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Abstract. Profile analysis of powder diffraction lines was used to determine the variations in lattice parameters as a function of temperature. Using this procedure, phase diagrams of $(K_{1-x}Na_x)MnF_3$ and $(K_{1-x}Li_x)MnF_3$ were obtained in the concentration range $x \leqslant 0.02$.

From the splitting of cubic (220) and (400) Bragg's lines the temperatures of the structural phase transitions and the types of distortion were determined.

The following sequence of distortions was observed: cubic → tetragonal → orthorhombic → monoclinic.

1. Introduction

This is a further paper in a series dealing with the problem of describing the influence of certain admixtures on the structural evolution of $KMnF_3$ crystals. The introduction of small quantities (usually less than 2%) of the admixtures into the crystal lattice causes stabilization of the low-symmetry distortions of perovskite cubic structure which for $KMnF_3$ crystals are observed below room temperature.

Three structural phase transitions have been observed in $KMnF_3$: at 186 K to a tetragonal phase, at 88 K to an orthorhombic phase (Gibaud *et al* 1991) and at 82 K to a monoclinic phase. The MnF_6 octahedra tilting phenomenon is very largely responsible for the above-mentioned distortions. The mechanism has been described in a number of papers dealing with the problem of the temperature dependence of $KMnF_3$ crystal structure evolution and similar effects in other types of tilting perovskite (Beckman and Knox 1961, Lockwood and Torrie 1974, Hidaka 1975, Hidaka *et al* 1986).

The following processes appear to affect the energy stabilization of the particular deformations:

(i) MnF_6 octahedra deformations whose presence may be as a consequence of introducing M^{2+} ions with diameters larger or smaller than those of the Mn^{2+} ions;

(ii) loose packing of MnF_6 octahedra which is the result of introducing smaller-diameter ions in place of the K^+ cations;

(iii) introducing small quantities of admixtures which may cause point defects, leading to the appearance of internal stresses, and hence to stabilization of the lattice deformations.

Gibaud *et al* (1989, 1991) reported the results of investigations on the influence of M^{2+} admixtures in MnF_6 octahedra on the nature of structural phase transitions in $KMnF_3$ crystals, where Ca^{2+} ($x \leqslant 0.05$) was substituted for Mn^{2+} cations.

A recent paper by Ratuszna *et al* (1992) presents the results of substituting Co^{2+} and Ni^{2+} ($x \leqslant 0.08$) for Mn^{2+} ions. In these papers it was established that a small admixture ($x < 0.05$) gives stabilization of low-symmetry lattice deformations (below 90 K) and broadens the temperature range of occurrence of this distorted phase.

Reported here are studies made on systems where the K^+ cation ($r_{K^+}^{XII} = 1.64$ Å) was replaced by other ions with much smaller radii: Na^+ ($r_{Na^+}^{XII} = 1.39$ Å) and Li^+ ($r_{Li^+}^{XII} = 1.15$ Å). In this case, in agreement with the concepts of Kassan-Ogly and Naish (1986) and Gibaud *et al* (1989), the tilting of octahedra is facilitated because of their loose packing and the occurrence of internal stresses caused by introducing additional point defects resulting from small quantities of admixtures.

2. Experimental details

$(K_{0.99}Na_{0.01})MnF_3$, $(K_{0.98}Na_{0.02})MnF_3$, $(K_{0.995}Li_{0.005})MnF_3$ and $(K_{0.99}Li_{0.01})MnF_3$ single crystals were grown by the Bridgman method in the laboratory of the Solid State Department, Silesian University. (A more detailed description of the method has been given by Skrzypek *et al* (1980).)

The crystals were powdered and examined by the x-ray diffraction technique. The Na^+ and Li^+ ion concentrations in $KMnF_3$ were determined by careful measurements of the lattice parameter a at room temperature, assuming its linear dependence in agreement with the Vegard law. Measurements were carried out in a low-temperature camera chamber cooled by a helium-vapour stream in the temperature range from 4.2 to 300 K.

