Pressure-induced critical behavior of $KMnF_3$ close to $P_c = 3.1$ GPa: X-ray diffraction results

S. Åsbrink
Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

A. Waśkowska
Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PL-50 950 Wrocław, Poland
(Received 25 April 1995; revised manuscript received 26 September 1995)

The critical behavior of $KMnF_3$ close to the pressure-induced cubic-to-tetragonal structural phase transition at $P_c = 3.1$ GPa has been studied by single-crystal x-ray diffraction. The pressure dependence of a primary order parameter has been determined from superlattice Bragg intensities and was found to fulfill the power law $Q = A(P - P_c)^{\beta}$. The transition with a small discontinuity of the intensities close to P_c shows deviations from the classical behavior similarly as in the temperature-dependent transition at 186 K, where the domain structure considerably affects the values of the critical parameters. However, the pressure inhibits formation of large, single domains of definite orientation. Instead, increased width of diffraction profiles points to the appearance of numerous, narrow domains which may influence the character of the transition.

Our recent high-pressure x-ray-diffraction studies on a single crystal of the cubic perovskite $KMnF_3$ (space group $Pm3m$ at ambient conditions) have shown that besides known and extensively described temperature-dependent structural and magnetic phase transitions (PT's),[1–4] there is also a pressure-induced structural PT at $P_c = 3.1$ GPa to the tetragonal phase, $I4/mcm$.[5,6] A detailed analysis of the crystal structure distortion as a function of pressure up to 6.9 GPa showed that the microscopic mechanism of the compression could be described by antiphase rotations of MnF_6 octahedra around the [001] axis in adjacent cells.[6] The shape of octahedra changes with pressure, since the Mn-F distances vary significantly (Fig. 1), so that the assumption of the constant shape of the octahedra is only approximate. Using Glazer's notation[7] this is an $a^{\circ}a^{\circ}c^{+}$ phase with enlarged unit cell: $a_t = a_c\sqrt{2}$, $c_t = 2c_c$, $(Z = 4)$. Considering these experimental data, the structural PT at 3.1 GPa appeared to be of the antiferrodistorsive nature, similarly as the corresponding temperature-dependent transition at 186 K.[8–10]

A number of theoretical treatments of temperature-dependent phase transitions in perovskites of the $SrTiO_3$-type were based on the Landau thermodynamical theory, according to which it is essential to define an order parameter Q describing the way in which a low-symmetry phase departs from the high-symmetry one.[11–14] The temperature-dependent structural instabilities in $KMnF_3$, related to the dynamics of the MnF_6 octahedra, have been characterized by a three-component order parameter $Q(Q_1, Q_2, Q_3)$ where only $Q_3 \neq 0$ below T_{c1}. Cases with $Q_1 \neq 0$ and $Q_2 \neq 0$ correspond to the other distorted phases[15–17] and are beyond the scope of this paper. The pressure dependence of Q can be expressed by the power law: $Q = A(P - P_c)^{\beta}$, where A is the amplitude of transition and β is the critical exponent describing the variation of the order parameter when $P \rightarrow P_c$. Since it is known that hydrostatic pressure changes the character of some PT's,[18,19] it was considered interesting to make comparative studies of the critical behavior of $KMnF_3$ close to the pressure-induced PT at $P_c = 3.1$ GPa. Being aware of the generally lower precision of the high-pressure experiments performed within a diamond-anvil cell compared to the low-temperature experiments, we have made an attempt to use the Landau thermodynamical approach for at least a qualitative description of the transition. For this purpose it was necessary to define a physical quantity which could be considered as an order parameter. It was established in[5] that above P_c the macroscopic strain ϵ_s is proportional to $(P - P_c)$, what means that ϵ_s is a secondary order parameter.[20,21] According to Nicholls and Cowley[10] and Cox[22] a primary order parameter of the transition $Pm3m \rightarrow I4/mcm$ can be related to the intensities of the superlattice reflections which arrive above P_c and are entirely caused by the F_1 atom displacement from the high-symmetry position. Assuming this displacement as a driving force for the transition we have extended our earlier investigations by measuring:

