PHYSICAL REVIEW B
CONDENSED MATTER

THIRD SERIES, VOLUME 44, NUMBER 6 1 AUGUST 1991-II

Phase diagram of $KMn_{1-x}Ca_xF_3$ ($x < 0.05$) determined by high-resolution x-ray scattering

A. Gibaud* and S. M. Shapiro
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

J. Nouet
Université du Maine, Faculté des Sciences, Route de Laval 72017, Le Mans, France

H. You
Argonne National Laboratory, Materials Science Division 223, 9700 South Cass Avenue, Argonne, Illinois 60439

(Received 29 August 1990; revised manuscript received 15 February 1991)

Precise high-resolution x-ray-diffraction measurements of the lattice parameters as a function of temperature are reported for the mixed system $KMn_{1-x}Ca_xF_3$ in the concentration range $x < 0.05$. From the splitting of the cubic (0,0,4) Bragg reflection it is possible to determine the transition temperatures of the structural phase transitions which occur in this system and to establish the phase diagram in the concentration range $x < 0.05$. Three structural phase transitions are observed in this system and the transition temperatures at which they occur are enhanced when Mn^{2+} ions are substituted by Ca^{2+} ions. The enhancement rates are, respectively, 5.8, 18, and 14 K/at. % Ca^{2+} ions. This shows that a crossover between the T_{c1} and the T_{c2} transitions should occur at the extrapolated critical concentration $x = 0.075$.

I. INTRODUCTION

Solids with the perovskite structure have been extensively studied in the past because of their simple structure and of their ability to undergo phase transitions. With the development of the soft-mode theory by Cochran and Anderson,[1] much attention has been focused on those compounds of this family which undergo structural phase transitions (SPT) by rotation of octahedra such as $SrTiO_3$, $KMnF_3$, and $RbCaF_3$. The reason for such an interest was that these compounds exhibit, in addition to the softening of a normal mode of vibration, an unexpected critical behavior. Inelastic neutron-scattering experiments first evidenced the presence of critical fluctuations occurring on two times scales, the shorter being associated with the soft mode and the longer with the so-called central peak.[2,3] X-ray-diffraction experiments have recently revealed that the critical fluctuations also occur on two lengths scales: the shorter is associated with the correlation length of the soft mode and the longer, the quasi-Bragg peak, believed to arise from tetragonal clusters developing above T_c in the cubic phase.[4-8] The departure from the classical theory is believed to be due to the presence of unknown defects. For this reason, one can expect to learn much from systems in which defects have been introduced in a controlled manner. In this framework, we have carried out the study of the doped material $KMn_{1-x}Ca_xF_3$ system with $x=0$, 1, 2, 3.75, and 5 at. %. This paper is devoted to the determination, by high-resolution x-ray scattering, of the phase diagram by measuring the lattice parameters as a function of temperature.

Nominally pure $KMnF_3$ undergoes several phase transitions related to the rotation of octahedra.[9] Table I is a summary of the observations. The first transition, which is slightly first order, occurs around $T_{c1} = 186$ K and corresponds to the softening of phonons having the R_{25} symmetry. The high-temperature cubic space group O_h^1 ($Pm3m$) becomes tetragonal D_{4h}^{18} ($I4/mcm$) with the tetragonal axis developing around the axis of rotation of the octahedra, namely, one of the [001] cubic axes. According to various authors,[10,11] this transition is followed at lower temperatures by two other successive transitions: a first-order SPT at $T_{c2} = 91$ K associated with the softening of phonons having the M_3 symmetry and a magnetic transition at $T_N = 88$ K associated with the appearance of an antiferromagnetic ordering of the Mn network.[10,11] There is disagreement about the nature of the transitions since measurements by Hidaka *et al.*[12] indicate that the T_{c2} transition is clearly second order and those of Shirane *et al.*[10] show a more first-order nature. The measurements of Heeger *et al.*[13] and Hidaka *et al.*[12] reveal the presence of a third transition at $T_{c3} = 82$ K which, according to these authors, is either a magnetic transition

TABLE I. Summary of the previous and present works performed in $KMnF_3$ showing the observed transition temperatures, the Q vector associated with the transition and its nature.