To obtain precise positions and splitting data for diffraction lines, the diffraction line profile was thoroughly examined in the region of the phase transition. An automatic diffractometer of DRON type with Cu $K\alpha$ radiation (35 kV; 20 mA) was used for the measurements. By controlling the helium-vapour stream the samples in the camera chamber were cooled continuously with temperature stabilization of ± 1 K. The temperature was measured with a chromel–gold thermocouple. Using a scanning method for diffraction line profile measurements with a step value set to $|\Delta(2\theta)| = 0.01°$, the number of counter pulses was measured in the time interval $\Delta\tau = 10$ s.

Data recorded by the counter controller were transmitted to a personal computer system. The experimental profiles were modelled with Pearson VII functions to obtain position, intensity and half-width value of the lines, and in the case of any distortions connected with structural phase transition it was possible to determine the number of overlapping lines (Ratuszna and Majewska 1990).

The temperature dependences of crystal lattice parameters were analysed using the $(220)_c$ and $(400)_c$ lines. At 10 K, additional profiles of the $(211)_c$ and $(222)_c$ lines were investigated with the aim of obtaining unit-cell distortion.

Figure 1 shows the evolution of the (400) line from cubic to tetragonal phase, and then to orthorhombic and to monoclinic distortion for the $(K_{0.99}Li_{0.01})MnF_3$ crystal. Similar behaviours were observed for the remaining samples.
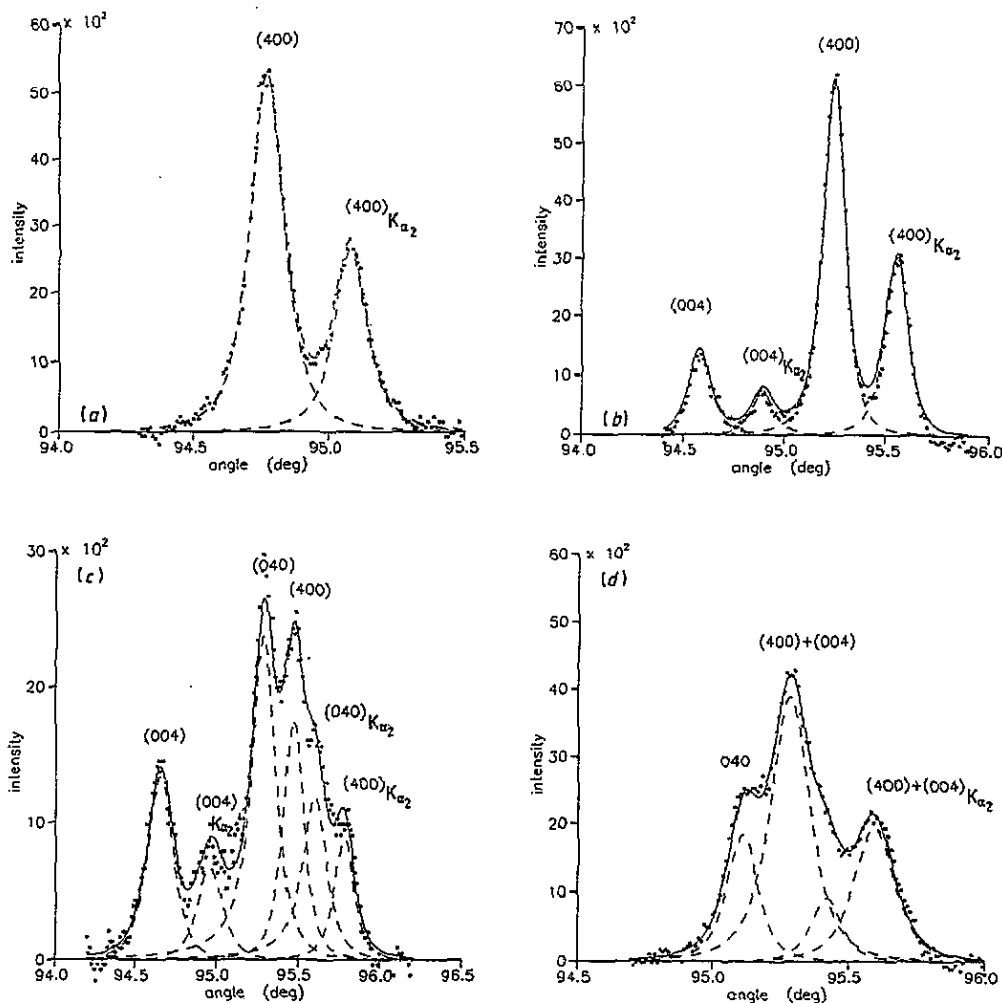
Figure 1. Temperature evolution of the $(400)_c$ diffraction line in $(K_{0.99}Li_{0.01})MnF_3$ for the observed lattice distortions: (a) cubic symmetry; (b) tetragonal distortion; (c) orthorhombic; (d) monoclinic. The subscript c refers to cubic symmetry.