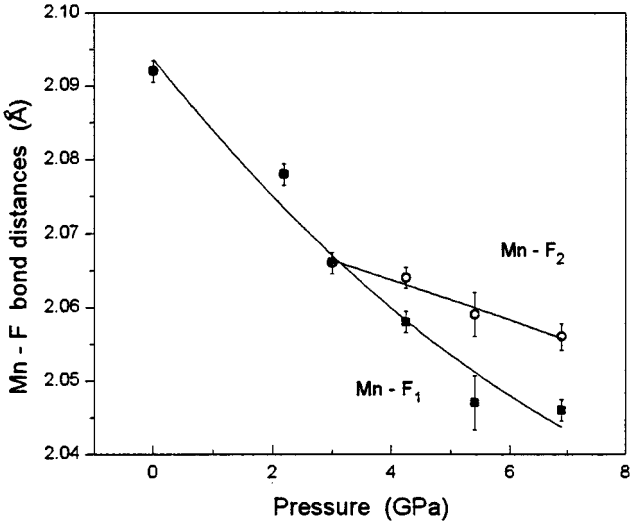

FIG. 1. The pressure-dependent octahedral change in $KMnF_3$ in the cubic and tetragonal phases. The ($Mn\text{-}F_1$) denotes equatorial, and ($Mn\text{-}F_2$) azimuthal bond distances in the octahedron.

(1) integrated intensity variation of the superlattice reflections $(211)_t$ and $(123)_t$,
(2) full width at half maximum (FWHM) of the main Bragg reflections $(400)_c$ and $(004)_c$ in connection with the arrival of a domain structure due to the tetragonal deformation.

The present experiment is concerned with the effects in the vicinity of P_c; thus the pressure range has been confirmed up to 4.1 GPa, which allowed the use of a relatively large sample, ensuring better counting statistics. A high-quality monodomain sample $\sim(150\times160\times50)$ μm was mounted in a diamond-anvil cell (Diacell products, DXR-4 UK) together with a crystal of fluorite for pressure calibration. A 4:1 mixture of methanol:ethanol was used as the pressure transmitting medium. The Inconel X-750 gasket had at the start a hole of the diameter $d=0.25$ mm. The x-ray-diffraction experiment was carried out on a STOE 4-circle diffractometer with graphite monochromated Mo $K\alpha$ radiation (60 kV, 40 mA). Before and after each pressure point the 2θ angles of two {111} fluorite reflections were measured and used to determine the pressure from the equation of state for CaF_2 (Ref. 23) with a precision of 0.04 GPa. Crystal offset errors and instrumental systematic errors were controlled by using a procedure of Hamilton,[24] modified by King and Finger.[25] The orientation of the sample was controlled at each pressure from setting angles of 12–14 strong reflections ($9°<2\theta<19°$) using the standard centering and double scan procedure ($\omega_-\theta_-$, $\omega_+\theta_+$) of the STOE software which allowed improving the precision (e.s.d.'s of unit-cell parameters from 0.01 to 0.001–0.002 Å). The intensities and profiles of superlattice reflections together with their Friedel pairs were measured with counting time 100 sec/step, using ω-scan technique. The long measuring time was used to obtain a better signal/background ratio. Normal Bragg reflections were measured with time 10 sec/step. The intensities were corrected for background, and Lorentz and polarization effects. Experimental constraints imposed by the high-pressure technique cause that the pressure intervals, dependent on the elastic properties of the gasket material, could not be controlled as precisely as the temperature in the cause of temperature dependencies. Thus, the reduced pressure range $p=(P-P_c)/P_c\leqslant0.2$ could not be covered with as many experimental points as wanted, although special care had been taken to slowly compress the sample in order to perform the measurements with as small pressure intervals as possible.

The evolution of the $(211)_t$ peak profile as a function of pressure in the tetragonal phase is shown in Fig. 2 (solid lines are eye guides only). The profile at $P=3.03$ GPa has been obtained after decreasing the pressure below P_c, but all the others were measured with the increasing pressure. The nonvanishing intensity below P_c can be attributed either to diffuse scattering—the experimental arrangement, however, was not suitable for a more quantitative study of the effect connected with short-range interactions—or to a hysteresis of about 0.15 GPa. It was observed that intensities corresponding to increased and decreased pressures were different within this pressure range. If we relate this effect to the pressure hysteresis, its magnitude appears slightly higher than three standard deviations of the pressure determination (0.04 GPa).

