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Temperature dependence of the wave vector of the incommensurate modulation in two BaMnF₄ crystals grown by different techniques ; neutron and X-ray measurements

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Résumé. — Des mesures précises en diffusion des neutrons de la variation avec la température du vecteur d'onde incommensurable δ dans deux cristaux de BaMnF₄ sont présentées. Le rôle des défauts est mis en évidence par la présence d'hystérésis global et par la valeur, différente d'un échantillon à l'autre, de l'incommensurabilité résiduelle à basse température.

Une faible déformation spontanée du réseau a été mise en évidence par une étude aux rayons X de la largeur des taches de Bragg.

Cet effet est en accord avec la prédiction théorique d'une ferroélasticité pour $T < T_0$ ($T_0 \simeq 250$ K).

Abstract. — Neutron elastic scattering measurements on two incommensurate BaMnF₄ crystals show that the incommensurability δ is temperature dependent. The large observed « global » hysteresis and the sample dependent residual value of the incommensurability at low temperature indicate the importance of lattice defects.

A very small angular lattice distortion has been observed below $T_0 \simeq 250$ K by means of X-ray measurements of the width of some Bragg spots.

This observation is in agreement with the theory of the structural transition in BaMnF₄ which predicts the possibility of a ferroelastic strain below $T < T_0$.

BaMnF₄ is an intensively studied compound which exhibits an incommensurate phase with special characteristics : the wave vector of the incommensurate modulation was reported to be independent of the temperature [1] and no incommensurate-commensurate « lock-in » transition could be observed. Recently, X-ray, electron, neutron scattering and specific heat measurements have shown that in some samples two phase transitions occur at 255 K and 247 K [2]. The superlattice spots below 247 K appear at (0.40, 0, 0.5) instead of (0.39, 0.5, 0.5) [1], and thus

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this phase would be commensurate with the orthorhombic A_{2am} disordered phase. These results are in disagreement with [1] and could be sample dependent [2, 3]. The authors of the first neutron scattering investigation [1] have recently repeated their measurements [4] which confirms their previous experiments : the phase below 247 K is incommensurate with a slight temperature dependence of the incommensurability [5] : the wave vector of the incommensurate modulation changes from $\mathbf{q}_\delta$ (250 K) $\simeq 0.389 \mathbf{a}^*$ to $\mathbf{q}_\delta$ (120 K) $\simeq 0.394 \mathbf{a}^*$. Slightly different $\mathbf{q}_\delta(T)$ curves were obtained on heating and cooling.

In this paper we present results of two neutron elastic scattering measurements, with two samples grown at the University of Le Mans by different methods. The sample « B » (Bridgman grown crystal) is parallelepipedic ($8 \times 6 \times 4.5 \text{ mm}^3$), clear, transparent, and pink. Its alignment on the three-axis spectrometer revealed that it contained at least three weakly misorientated crystals. The largest was chosen for the first investigation.

In the second experiment we used a larger sample, « C » (Czocharalski grown crystal) of $15 \times 10 \times 10 \text{ mm}^3$. This sample contains only one single crystal, as revealed by the neutron investigation.

The two neutron scattering measurements were carried out using the three-axis spectrometer IN2 at the I.L.L. high flux reactor in Grenoble. The experiments were done with a fixed incoming neutron energy of 5 meV. A beryllium filter was used to reduce higher order contamination. Horizontal collimation, with respect to the outgoing beam was $60', 40', 40', 40'$. In both cases, the samples were mounted with the $|100|$ and $|011|$ directions in the scattering plane and special attention was paid not to reverse the temperature variation between 300 K and 4 K.

We present also X-ray measurements of Bragg spots widths in the disordered and in the incommensurate phase on samples B' having the same origin as sample B (Bridgman), but with a spherical shape and a diameter of about 0.2 to 0.6 mm. Our results are summarized and then discussed.

1. Elastic neutron scattering results.

Figure 1 shows the temperature dependence of the incommensurate modulation δ

$\left| \mathbf{q}_\delta = \left(\delta \mathbf{a}^*, \frac{\mathbf{b}^*}{2}, \frac{\mathbf{c}^*}{2} \right) \right|$ obtained with the « B » and « C » samples. We have also reported Cox's results [5].

Fig. 1. — Temperature dependence of δ of the incommensurate wave vector $(\delta, 0.5, 0.5)$. a) dotted line : results from Cox *et al.* [5]; b) dashed line : results obtained with the « B » sample (■ : 1st order satellites for decreasing temperature; □ : *idem* on heating; ○ : 2nd order satellite on cooling; ⊙ : *idem* on heating); c) solid line : results obtained with the « C » sample (× = on cooling; ● on heating).