3. Results

The temperature dependences of the lattice parameters for the crystals investigated are presented in figures 2–5. In the samples with admixture concentrations $x \leqslant 0.01$ (irrespective of the kind of admixture), three structural phase transitions can be seen, in a similar way to those in pure $KMnF_3$ crystals (Gibaud *et al* 1991). A slightly different picture is observed for samples with higher concentrations (i.e. $x = 0.02$) of Na^+ ions in $KMnF_3$. In figure 3 showing the temperature variations in the lattice parameters there is an evident lack of transition from tetragonal to orthorhombic phase for this sample. This transition was observed, but only during heating of the sample.

The calculated lattice parameters of the cubic unit cell at $T = 300$ K are given in table 1, together with the values of the Goldschmidt tolerance parameter. This
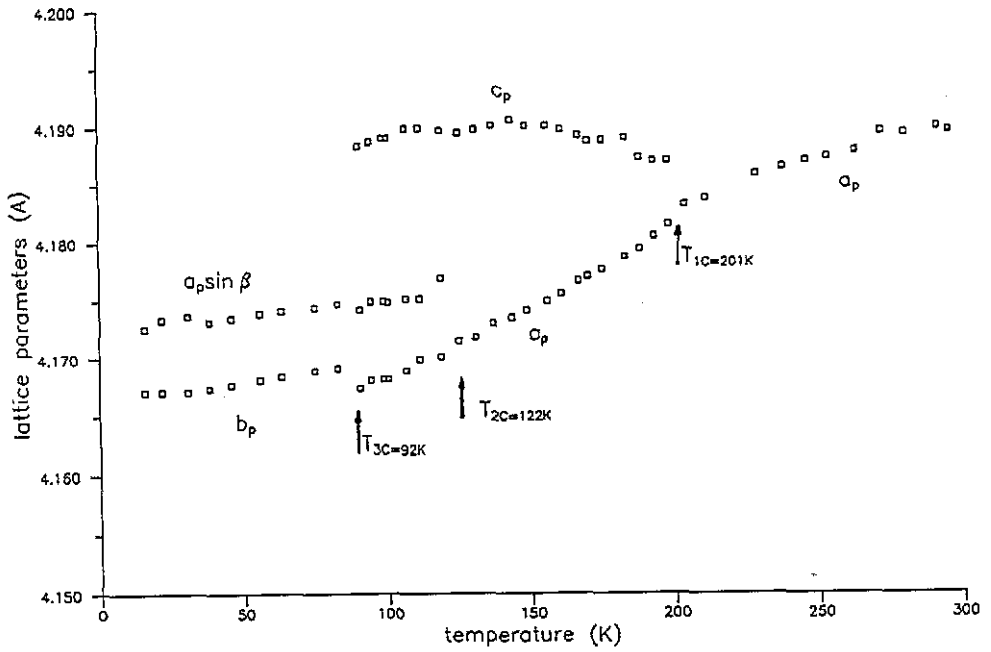