	Transition temperature Other experiments (in K)	present work (in K)	Q vector	Nature
T_{c1}	186.6 (Refs. 8 and 9)	186.7	R point $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	Slightly first-order SPT
T_{c2}	91 (Ref. 10)		M point $(\frac{1}{2},\frac{1}{2},0)$	First-order SPT
	91 (Ref. 12)		M point	Second-order SPT
	88		M point	First-order SPT
T_N	88 (Refs. 10 and 12)	Not studied	R point	Antiferromagnetic transition
T_{c3}	82 (Ref. 13)			Magnetic Transition due to the canting of the spins
	82 (Ref. 12)		R-point (magnetic)	Magnetic and first-order SPT
		82	?	First-order SPT (no magnetic studies performed)

due to the canting of the Mn^{2+} spins or a first-order SPT accompanied by a magnetic one (all these results are summarized in Table I).

These compounds have a loose-packed structure[14] and for this reason it was shown that they undergo SPT.[14] Therefore, the substitution of Mn^{2+} ions by Ca^{2+} ions, which have a bigger ionic radius, is likely to provide an important perturbation in the temperature of these phase transitions. Simple considerations about ionic radii have already allowed a quantitative determination of the amount and the direction of the shift of T_{c1}.[15,16] Very good agreement was obtained between the predicted and observed temperatures in the concentration range $x<0.1$. However, at this time, attention was only focused on the highest-temperature phase transition. In this paper, we report that the other transitions are much more affected by the substitution and that a crossover between the R and M transitions should take place.

II. EXPERIMENT

Single crystals of $KMn_{1-x}Ca_xF_3$ were grown by the Bridgman technique at PEC Laboratory (Université du Maine, Le Mans, France). Typical pink-colored crystal boules of several cm^3 were obtained with a natural trend to cleave perpendicular to the $\langle 100 \rangle$ cubic directions. From the crystal boules, small rectangular pieces about $5\times5\times2$ mm^3 were cleaved for the purpose of x-ray experiments.

Samples were glued on a copper holder and inserted in a Be can filled with He gas to obtain good thermal contact. The can was attached, in turn, to the cold finger of a closed-cycled cryogenerator.

X rays were produced by a Rigaku copper rotating anode operating at (45 kV, 200 mA). The $K\alpha_1$ wavelength was selected by reflection on the (111) planes of a silicon monochromator and $K\alpha_2$ was cut off with a sharp edge slit. The diffracted beam was collimated by a silicon (111) analyzer. The resolution thus achieved was typically 0.019° in a θ-2θ scan at $2\theta=95°$ corresponding to a Q resolution of $\delta Q=0.002$ Å^{-1}. Let us point out that, with such a resolution, the detector offset can be considered as negligible and that, at this angle, a direct and absolute determination of the lattice parameters is thus possible with a relative accuracy better than 0.03%. However, as the samples transform into several domains at the phase transitions, the correct determination of the lattice parameters is only possible if the intensity is measured when the sample is oscillating at each position of the detector during the θ-2θ scan, thus integrating over all the present domains.

Measurements were performed around the (0,0,4) Bragg reflection of the cubic phase and transition temperatures were determined by monitoring the splitting of this reflection as shown in Fig. 1 for $KMn_{0.98}Ca_{0.02}F_3$. The determination of the Ca^{2+} concentration was checked by measuring the lattice parameter a for each sample at room temperature and assuming a linear relationship between a and x as expected from Vegard's law. In the range $x<0.05$, it was found, as shown in Fig. 2, that the nominal concentration was in reasonable agreement with that determined by the starting materials. One of the nominal $x=0.05$ samples did not fit on this curve and its composition was found to be $x=0.0375$.

III. RESULTS

A. Nominally pure $KMnF_3$

Figure 3 shows the evolution of the lattice parameters as a function of temperature in nominally pure $KMnF_3$. There are three structural phase transitions which is consistent with previous measurements. However, our measurements of the lattice parameters clearly show a first-order SPT at $T_{c2}=88$ K and a first-order SPT at $T_{c3}=82$ K. The T_{c3} result is consistent with the observation of Hidaka *et al.*,[12] but the T_{c2} result, which coincides with the measurement of the Néel temperature, does not agree with previous measurements[10,12] which show a SPT at 91 K. In order to check the validity of this measurement, we measured, in the high-resolution mode, the temperature dependence of the intensity at the (0.5,0,2.5) M point

