^2\sum_n\sum_{n'}\delta_n^\alpha\delta_{n'}^\alpha \qquad (1)$$

where n and n' enumerate the neighbouring fluoride planes, and δ_n^α is the Ising operator with eigenvalue ± 1, indicating fluoride-ion displacement from the equilibrium position in the direction $\alpha = x, y, z$. The total Hamiltonian is $H = \sum_\alpha H_\alpha$.

(*d*) The energy of the system is defined as

$$E = \sum_\alpha E_\alpha = -V\sum_\alpha(\Delta_\alpha)^2\eta_\alpha \qquad (2)$$

where $\eta_\alpha = \langle\delta\rangle^2$. The order parameter may be derived from the Ising model, *i.e.* $\langle\delta\rangle = \tanh J\langle\delta\rangle$, and in the high-temperature cubic phase this parameter is taken as having a zero value. In the case of the Kassan-Ogly & Naish model the 'order parameter' is defined as

$$\eta_\alpha = \tanh(J_\alpha) = \tanh\frac{V(\Delta_\alpha)^2}{kT} \qquad (3)$$

which differs from zero in the cubic phase. The model assumes that lattice parameters vary with temperature as follows

$$\begin{aligned} a_x &= a_p = a_o(1 - t'\eta_y)(1 - t'\eta_z)\\ a_y &= b_p = a_o(1 - t'\eta_x)(1 - t'\eta_z)\\ a_z &= c_p = a_o(1 - t'\eta_x)(1 - t'\eta_y) \end{aligned} \qquad (4)$$

where a_o is the lattice constant in the cubic system (high symmetry), t' a parameter associated with the packing of ions in the high-symmetry phase ($t' < 1$).

In a similar manner it is possible to determine the temperature dependence of ion displacement from the equilibrium position Δ_α

$$\begin{aligned} \Delta_x &= \Delta(1 - l\eta_x)(1 - t\eta_y)(1 - t\eta_z)\\ \Delta_y &= \Delta(1 - t\eta_x)(1 - l\eta_y)(1 - t\eta_z)\\ \Delta_z &= \Delta(1 - t\eta_x)(1 - t\eta_y)(1 - l\eta_z) \end{aligned} \qquad (5)$$

where Δ is the amplitude of the fluoride-ion oscillation at $T = \infty$ (in the cubic phase). The meaning of parameters t and l is the same as previously.

For parameters Δ_α defined in this way, equations (3) may now be written explicitly, *i.e.*

$$\begin{aligned} \eta_x &= \tanh[(T_0/T)(1 - l\eta_x)(1 - t\eta_y)(1 - t\eta_z)]\\ \eta_y &= \tanh[(T_0/T)(1 - t\eta_x)(1 - l\eta_y)(1 - t\eta_z)]\\ \eta_z &= \tanh[(T_0/T)(1 - t\eta_x)(1 - t\eta_y)(1 - l\eta_z)] \end{aligned} \qquad (6)$$

where $T_0 = (|V|/k)\Delta^2$, resulting in an expression for the energy of the system

$$\begin{aligned} E &= -V\textstyle\sum_\alpha(\Delta_\alpha)^2\eta_\alpha\\ &= -V[\eta_x(\Delta_x)^2 + \eta_y(\Delta_y)^2 + \eta_z(\Delta_z)^2\\ &= -V\Delta^2[\eta_x(1 - l\eta_x)^2(1 - t\eta_y)^2(1 - t\eta_z)^2\\ &\quad + \eta_y(1 - t\eta_x)^2(1 - l\eta_y)^2(1 - t\eta_z)^2\\ &\quad + \eta_z(1 - t\eta_x)^2(1 - t\eta_y)^2(1 - l\eta_z)^2]. \end{aligned} \qquad (7)$$

The temperature dependence of tilting angles of the octahedra ψ_α may also be easily found, *i.e.*

$$\begin{aligned} \psi_x &= \tan^{-1}(2\eta_x\Delta_x/b)\\ \psi_y &= \tan^{-1}(2\eta_y\Delta_y/c)\\ \psi_z &= \tan^{-1}(2\eta_z\Delta_z/a). \end{aligned} \qquad (8)$$

Structural distortion in $KMnF_3$ – experimental data

The distortion of the $KMnF_3$ unit cell was determined from measurements of the lattice parameters as a function of temperature. Experiments were performed on an X-ray powder diffractometer.* Displacement and splitting of the chosen diffraction lines {200}, {211} and {222} were observed in the temperature range 4.2 to 300 K. Lines were measured by profile scanning and subsequent fitting to a Pearson VII type function as described in the paper by Ratuszna & Majewska (1990). Fig. 1 shows the experimental plots of lattice parameters as a function of temperature (Ratuszna & Glazer, 1988; Ratuszna & Majewska, 1990).