Figure 2. Lattice parameter as a function of temperature for $(K_{0.99}Na_{0.01})MnF_3$ samples. In this diagram and the following, symmetry changes were determined during the cooling cycle (the subscript p refers to the pseudo-cubic cell).
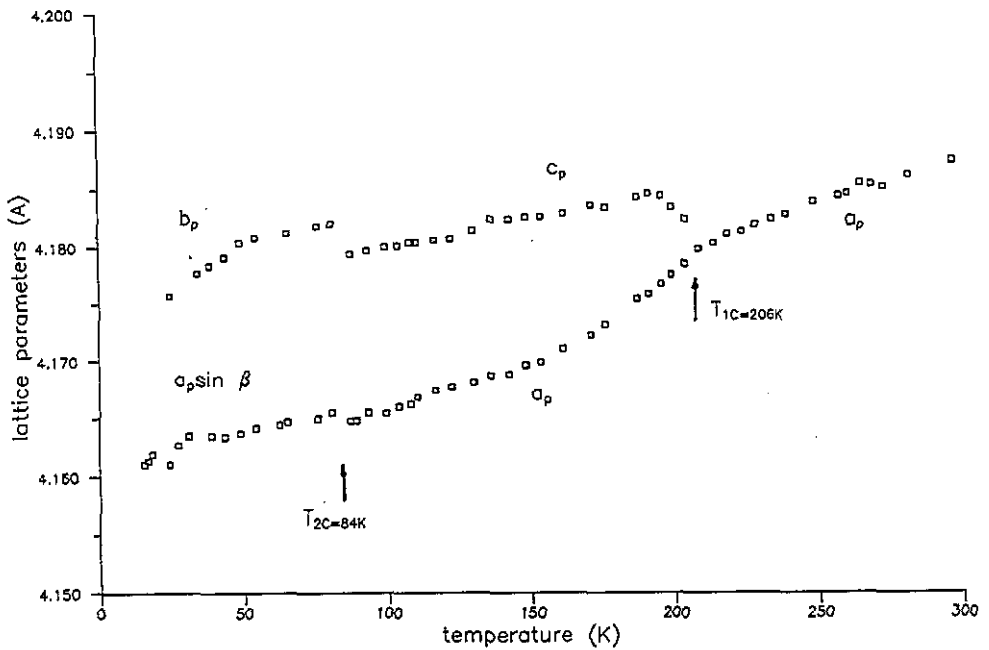
Figure 3. Lattice parameter as a function of temperature for $(K_{0.98}Na_{0.02})MnF_3$ samples.
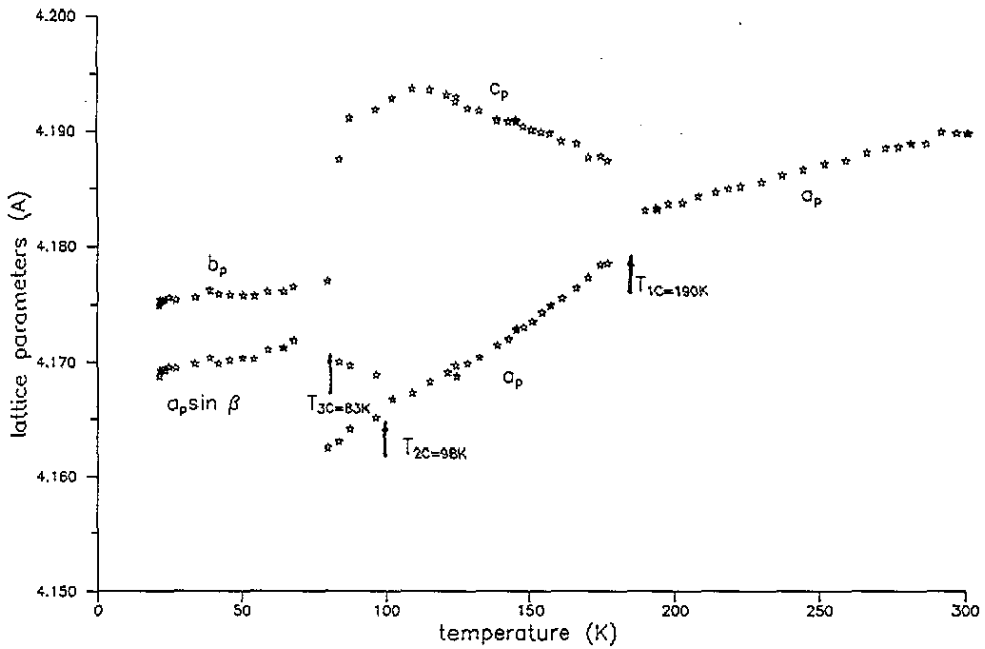
Figure 4. Lattice parameter as a function of temperature for $(K_{0.995}Li_{0.005})MnF_3$ samples.
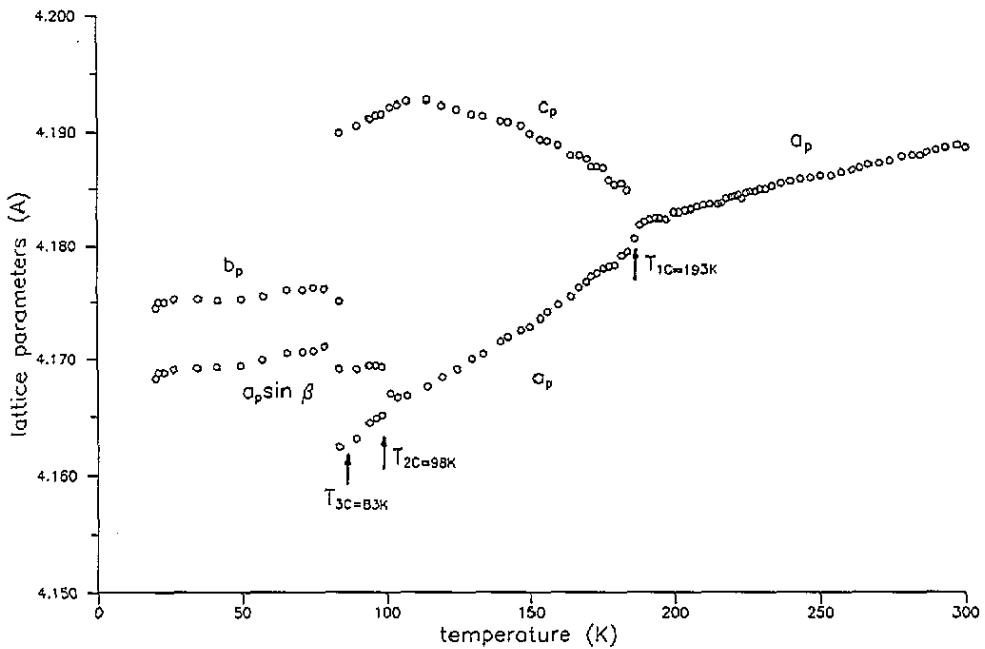