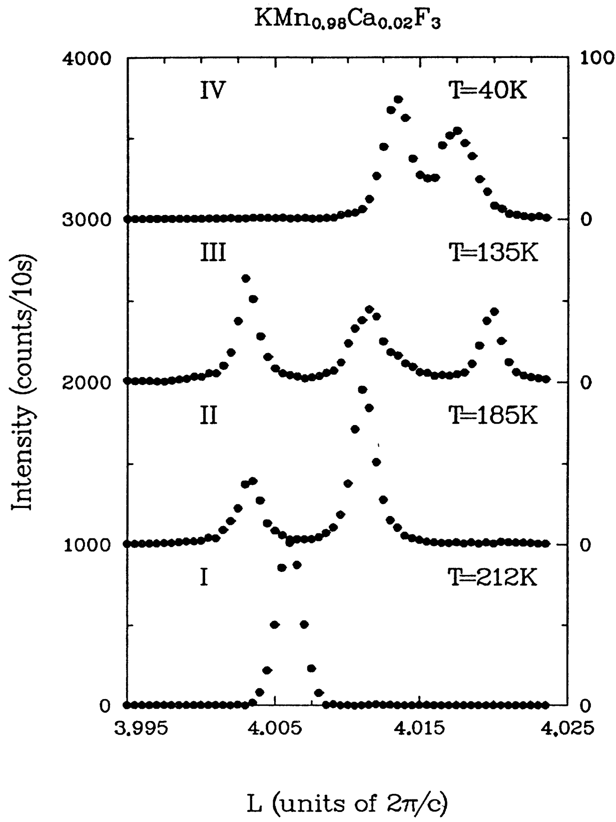

FIG. 1. Q-scans showing the evolution of the splitting of the (0,0,4) Bragg reflection at different temperatures in phases I, II, III, and IV in $KMn_{0.98}Ca_{0.02}F_3$ (at room temperature $a=4.193$ Å).

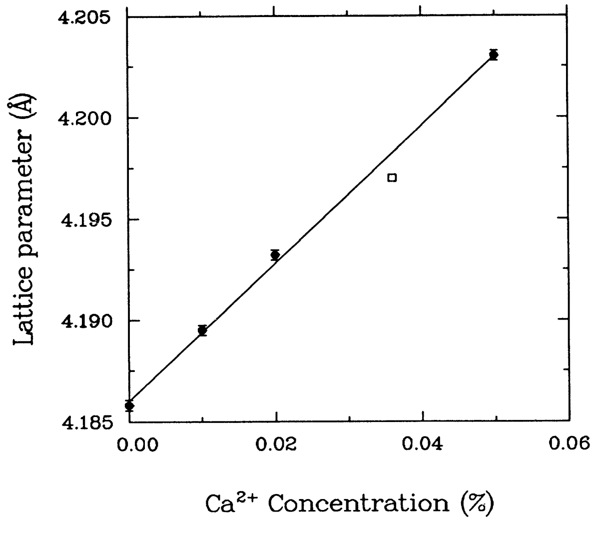

FIG. 2. Evolution of the lattice parameters for various nominal concentrations in Ca^{2+} (solid circles); the straight line is calculated from Vegard's law. The open square is the measured lattice parameter of a crystal with nominal concentration $x=0.05$.

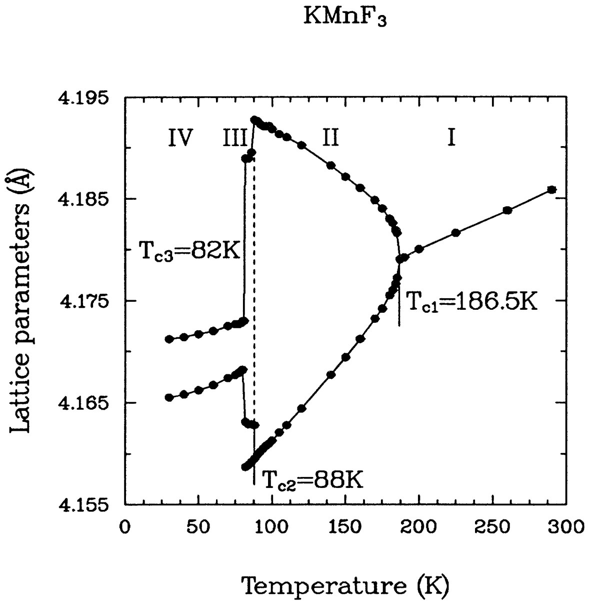

FIG. 3. Evolution of the lattice parameters in pure $KMnF_3$ as a function of temperature showing the presence of three SPT's at $T_{c1}=186.5$ K, $T_{c2}=88$ K, and $T_{c3}=82$ K (solid lines are used only as guides).

of the cubic Brillouin zone (see Fig. 4). Consistently we observed that the intensity of the superlattice reflection steadily increased around 88 K indicating the occurrence at this temperature of a SPT. Let us, however, point out that the intensity measured at the M point does not jump at T_{c2} and that the intensity measured above T_{c2}, though weak, was not negligible even 10 K above T_{c2}. This discrepancy between the nature and the value of T_{c2}