At high temperature $KMnF_3$ crystallizes in a cubic system forming an 'ideal' perovskite structure. With

* Powder diffraction data at 297 K have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54666 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

decreasing temperature, deformation of this cell may be observed due to the freezing of the fluoride-ion oscillations to one plane only, perpendicular to z. According to Kassan-Ogly & Naish (1986), this is associated with the occurrence of spontaneous z-tilting of the MnF_6 octahedra. The system transforms to the tetragonal phase at $T_1 = 186.5$ K; the cubic cell is deformed to $a_p = b_p = a_o(1 - t'\eta_z)$ and $c_p = a_o$. The real unit cell has doubled lattice parameters, which are associated with the tilting of the octahedra of type $a^0a^0c^-$ (the symbol a^0 means there is zero tilt about the [100] and [010] pseudocubic axis and c^- indicates successive octahedra along the [001] axis have the opposite tilt of magnitude ψ_z). A more detailed description of the tilted octahedra in perovskite can be found in the original paper by Glazer (1972). The space group describing this symmetry is *I4/mmm*. The doubled lattice parameters are confirmed by the appearance of additional lines on the powder diffraction diagrams (superstructure lines of half indices).

The next phase transition, at $T_2 = 91$ K, causes deformation of the cell to monoclinic, which this time is associated with the appearance of spontaneous x-tilting and y-tilting of the octahedra about the pseudocubic axis. The unit cell is orthorhombic and contains four deformed monoclinic pseudocubic subcells; the space group is *Pnma*.

According to the notation of Glazer (1972), deformations in the $KMnF_3$ crystal are the result of freezing of rotations of the MnF_6 octahedra in the sequence:

$$\underset{\text{Cubic}}{a^0a^0a^0} \xrightarrow{186.5\text{ K}} \underset{\text{Tetragonal}}{a^0a^0c^-} \xrightarrow{91\text{ K}} \underset{\text{Monoclinic}}{a^-b^+a^-}.$$

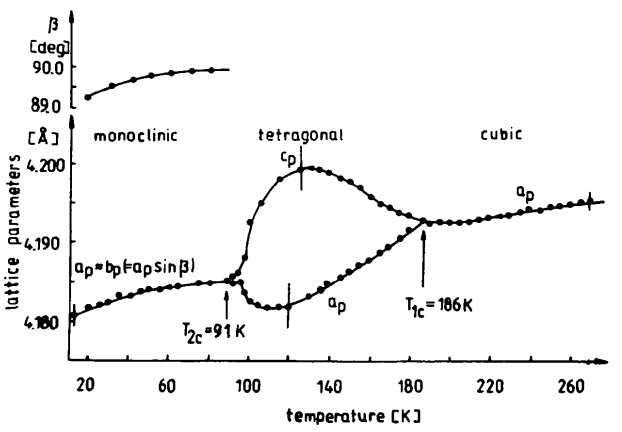

Fig. 1. Experimentally determined temperature dependences of lattice parameters for a $KMnF_3$ crystal. Parameters a_p, b_p, c_p describe the deformation of the perovskite cell. In the tetragonal phase the real cell has dimensions $2a_p \times 2a_p \times 2c_p$, and in the orthorhombic phase $2a_p\cos\beta/2 \times 2b_p \times 2a_p\sin\beta/2$ (the bars indicate values of Δa). T_{1c} and T_{2c} are the temperatures of the structural phase transitions (subscript c indicates that T was determined during the cooling process).

The lattice parameters a_p, b_p, c_p mentioned in the text and shown in Fig. 1 refer to the pseudocubic cell. For this reason we use the name distortion or deformation of the lattice to mean the distortion undergone by the initial cubic cell due to tilting of the fluoride-ion octahedra.

Intrinsic chaotization model in $KMnF_3$ – calculation of model parameters

The temperature dependence of the lattice parameters, temperatures of structural phase transitions and types of distortion occurring for $KMnF_3$ are shown in Fig. 1. Based on these experimental data, an attempt was made to calculate the order parameter according to equation (6). Assuming that $\eta_x = \eta_y = \eta_z = \eta_1$, for the cubic phase a symmetrical solution was obtained

$$\eta_1 = \tanh[(T_0/T)(1 - l\eta_1)^2(1 - t\eta_1)^4] \qquad (9)$$

and associated with this solution, the energy describing the cubic system crystal

$$E_1 = -3V\Delta\eta_1(1 - l\eta_1)^2(1 - t\eta_1)^4. \qquad (10)$$

For the tetragonal phase, for which $\eta_x = \eta_y = \eta_2$, $\eta_z = \eta_2'$, two equations were obtained