Figure 5. Lattice parameter as a function of temperature for $(K_{0.99}Li_{0.01})MnF_3$ samples.

parameter is used as a measure of packing in a perovskite crystal lattice and hence
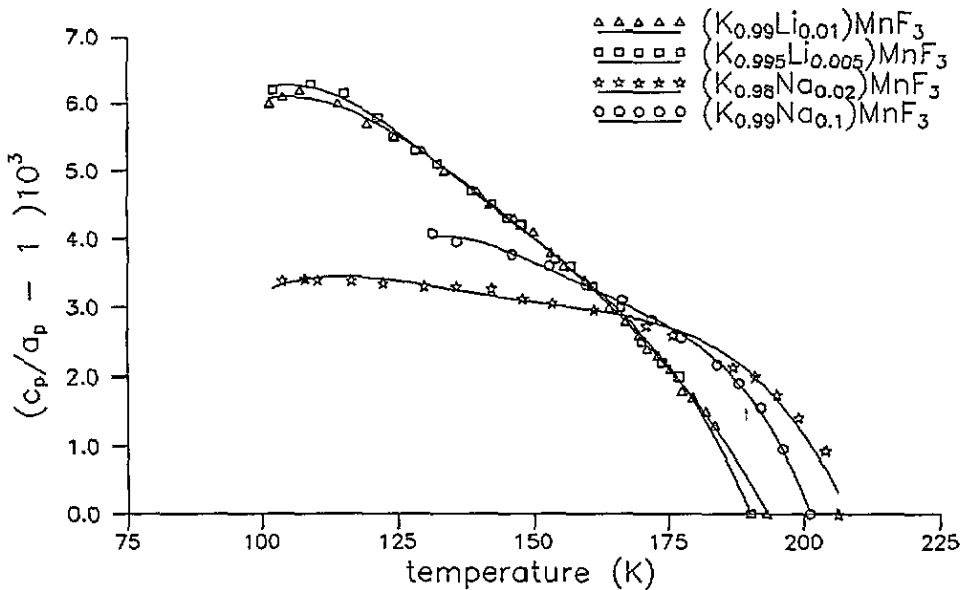
Figure 6. Evolution of the tetragonality parameter versus temperature in the range $T_2 < T < T_1$ for all measured samples: ——, least-squares fit to the data.

Table 1. Cubic cell lattice parameter and Goldschmidt tolerance parameter τ: $\tau = (r_A + r_X)/2(r_B + r_X)$, where $r_A = r_{K+}^{XII} = 1.64$ Å, $r_{Na+}^{XII} = 1.39$ Å, $r_{Li+}^{XII} \simeq 1.15$ Å, $r_X = r_{F-}^{VI} = 1.33$ Å and $r_B = r_{Mn^{2+}}^{VI} = 0.83$ Å. Ionic radii were taken from Shannon's (1976) table.

Compound	$a_p(T = 300$ K) (Å)	τ
KMnF$_3$	4.1926(7)[a]	0.972
(K$_{0.99}$Na$_{0.01}$)MnF$_3$	4.189(6)	0.971
(K$_{0.98}$Na$_{0.02}$)MnF$_3$	4.187(4)	0.970
(K$_{0.995}$Li$_{0.005}$)MnF$_3$	4.189(8)	0.971
(K$_{0.99}$Li$_{0.01}$)MnF$_3$	4.188(6)	0.970

[a] From Ratuszna *et al* (1979).

is a measure of the crystal stability.

It is an experimentally observed phenomenon that introducing a small quantity of Na$^+$ and Li$^+$ cations into the KMnF$_3$ lattice causes a distinct shift in the transition points T_1 (the temperature of the cubic-to-tetragonal phase transition) and T_2 (the temperature of the tetragonal-to-orthorhombic transition) to higher temperatures.

The next very interesting experimental fact is that the temperature region of existence of the orthorhombic phase in the samples becomes wider. The temperature T_3 (the temperature of the orthorhombic-to-monoclinic transition) is slightly shifted and this gives a broadening of the range of orthorhombic phase to 30 K, compared with 6 K in pure KMnF$_3$.

The next phase transition is observed below the temperature T_3, with deformation of the pseudo-cubic cell to monoclinic. For all the crystals tested, the splitting of

additional lines $(211)_c$ and $(222)_c$ at $T = 10$ K was measured and this allowed the lattice parameters of the distorted cell to be determined.

Table 2 gives the temperatures of the structural phase transitions in the tested crystals, obtained during the cooling process.

Table 2. Temperatures of the structural phase transitions observed in the samples tested.