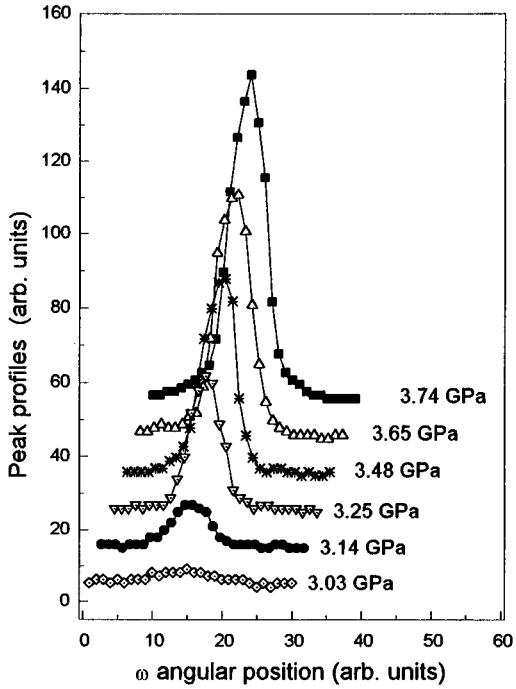

FIG. 2. Evolution of peak profiles (ω scan) of superstructure reflection $(211)_t$ with pressure. The solid lines are guides to the eye.

The integrated intensities of the $(211)_t$ and $(123)_t$ reflections between 2.5 and 4.1 GPa across P_c were measured and individually fitted by the least-squares method to the experimental power law: $I=A(P-P_c)^{2\beta}$, with A, β, and P_c as the refined parameters [Fig. 3(a)]. In Fig. 3(b) the squared intensities are plotted against the reduced pressure. It is seen that the two reflections differ in character: the strong $(211)_t$ shows the features corresponding to a first-order transition, while the weak $(123)_t$—due to the poorer counting statistics—changes less rapidly above P_c.

Taking into account the deviation of $(211)_t$ superlattice reflection from the classical behavior (Fig. 3), we have used the formula for the free energy extended to a first-order transition by adding a term of the sixth power of the order parameter Q:

$$F=1/2a(P-P_c)Q^2+1/4bQ^4+1/6cQ^6, \tag{1}$$

the coefficients a and c are positive and b is negative.[13]

Minimization of (1) gives the well-known formula:

$$Q^2=A_1\{1+[1-A_2(P-P_c)]^{1/2}\}, \tag{2}$$

where $A_1=-b/2c$ and $A_2=4ac/b^2$. Fitting the data $I=K(P-P_c)^{2\beta}$ to Eq. (2) we find that $K^2A_1=173(31)$, $A_2=0.21(15)$, and $P_c=3.12(5)$ GPa. From the positive sign of A_1 it follows that $b<0$. As the parameters A_1 and A_2 are highly correlated one may only state that the probability for the transition to be of first order is higher than it is of second order.

Examination of the domain formation is essential in considering the effects influencing the transition character. One of the ways of observation of the domain appearance in the tetragonal phase is to measure the full width at half maximum (FWHM) of $(400)_c$ and $(004)_c$ reflections as a function