$$\eta_2 = \tanh[(T_0/T)(1 - l\eta_2)^2(1 - t\eta_2)^2(1 - t\eta_2')^2]$$
$$\eta_2' = \tanh[(T_0/T)(1 - l\eta_2')^2(1 - t\eta_2)^4] \qquad (11)$$

corresponding to an energy

$$E_2 = -V\Delta(1 - l\eta_2')^2(1 - t\eta_2')^4\eta_2 - 2V\Delta(1 - l\eta_2')^2 \times (1 - t\eta_2')^2(1 - t\eta_2)^2\eta_2'. \qquad (12)$$

For the monoclinic distortion, in which the pseudocubic cell has lattice parameters: $a_p = c_p$, $b_p = a_p\sin\beta$ and $\beta \simeq 90°$, the order parameters fulfil the equality: $\eta_x \simeq \eta_y \simeq \eta_z$. For this reason from the possible solutions listed in Kassan-Ogly & Naish (1986), the symmetrical solutions which exist over the whole temperature region were chosen. Fig. 2 shows the calculated symmetrical and tetragonal numerical solutions for $KMnF_3$.

The symmetrical solution was assumed for the cubic phase ($T_1 > 186.5$ K) and also for temperatures below $T_2 = 91$ K where monoclinic distortions had already been observed. The tetragonal solution describes the interval $91 < T < 186.5$ K, where tetragonal deformation was observed. The parameters t, l and T_0, appearing in equation (6), were fitted and their values are given in Table 1. Fig. 2 shows their temperature dependence. For calculated values η, the energy of the system was determined from equations (10) and (12).

The model envisages temperature variations of the lattice parameters [equation (4)] modulated by changes in the order parameters. These values of the

Table 1. *Model parameters obtained from fitting procedure*

Crystal	t	l	t'	T_0 (K)
$KMnF_3$	0.673 (2)	0.09 (12)	0.002 (6)	4000

lattice parameters are compared in Fig. 3 with values determined directly from X-ray diffraction measurements.

The angles ψ_α, *i.e.* the tilting of the MnF_6 octahedra as calculated from equation (8), are shown in Fig. 4. As a consequence of the non-zero order parameter $\eta_\alpha = \tanh J_\alpha$ in the cubic phase, the tilting angles are also non-zero in this phase. For this reason Kassan-Ogly & Naish (1986) propose the name pseudocubic for the high-temperature phase, and similarly, we use the name pseudotetragonal for the tetragonal phase where $\psi_x = \psi_y \neq 0$.

Discussion

The present paper attempts to apply the Kassan-Ogly & Naish (1986) model to a description of the temperature evolution of the structure in an ionic perovskite crystal of the tilting type with intrinsic chaotization. The cause of this chaos is the loose packing of ions in the crystal, making displacement from the equilibrium position possible (by a value of Δ_α) without destroying the symmetry at high temperatures. With decreasing temperature the interatomic distances also decrease and strong interactions appear between the oscillating ions.

In crystals of the tilting type a strong correlation may be observed between vibrations of fluorine ions in a plane, which may be associated with rotation of the MnF_6 octahedra. Freezing the fluoride-ion displacements in the planes is equivalent to freezing the tilting of the octahedra which is responsible for deformation of the elementary cell.

Temperature plots calculated from the model for values such as the order parameter, the energy of the system or tilting angles of the octahedra would appear to be correct. Nevertheless, it is not possible to measure any of these values directly (even the ψ_α angles are functions of the lattice parameters), hence no comparisons are made between the model and experimental values. The lattice parameters are the only values which can be determined directly from X-ray measurements and therefore only this comparison has been made here. It has not been possible to obtain quantitative agreement throughout the whole temperature range by fitting parameters t, l, t' and T_0, but qualitatively these variations are described quite satisfactorily. The model confirms the existence of the tetragonal and monoclinic (symmetrical) distortion, since the appropriate energies E_1 and E_2 associated with solutions for the given symmetry reach a minimum in the regions where the given phase occurs.