Compound	T_{1c} (K)	T_{2c} (K)	T_{3c} (K)
$KMnF_3^a$	186	88	82
$(K_{0.99}Na_{0.01})MnF_3$	201	122	92
$(K_{0.98}Na_{0.02})MnF_3$	206	—	84
$(K_{0.995}Li_{0.005})MnF_3$	190	98	83
$(K_{0.99}Li_{0.01})MnF_3$	193	98	83

[a] From Gibaud *et al* (1991).

Values of the lattice cell parameters determined at 10 K are presented in table 3.

Table 3. Lattice parameters for monoclinic distortion of the unit cell. a_p, b_p and c_p are the relative pseudo-cubic subcell parameters (Glazer 1972) at 10 K.

Compound	$a_p = c_p$ (Å)	b_p (Å)	β
$KMnF_3$	4.186(4)	4.171(4)	89°50'
$(K_{0.99}Na_{0.01})MnF_3$	4.167(1)	4.172(6)	89°46'
$(K_{0.98}Na_{0.02})MnF_3$	4.161(1)	4.175(7)	89°42'
$(K_{0.995}Li_{0.005})MnF_3$	4.168(8)	4.174(9)	89°45'
$(K_{0.99}Li_{0.01})MnF_3$	4.168(3)	4.174(4)	89°43'

4. Discussion

The object of these investigations was to study the influence of the controlled quantities of admixtures in the lattice $(x \leqslant 0.02)$ on structural phase transitions in $KMnF_3$ crystals. It is well known that in ionic crystals of perovskite type the microstresses caused by point defects play an important role in the appearance of unit-cell distortions. These stresses affect the A–F bond length, causing 'freezing' of the tilting of MnF_6 octahedra which is mainly responsible for these distortions (Kassan-Ogly and Naish 1986, Ratuszna and Kachel 1992).

An important factor in the description of the phase transition mechanism is the packing parameter of ions in the crystal lattice, but in this case we are dealing with relatively small quantities of admixture and this effect can be neglected as the Goldschmidt parameters are virtually the same for all the tested crystals, their magnitudes being close to the τ-value for pure $KMnF_3$.

The very important role of internal stresses in structural phase transition phenomena may be confirmed by tracing the history of pure $KMnF_3$ investigations, where all the papers describing the phase transition below 90 K are ambiguous as to the exact determination of the transition temperatures and the types of distortion

(Beckman and Knox 1961, Lockwood and Torrie 1974, Hidaka 1975). Using the method of high-resolution x-ray scattering, recently Gibaud *et al* (1991) observed the region of a new phase described as orthorhombic.

In our investigations of pure KMnF$_3$ (using the powder x-ray diffraction method) we noticed a similar behaviour, but the diffraction lines were broadened so that it was difficult to decide whether this phenomenon is a new type of lattice distortion or a state of coexistence of two different phases. The introduction of admixtures into the lattice makes the phenomenon clearer; the $(400)_c$ line splits into three lines, i.e. corresponding to the parameters $a_p \neq b_p \neq c_p$. Admixtures cause stabilization of the orthorhombic phase in the transient region and as a consequence the MnF$_6$ octahedra tilting around the $[010]_c$ axis becomes 'frozen'. The next unit cell distortion takes place below T_3 and leads to the monoclinic phase by 'freezing' the anti-tilting octahedra around the $[100]_c$ axis.

The observed deformations of the cubic perovskite unit cell for the crystal with admixtures may be summarized as follows.

(i) $T > T_1$. In this temperature region the cubic phase of perovskite type is observed. In agreement with the Glazer classification, tilting of MnF$_6$ octahedra around all three cubic axes is of $a^0a^0a^0$ type; hence the average value of their rotation angles equals zero (the so-called para-tilting). (The space group is $Pm3m$.)

(ii) $T_2 < T < T_1$. In this temperature region the tetragonal phase occurs, its appearance being governed by spontaneous freezing of the tilting of octahedra around only one axis, e.g. $[001]_c$. This type of tilting may be described in this notation as $a^0a^0c^-$ (i.e. anti-tilting along the c axis). The real tetragonal unit cell has dimensions $2a_p \times 2a_p \times 2c_p$, where the subscript p refers to relative pseudo-cubic parameters. (The space group is $I4/mcm$.)