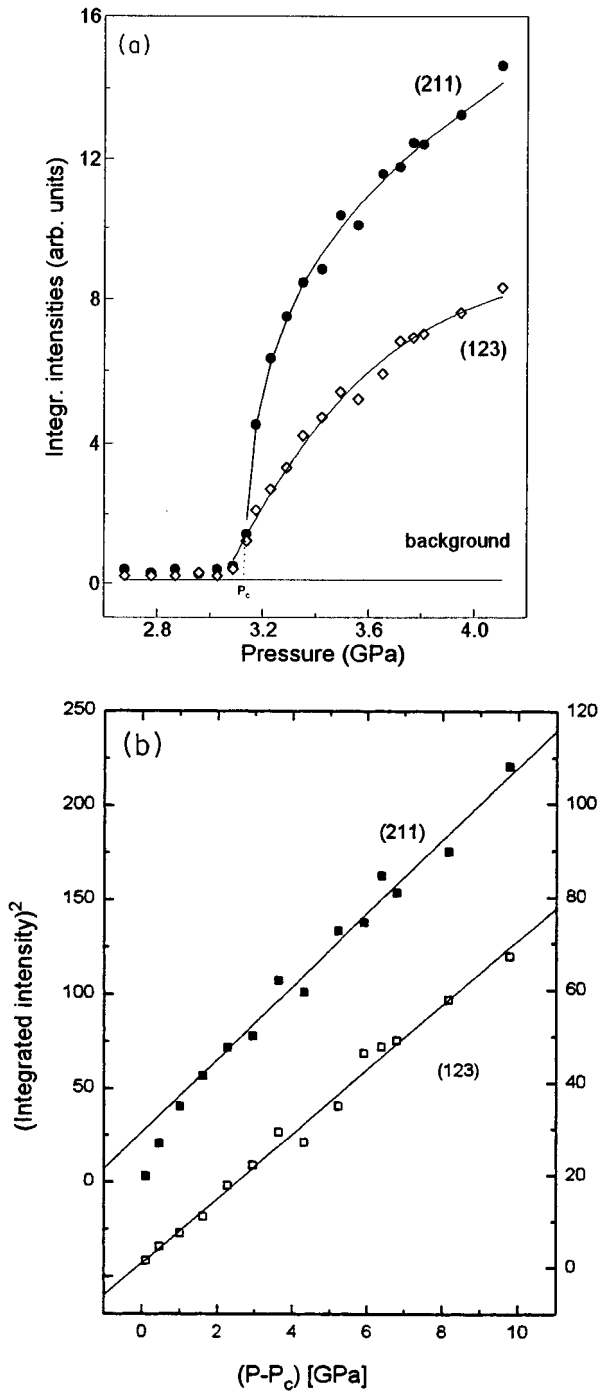

FIG. 3. (a) Integrated intensities of $(211)_t$ and $(123)_t$ reflections as a function of pressure. The solid lines are least-squares fits to the power law: $I=A(P-P_c)^{2\beta}$, where P_c' shows the transition pressure from $(211)_t$, averaged $\beta=0.24(7)$. (b) Squared integrated intensities of $(211)_t$ and $(123)_t$ reflections *versus* $(P-P_c)$. The left- and right-side Y axes correspond to $(211)_t$ and $(123)_t$ reflections, respectively.

of pressure. A Gaussian fit to the peak profiles showed rapid broadening of both reflections in the vicinity of P_c (Fig. 4), which means that each cubic axial reflection splits into a number of tetragonal peaks. High-resolution x-ray studies of the temperature-dependent domain distribution in $KMnF_3$ (Ref. 22) and related $RbCaF_3$ (Refs. 26–29) showed that the simple model of three orthogonal clusters[29] was considerably

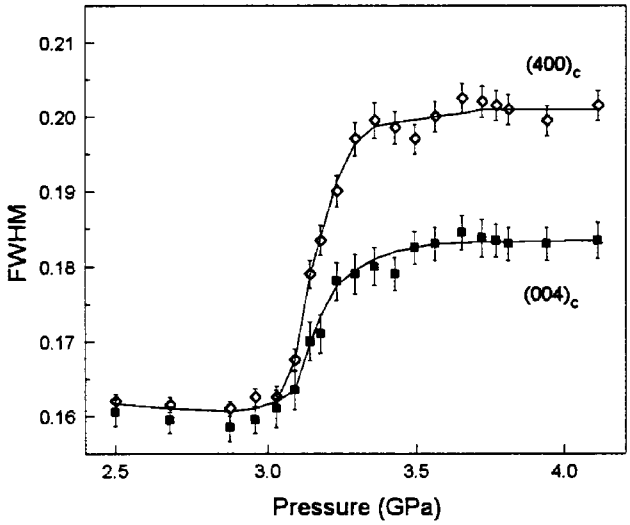

FIG. 4. Full width at half maximum (FWHM) (arc deg in ω), of the reflections $(400)_c$ and $(004)_c$ as a function of pressure.

more complicated, and in Ref. 28 it was exhibited that the cubic reflection $(h00)_c$ could split into as many as ten tetragonal peaks. This process seriously affected the intensity of superlattice reflections, because the relative proportions of the particular domains were temperature dependent. In the present investigation the domain formation takes place mainly close to P_c as it is seen from Fig. 4. In the high-pressure phase apart from the transition pressure the FWHM did not change significantly, as long as the sample was not decompressed below P_c. It seems that hydrostatic pressure suppresses the creation of large domain clusters with definite orientation which was observed in the temperature-dependent transition. Instead, numerous, narrow domains were formed and they could be a reason for the intensity tail below P_c (Fig. 2).