The object of this investigation was not to defend the Kassan-Ogly & Naish model but to demonstrate that, despite the inadequacies of its assumptions (widely discussed by the authors themselves), this model provides the means by which a system may be

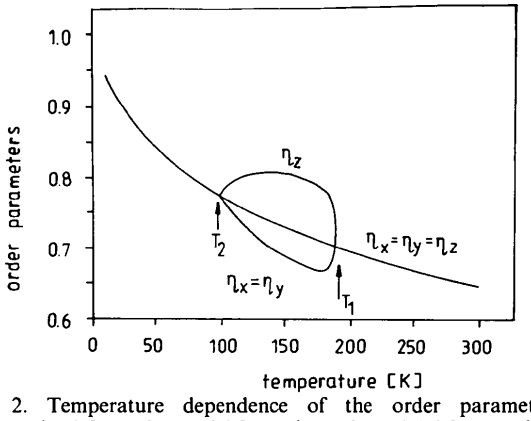

Fig. 2. Temperature dependence of the order parameters determined from the model [equations (3) and (10)]; T_1 and T_2 correspond to the temperatures of structural phase transitions.

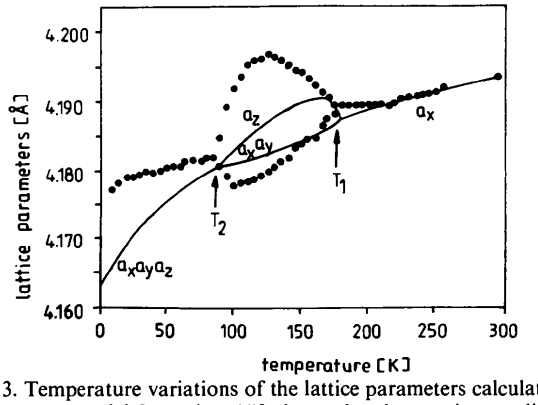

Fig. 3. Temperature variations of the lattice parameters calculated from the model [equation (4)] shown by the continuous line. Filled circles indicate experimental data (from Fig. 1).

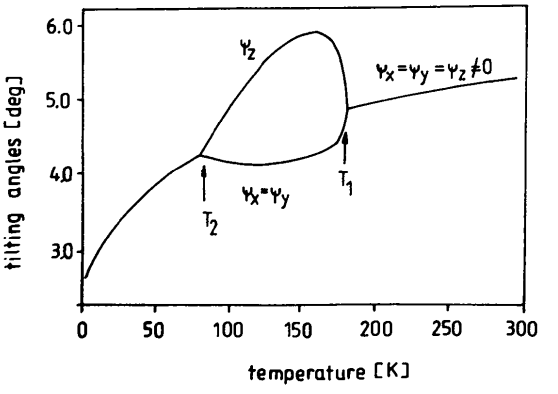

Fig. 4. Angles of tilting of the octahedra as functions of temperature calculated from the model [equation (8)].

described with a relatively simple initial structure in which, due to packing of the ions and the stresses resulting from this, a great number of structural deformations occur.

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Four-Dimensional Crystallographic Analysis of the Incommensurate Modulation in a $Bi_2Sr_2CaCu_2O_8$ Single Crystal

BY X. B. KAN AND S. C. MOSS

Physics Department and Texas Center for Superconductivity, University of Houston, Houston, TX 77204–5504, *USA*

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Abstract

The incommensurately modulated structure in single crystals of nominal composition $Bi_2Sr_2CaCu_2O_8$ has been solved with the aid of four-dimensional crystallography. 700 unique X-ray reflections were collected, including 265 fundamentals, 350 first-order and 85 second-order satellites. The overall weighted R factor (wR) is 0.073, while the partial wR values for fundamentals and first- and second-order satellites are 0.066, 0.086 and 0.133 respectively. Up to second-order harmonics were included in the modulation function along with the temperature factors, B_{ij}. In addition, Ca is partially replaced by Sr and Bi, and Sr sites have some vacancies; Bi has a large first- and second-order modulation of the B factor, which suggests a static disorder in the Bi sites; and the CuO_2 planes suffer a measurable modulation of their average structure. These findings are in fair agreement with earlier results by Petricek, Gao, Lee & Coppens [*Phys. Rev. B* (1990), **42**, 387–392]. However, our moduation amplitudes are in significant disagreement. A small c-axis component to the modulation wavevector was observed along with substantial disorder in the interplanar phasing of the modulation waves. Diffuse scattering at 'unallowed' Bragg positions was also measured.

Introduction

Following the observation of superconductivity at 20 K by Michel, Hervieu, Borel, Grandin, Deslandes, Provost & Raveau (1987) for the BiSrCuO system, the addition of Ca to this ternary system led Maeda, Tanaka, Fukutomi & Asano (1988) to the discovery of bulk superconductivity at 85 K and evidence of superconductivity at 110 K in the BiSrCaCuO system. The compound with a formal composition of $Bi_2Sr_2CaCu_2O_{8+x}$ (hereafter denoted Bi2212) was found to be responsible for superconductivity at 85 K in the Bi system and its basic structure was soon established (Tarascon, Le Page, Barboux,

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