(iii) $T_3 < T < T_2$. From measurements of the diffraction lines and values of lattice parameters obtained, the type of unit-cell deformation occurring in this temperature range is described as orthorhombic. On analysis of the values of the lattice parameters $a_p < b_p \neq c_p$ it may be concluded that distortion formation is the result of the 'freezing' of MnF$_6$ octahedra tilting around the next pseudo-cubic axis, i.e. $[010]_c$. This kind of deformation can be denoted as $a^0b^+c^-$, and the dimensions of the real orthorhombic cell as $2a_p \times 2b_p \times 2c_p$. (The space group is $Bmmb$).

(iv) $T < T_3$. The next deformation of the pseudo-cubic unit cell below T_3 leads to the monoclinic phase. Owing to internal stresses and interactions the following tilting around the $[100]_c$ axis becomes 'frozen'. The tilting angles of octahedra around the $[100]_c$ and $[001]_c$ axes are nearly equal ($a_p = c_p$) and the corresponding lattice parameters are related to tilting of $a^-b^+a^-$ type. This allows transformation from the monoclinic cell to the orthorhombic cell with dimensions $2a_p \cos(\beta/2) \times 2b_p \times 2a_p \sin(\beta/2)$ (where β is the angle of the monoclinic unit cell). (The space group is $Pnma$.)

Let us emphasize the differences between the $Bmmb$ and the $Pnma$ phases. In the $Bmmb$ phase the pseudo-cubic cell is distorted to orthorhombic symmetry, while in the $Pnma$ it is distorted to monoclinic.

Careful analysis showed a major influence of admixtures in the KMnF$_3$ lattice on its deformation in the tetragonal phase and on the nature of variations in this parameter, which is a measure of deformations below the phase transition point T_1. It was assumed that the magnitude $c_p/a_p - 1$ is a measure of the deformations in this phase and its temperature dependence is expressed by

$$c_p/a_p - 1 = A(T'_{1c} - T)^{2\beta'}$$

where the exponent β' has the meaning of an order parameter (Gibaud *et al* 1991).

Figure 6 shows the evolution of the tetragonality parameter as a function of temperature, in the region below T_1, for all the samples, and table 4 lists the calculated values of the parameters β'. If $\beta' = 0.310$ for pure $KMnF_3$ and this exponent is in good agreement with the $d = 3$ of the Ising model, it may be concluded that introducing admixtures to the $KMnF_3$ lattice causes a slow increase in β', and hence this process may be claimed as changing the nature of the transition.

Table 4. Values of the parameter β' obtained experimentally for the high-temperature phase transition.

Compound	β'
$KMnF_3^a$	0.310 ± 0.005
$(K_{0.99}Na_{0.01})MnF_3$	0.325 ± 0.007
$(K_{0.98}Na_{0.02})MnF_3$	0.333 ± 0.007
$(K_{0.995}Li_{0.005})MnF_3$	0.321 ± 0.005
$(K_{0.99}Li_{0.01})MnF_3$	0.320 ± 0.005

[a] From Ratuszna (1978).

5. Conclusions

In $KMnF_3$ crystals the introduction of small quantities of admixtures of type Na^+ and Li^+ into the $KMnF_3$ lattice causes the following fundamental effects.

(a) The characteristic transition temperatures T_1 and T_2 observed for pure $KMnF_3$ are increased. The admixtures appear to interact with point defects, leading to an increase in internal stresses and thus relatively 'easier freezing' of MnF_6 octahedra tilting at suitable higher temperatures.

(b) These newly created stresses stabilize the orthorhombic phase below the temperature T_2 and broaden its temperature range of occurrence to 30 K for the $(K_{0.99}Na_{0.01})MnF_3$ crystal, compared with 6 K for pure $KMnF_3$.

(c) Introduction of admixtures changes the nature of the high-temperature phase transition.

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