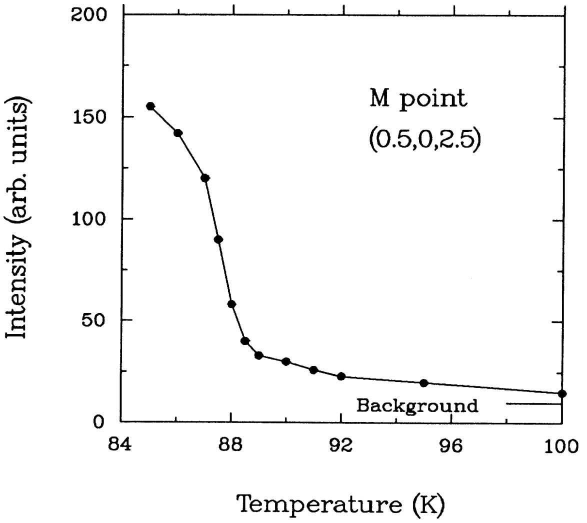

FIG. 4. Integrated intensity measured as a function of temperature in the high-resolution mode at the M point (0.5,0,2.5) of the cubic Brillouin zone (note the intensity present 10 K above T_c) (the solid line is a guide to the eye).

might be related to the presence of anomalous scattering such as the "*quasi-Bragg*" peak clearly observed at the T_{c1} transition[8] in this material and also to strong thermal diffuse scattering of a soft phonon mode which can perturb the determination of the transition temperature. This is more serious if measurements are performed in a low-resolution mode. No hysteresis of this transition was observed.

The first-order character of the T_{c3} transition is obvious in the lattice parameter determination and is enhanced by the observation of some hysteresis at the location of the (0,0,4) Bragg reflections (this reflection is split and only one of the peaks was used to measure the hysteresis) as shown in Fig. 5.

The space-group determination of the different phases is not possible from only the measurements of the lattice parameters and clearly deserves a further detailed study. However, $KMnF_3$ has been extensively studied and in this context it can be pointed out that our measurements are consistent with the presence of (see Table I) the following.

(1) A cubic phase called phase I above T_{c1}.

(2) A tetragonal phase called phase II in the range $T_{c2} < T < T_{c1}$, which, owing to the rotation of the octahedra around the tetragonal c axis, leads to $c_t/a_t > 1$. The development of the tetragonal phase can be characterized by a tetragonal distortion $(c_t/a_t)-1$ which, as shown in Fig. 6, can be described as a power law:

$$\frac{c_t}{a_t}-1=A(T'_{c1}-T)^{2\tilde{\beta}}$$

with $\tilde{\beta}$ being the exponent of the order parameter of the transition. A least-squares fit to the data yields the value $\tilde{\beta}=0.316\pm0.005$ and $T'_{c1}=189.6\pm0.3$ K (the shift in T_{c1} arises from the first-order character of the transition).

(3) An orthorhombic phase called phase III in the range $T_{c3} < T < T_{c2}$ in which octahedra are still rotated around the previous tetragonal axis and slightly rotated around one of the tetragonal a_t axes as expected from the condensing of the M_3 soft mode.

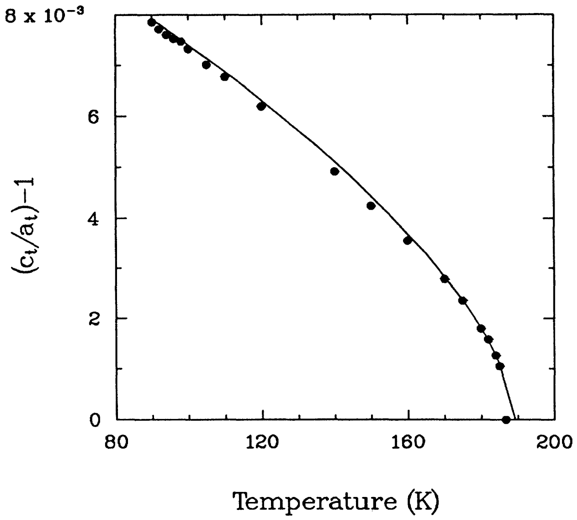

FIG. 6. Evolution of the tetragonality $[(c_t/a_t)-1]$ as a function of temperature below T_{c1}; the solid line is a least-squares fit to the data.