The present study demonstrates that high-pressure single-crystal diffraction results, used to characterize a phase transition in terms of Landau theory, enables the approximation of an order parameter. It is known that critical fluctuations, leading to hysteresis effects and influencing the transition pressure, may cause the transition to show features of the first order. Although we were not able to measure the lattice diffuse scattering, we have, in fact, observed that P_c was shifted towards the higher pressures on increasing pressure, while on decompression, when P_c was approached from above, the nonvanishing intensity of the superlattice reflections persisted below P_c. The shift of the transition pressure, $\Delta P_c=0.15(4)$ GPa (1.5 kbar), shows the metastability limits. The transition at 3.1 GPa might be correctly described as a weak first-order transition. The phenomena related to the first-order character of the transition are limited to the narrow critical pressure region and thus are difficult to access in the high-pressure experiment.

We are grateful to Dr. A. Ratuszna for excellent samples. The valuable discussions with Dr. Ewa Gałdecka are also gratefully acknowledged. Financial support was provided by the Royal Swedish Academy of Sciences, the Swedish Natural Science Research Council, and the Polish Academy of Sciences.

[1] V. J. Minkiewicz, Y. Fujii, and Y. Yamada, J. Phys. Soc. Jpn. **28**, 443 (1970).
[2] G. Shirane, V. J. Minkiewicz, and A. Linz, Solid State Commun. **8**, 1941 (1970).
[3] K. Gesi, J. D. Axe, G. Shirane, and A. Linz, Phys. Rev. B **5**, 1933 (1972).
[4] S. M. Shapiro, J. D. Axe, G. Shirane, and T. Riste, Phys. Rev. B **6**, 4332 (1972).
[5] S. Åsbrink, A. Waśkowska, and A. Ratuszna, J. Phys. Chem. Solids **54**, 507 (1993).
[6] S. Åsbrink and A. Waśkowska, Eur. J. Solid State Inorg. Chem. **31**, 747 (1994).
[7] A. M. Glazer, Acta Crystallogr. B **28**, 3384 (1972).
[8] A. Gibaud, S. M. Shapiro, J. Nouet, and H. You, Phys. Rev. B **14**, 2437 (1991).
[9] A. Ratuszna and A. Kachel, Acta Crystallogr. B **48**, 118 (1992).
[10] U. J. Nicholls and R. A. Cowley, J. Phys. C **20**, 3417 (1987).
[11] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, Oxford, 1962).
[12] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectric and Related Materials* (Clarendon, Oxford, 1977).
[13] R. A. Cowley, Adv. Phys. **29**, 1 (1980).
[14] A. D. Bruce, Adv. Phys. **29**, 111 (1980).
[15] V. J. Minkiewicz and G. Shirane, J. Phys. Soc. Jpn. **26**, 674 (1969).
[16] M. Hidaka, N. Ohama, A. Okazaki, H. Sakashita, and S. Yamakawa, Solid State Commun. **16**, 1121 (1975).
[17] M. Hidaka, H. Fujii, and S. Maeda, Phase Transitions **6**, 101 (1986).
[18] K. Gesi, J. Phys. Soc. Jpn. **58**, 1532 (1989).
[19] T. G. Worlton and R. A. Beyerlein, Phys. Rev. B **12**, 1899 (1975).
[20] A. Aizu, J. Phys. Soc. Jpn. **28**, 717 (1970).
[21] J.-C. Toledano and P. Toledano, Phys. Rev. B **21**, 1139 (1980).
[22] U. J. Cox, J. Phys. Condens. Matter. **1**, 3565 (1989).
[23] L. Gerward, J. Staun Olsen, S. Steenstrup, M. Malinowski, S. Åsbrink, and A. Waśkowska, J. Appl. Crystallogr. **25**, 578 (1992).
[24] W. C. Hamilton, *International Tables for X-ray Crystallography* (Kynoch, Birmingham, England, 1974), Vol. IV, p. 275.
[25] H. E. King and L. W. Finger, J. Appl. Crystallogr. **12**, 374 (1979).
[26] T. W. Ryan, R. J. Nelmes, R. A. Cowley, and A. Gibaud, Phys. Rev. Lett. **56**, 2704 (1986).
[27] A. Gibaud, T. W. Ryan, and R. J. Nelmes, J. Phys. C **20**, 3833 (1987).
[28] H. Jex, J. Maetz, and M. Müllner, Phys. Rev. B **21**, 1209 (1980).
[29] J. Maetz, M. Müllner, H. Jex, and K. Peters, Solid State Commun. **28**, 555 (1978).