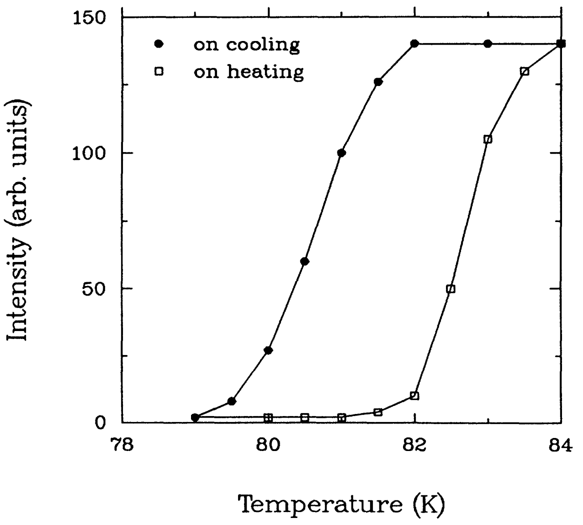

FIG. 5. Evolution through T_{c3} of the Bragg (0,0,4) peak intensity when the instrument is set for a fixed Q vector showing the presence of a 2-K hysteresis loop.

(4) A tetragonal (or pseudo-orthorhombic) phase called phase IV below T_{c3} in which octahedra are rotated around all the ⟨001⟩ directions of the cubic phase by roughly the same amount as previously observed in the low-temperature phase of the isomorphic tilting perovskite $RbCaF_3$ by Bulou *et al.*[17]

Let us also note that the series of three SPT observed in $KMnF_3$ is quite reminiscent of what has been observed in the nonmagnetic isomorphous compound $CsPbCl_3$.[18] However, in this latter case, the first SPT occurs at the M point of the cubic Brillouin zone instead of the R point and is then followed by SPT at the R and X points.

B. Ca^{2+}-doped $KMnF_3$

Figure 7 shows the evolution of the lattice parameters in doped $KMn_{1-x}Ca_xF_3$ and it is very similar to that observed in nominally pure $KMnF_3$. However, the temperatures of all the transitions are strongly enhanced by the substitution of Ca^{2+} for the Mn^{2+} ions. As already explained in detail in Refs. 15 and 16, this is the consequence of the larger ionic radius of the Ca^{2+} ions. As this ion is bigger than Mn^{2+}, it forces a displacement of the fluorines off their symmetry positions and it stabilizes the lower symmetry phase. Therefore, one expects an increase of T_c with x. In addition, it can be seen that the temperature domain of existence of phase III increases with the concentration of Ca^{2+} ions. The phase diagram in Fig. 8 shows that the enhancement of the transition temperatures follows a straight line as a function of the Ca^{2+} concentration. The increases are 5.8 ± 0.1 K/% of Ca^{2+} for T_{c1}, 18.0 ± 0.1 K/% for T_{c2} and 14.0 ± 0.1 K/% for T_{c3}. This clearly evidences that a crossover should occur between the R-point and the M-point transitions. It can be inferred that the critical Ca^{2+} concentration at which both the R-point and the M-point should simultaneously condense is roughly $x=0.075$ and that the transition temperature should be 228 K. (This statement, of course, assumes a linear extrapolation which is purely speculative.) It is also clear that when the Ca^{2+} concentration is increased, the two first transitions tend to be more and more rounded and become second order. This has already been observed in previous experiments.[15,19]

IV. DISCUSSION

The direct measurements of the lattice parameters in the doped system $KMn_{1-x}Ca_xF_3$ in the range $x<0.05$ is a powerful tool to investigate the sequence of SPT in this system. In nominally pure $KMnF_3$, it appears clearly for the first time that, independent of any magnetic phase transitions which are not normally observable with x-rays, there are two first-order SPT's at $T_{c2}=88$ K and $T_{c3}=82$ K which occur below the well-known cubic to tetragonal transition at $T_{c1}=186.7$ K. From the evolution of the lattice parameters in the range $T_{c1}<T<T_{c2}$, it is shown that the tetragonal distortion evolves as $(T'_{c1}-T)^{2\beta}$ with $\beta=0.316\pm0.005$ and $T'_{c1}=189.3\pm0.3$ K. This exponent is in good agreement with the $d=3$ Ising model giving $\beta=0.315(2)$. It is usually believed that pure $KMnF_3$ should behave as a Heisenberg ($n=3$, $d=3$) model with $\beta=0.367$, but in most of the cases the experimental determination of β has contradicted this expectation[8,19] and led to smaller β values. The Ising behavior can be attributed to the presence of strain fields which tend to transform the sample into a single domain at T_{c1}. Indeed, in most cases, there is not an equal amount of each domain and one domain dominates the others indicating the presence of a strong anisotropy.

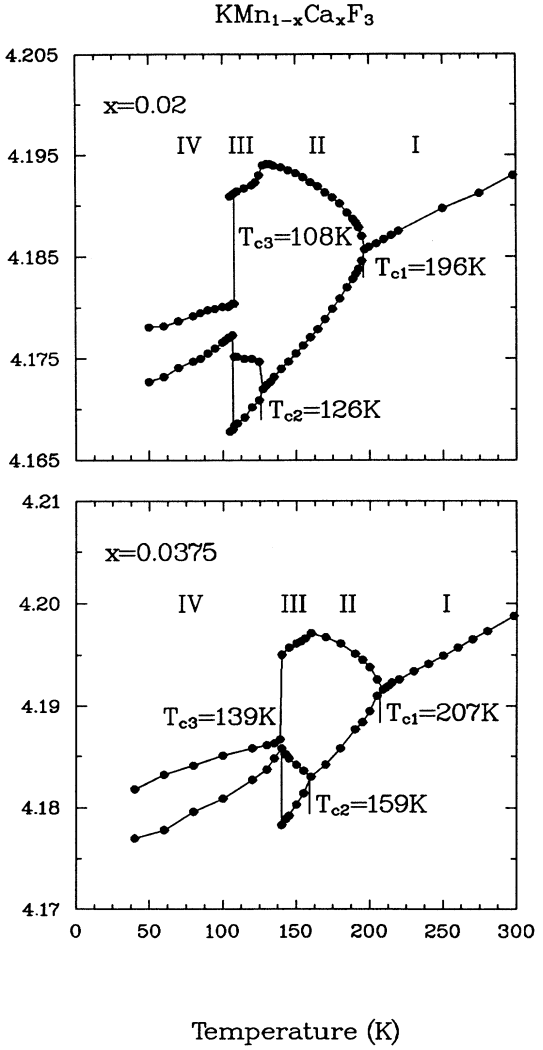

FIG. 7. Lattice parameters for $x=0.02$ (top) and $x=0.0375$ (bottom) as a function of temperature (the solid lines are used only as guides).

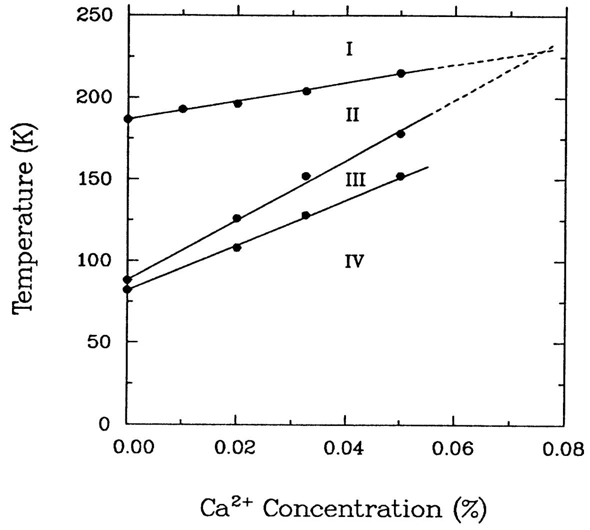

FIG. 8. Phase diagram of $KMn_{1-x}Ca_xF_3$ in the range $0<x<0.08$ showing the evolution as a function of temperature of the three SPT's and the inferred existence of a critical Ca^{2+} concentration at which the R- and M-point transitions should cross (dashed lines are extrapolated and solid lines are used only as guides).

The tetragonal distortion is followed at T_{c2} by an orthorhombic distortion which, in the pure system, very quickly evolves towards a new pseudotetragonal distortion. All these distortions of the initial cubic structure are mainly due to the rotation of the octahedra about the $\langle 001\rangle$ cubic axes. From the evolution of the lattice parameters it should be possible to determine what are the angles of rotation of the octahedra in each phase. As demonstrated by Glazer,[20] the lattice parameters are related to the angles of rotation ϕ_x, ϕ_y, ϕ_z about the (x,y,z) axes of the cubic phase (i.e., the $\langle 100\rangle$ cubic axes) and to the temperature-dependent bond length F-Mn-F. The temperature evolution of the bond length is unfortunately unknown so that the calculation of the angles of rotation in each phase is not possible. However, one can qualitatively describe this evolution: in the cubic phase, $a=b=c$ so that $\phi_x=\phi_y=\phi_z$; in phase II, $a=b<c$ and thus $\phi_x=\phi_y<\phi_z$; in phase III, $a<b<c$ so that $\phi_x<\phi_y<\phi_z$. Finally, in phase IV, it is very clear from our measurements, and assuming a tetragonal phase, that $a=b\neq c$ so that $\phi_x=\phi_y\neq\phi_z$. However, owing to the small difference in the lattice parameters, it is clear that, in this phase, ϕ_z should not differ much from ϕ_x.

In the doped system, the experimental results clearly show that the phase diagram is drastically affected by the substitution of Ca^{2+} ions for Mn^{2+} in the concentration range $x<0.05$. A similar effect was reported in $Na_{1-x}WO_3$.[21] The temperature dependence of 5.8 K/at. % of Ca^{2+} of the first phase transition is very consistent with the theoretical value 5.4 K at. % recently calculated from ionic radii considerations.[15,16] The most striking feature in the mixed materials is certainly the fact that the T_{c2} and T_{c3} transitions are found to be more sensitive to the Ca^{2+} concentration than the T_{c1} transition is. This demonstrates the major role played by this ion in the rotation of the octahedra and evidences that the very reason to observe the SPT in this system is related to the compactness of the unit cell as clearly shown by Kassan-Ogly and Naish.[14] The evolution of the angles of rotation in the mixed compounds should not differ much from what happens in the pure compound. However, due to the upwards shift of the T_{c2} transition temperature, it is clear that the ϕ_z tilt angle in phase II must become less and less important when x is increased and that, subsequently, the tetragonality at T_{c2} also becomes less and less pronounced. This is, in a certain way, a paradox since it is obvious that Ca^{2+} ions favor the rotation of the octahedra. However, it is very clear from our results that this behavior is due to the competition which develops between the R-point transition characterized by opposite rotation of the octahedra along the z axis and the M-point transition characterized by rotation of the octahedra in the same direction along the z axis.

The reason for which the Ca^{2+} ions should induce a crossover between the M-point and R-point transitions is not known. However, one can notice that the transition at the R point occurs first in perovskites ABX_3 where the tolerance factor introduced by Goldschmidt,[22]

$$\tau=\frac{(r_A+r_X)}{\sqrt{2}(r_B+r_X)}\ ,$$

is close but less than one, as in $RbCaF_3$, $KMnF_3$, and $SrTiO_3$ (in this formula r stands for the ionic radius of the A, B, or X ions). When this factor is, equal to one, all the ions touch together and the perovskite is ideal. Such a perovskite does not undergoe any SPT as, for example, $RbMnF_3$, for which $\tau=1.002$ (the calculation of τ is performed according to Shannon's table of ionic radii[23]). The further away from $\tau=1$ this factor is, the more unstable the perovskite. The introduction of Ca^{2+} in $KMnF_3$ dramatically reduces the Goldschmidt factor since $\tau_{KMnF_3}=0.9779$ and $\tau_{KCaF_3}=0.9052$. For this reason, the doped perovskite $KMn_{1-x}Ca_xF_3$ is bound to be more unstable than pure $KMnF_3$. This is evidenced in our study by the gradual increase in the T_{c1} transition temperature which follows the evolution of the Goldschmidt factor but also by the inferred existence of a crossover between the R-point and M-point transitions. As a matter of fact, it seems a general rule that perovskites having a small τ factor display the M-point transition first at relatively high temperatures and then the R-point transition. This is, for instance, the case in $KCaF_3$ ($\tau=0.9052$) and $CsPbCl_3$ (Ref. 18) ($\tau=0.8689$).

From a microscopic standpoint, the crossover is also related to the well-established presence in these compounds of the nearly flat R to M branch of phonons. The existence of such a flat branch indicates that rotation (M-point transition) or antirotation (R-point transition) of the octahedra around the z axis of the cubic phase have almost the same probability. As shown by Cowley[24] in $SrTiO_3$ and later on in $RbCaF_3$ by Rousseau[25] and Rousseau *et al.*,[26] this behavior is due to the competition between short-range forces and electrostatic Coulomb forces. Such a competition can either favor the R transition or the M transition and certainly can be drastically altered by small changes in composition since the phonon frequencies are strongly dependent upon both the composition (force constant) and the distance between ions. It is clear in our study, that the competition between the R-point and the M-point transitions is enhanced by the substitution of Mn^{2+} ions by Ca^{2+} ions and that, for an estimated concentration $x=0.075$, the R-point and the M-point frequencies should vanish simultaneously. The existence of such a critical concentration is very promising since it is not yet clear whether the system will evolve towards a glassy system or an incommensurate phase. The study of the doped system at this concentration is now in progress.

Finally, let us also point out that, since Ca^{2+} ions are nonmagnetic, our work clearly demonstrates that the T_{c2} and T_{c3} phase transitions are real SPT since it is very unlikely to raise T_N by dilution. Another reason is that Mn^{2+} ions do not favor any spin-lattice coupling and that, therefore, no magnetostriction effects are expected in this system. In the pure system it is purely coincidental that the Néel temperature[10,11] is the same as T_{c2}. However, T_N for the present sample has not been measured. The study of the magnetic transition in this system by neutron diffraction will be reported later on.

ACKNOWLEDGMENTS

This work was supported by a joint grant from the Centre National de la Recherches Scientifique (CNRS) and National Science Foundation (NSF) under Contract No. 62513 and by North Atlantic Treaty Organization (NATO) Grant No. 0477187. We wish to thank A. Roberts and B. Shoening for their technical assistance during the course of the x-ray measurements and G. Niesseron for the crystals growth. The work at Brookhaven National Laboratory (BNL) was carried out under Contract No. DE-AC02-76CH00016 with the Division of Materials Sciences, U.S. Department of Energy. The Université du Maine, Faculté des Sciences is Unité Associée an Centre National de la Recherches Scientifique No. 807.

*Permanent address: Université du Maine, Faculté des Sciences, Route de Laval 72017, Le Mans, France.

[1] W. Cochran, Adv. Phys. **9**, 387 (1960); P. W. Anderson, in *Fizika Dielectrikov,* edited by G. I. Skanavi (Acad. Nauk SR, Moscow, 1960).

[2] T. Riste, E. J. Samuelsen, K. Ones, and J. Feder, Solid State Commun. **9**, 1455 (1971).

[3] S. M. Shaprio, J. D. Axe, G. Shirane, and T. Riste, Phys. Rev. B **6**, 4332 (1972).

[4] T. W. Ryan, R. J. Nelmes, R. A. Cowley, and A. Gibaud, Phys. Rev. Lett. **40**, 237 (1986).

[5] A. Gibaud, T. W. Ryan, and R. J. Nelmes, J. Phys. C **20**, 3833 (1987).

[6] A. Gibaud, R. A. Cowley, and P. W. Mitchell, J. Phys. C **20**, 3849 (1987).

[7] S. R. Andrews, J. Phys. C **19**, 3712 (1986).

[8] U. Nicholls and R. A. Cowley, J. Phys. C **20**, 3417 (1987).

[9] V. J. Minkiewicz, Y. Fujii, and Y. Yamada, J. Phys. Soc. Jpn. **28**, 443 (1970).

[10] G. Shirane, V. J. Minkiewicz, and A. Linz, Solid State Commun. **8**, 1941 (1970).

[11] O. Beckman and R. Knox, Phys. Rev. **121**, 376 (1961).

[12] M. Hidaka, M. Ohama, A. Okasaki, H. Sakashita, and S. Yamakawa, Solid State Commun. **16**, 1121 (1975).

[13] A. J. Heeger, O. Beckman, and A. M. Portis, Phys. Rev. **123**, 1652 (1961).

[14] F. A. Kassan-Ogly and V. E. Naish, Acta Crystallogr. B **42**, 307 (1986).

[15] A. Gibaud, R. A. Cowley, and J. Nouet, Phase Transitions **14**, 129 (1989).

[16] U. J. Cox, A. Gibaud, and R. A. Cowley, Phys. Rev. Lett. **61**, 982 (1988).

[17] A. Bulou, C. Ridou, M. Rousseau, and J. Nouet, J. Phys. **41**, 87 (1980).

[18] Y. Fujii, S. Hoshino, Y. Yamada, and G. Shirane, Phys. Rev. B **9**, 4549 (1974).

[19] U. J. Cox, J. Phys. Condens. Matter **1**, 3565 (1989).

[20] A. M. Glazer, Acta Crystallog. A **31**, 756 (1975).

[21] R. Clark, Phys. Rev. Lett. **39**, 1550 (1977).

[22] V. W. Goldschmidt, J. Math. Naturvid. Klass **2**, 97 (1926).

[23] R. D. Shannon, Acta Crystallogr. A **32**, 751 (1976).

[24] R. A. Cowley, Phys. Rev. **134**, 981 (1964).

[25] M. Rousseau, J. Phys. Lett. **40**, 439 (1979).

[26] M. Rousseau, J. Nouet, and R. Almairac, J. Phys. **38**, 1423 (1977).