Curve b gives the variation of δ in the « B » sample, obtained by decreasing the temperature and by averaging over five first order satellite positions. Measurements of the second order satellite (1.21, 0, 0) are also reported. The error bars estimated to ± 0.001 take into account the errors on the crystal parameters and the misalignment of the spectrometer. We notice a small increase of δ between 220 K (0.392) and about 65 K (0.396) and no appreciable variation of δ below 65 K. On heating, we observed on the second order satellite that δ keeps the same value as in the lower temperature range up to 150 K. This is an indication of hysteresis in the incommensurate phase in agreement with the observations of [5]. Although the maximum value of δ is near the commensurate $2/5$ value, it is however unambiguously incommensurate. Therefore these results show that, in disagreement with [2], the BaMnF_4 sample « B » exhibits an incommensurate phase below $T_0 \simeq 250$ K. It is clear also that the residual value of the incommensurability at low temperature is sample dependent : the maximum value of δ in [5] is certainly < 0.395 .

Our second neutron scattering experiment was performed with the sample « C ». A systematic investigation of the hysteresis of δ was undertaken ; a hysteresis on the intensities of the incommensurate satellites peaks and on the Bragg peak (200) was observed also.

In figure 1, curve c represents the variation of δ with temperature. The most noticeable features of δ 's behaviour are : the incommensurate deviation $\delta' = \frac{2}{5} - \delta$ slightly decreases with decreasing temperature. δ increases from 0.389 at 250 K to 0.399 at about 65 K, a value which is, within the experimental accuracy, commensurate. Below 65 K, δ remains constant. On heating the crystal, δ keeps its constant value up to about 170 K and then decreases down to 0.389 at about 250 K. So, there is a large temperature range (~ 65 to ~ 250 K) showing « global » hysteresis in the δ value. This hysteresis has the same order of magnitude as in the $\{\text{N}(\text{CD}_3)_4\}_2\text{ZnCl}_4$ [6] and is about ten times smaller than in barium-sodium-niobate (BSN) [7]. However the temperature dependence of δ' in BaMnF_4 exhibits some analogy with that of δ in the incommensurate phase II of BSN : small remaining constant incommensurability in the lower temperature range, and large thermal hysteresis above.

Curve c of figure 1 was obtained by averaging the measured positions of two first order satellites.

The experiment was done two times, at the beginning and at the end of a hydrostatic pressure experiment of ten days on the sample « C ». The two runs give reproducible data.

In figure 2a we have plotted the intensity of the ($\pm 0.39, 1.5, 1.5$) satellites as a function of

Fig. 2. — Intensity of the incommensurate satellite on heating (●), and cooling (×). Intensity of the Bragg (011) on heating (□) and cooling (■). Intensity of the Bragg (200) on heating (Δ) and cooling (○). The scales are different for the three.

the temperature on heating and cooling. The intensity on heating is about 10 % larger than the intensity at the same temperature on cooling. This small hysteresis is observed below about 200 K. During the same temperature cycle, the Bragg peak (011) exhibits no hysteresis within the experimental accuracy (Fig. 2b). On the contrary, in figure 2c is plotted the intensity of the Bragg (200). Between about 60 K and 230 K, the intensity on heating is roughly 10 % smaller than the intensity on cooling.

2. Spontaneous deformation in the incommensurate phase.

X-ray measurements of the angular width of the Bragg spots have been performed on a 3-circle diffractometer using different sources : Mo- K_{α} , Mo- K_{β} and Cu- K_{β} . Evidence for a temperature dependence of the angular width has been made by performing (ω) scans. Coupled (ω) and ($\theta - 2\theta$) scans were used in order to draw intensity contour maps at room temperature and 80 K.

A summary of the results is shown on figure 3 : the scans are either parallel to one of the 3 crystallographic axes, or oblique (as for 404). All the spots indicated on figure 3 have been scanned at room temperature and at 80 K. If a significant change in the angular width ($> 0.03^\circ$) is observed between these two temperatures, the corresponding scan is indicated by a double line and the change of the width is given. With the instrumental resolution used (FWHM = 0.15° , in the best case) only one type of effect has been evidenced, namely the angular width parallel to the b^* axis increases for all spots hkl which have l different from 0. The amplitude of this effect does not depend on the observed spot so that a mean change of 0.07° can be deduced between room temperature and 80 K.

Fig. 3. — Summary of all X-ray scans performed on the Bragg spots. The direction of the different scans is indicated by arrows. When a change in the width is visible between 80 K and room temperature the corresponding scan is indicated by a double line. The angular change of the corresponding Bragg spot width is given.

A possible interpretation of this effect can be given if it is assumed that the α angle (between b^* and c^*) slightly departs from 90° for T below T_c . As the two cases ($90^\circ - \eta$) and ($90^\circ + \eta$) are equally probable the c^* axis is double and the change in the angular width roughly represents the angle 2η (a true deconvolution of the data has not been tried).

The angular width change of the (002) spot obtained by increasing temperature, is shown in figure 4. Points obtained by decreasing temperature fall on the same curve within the error bars.

Fig. 4. — Temperature dependence of the angular width of the (002) Bragg spot. The solid line reproduces the intensity of a first order satellite [1].

In the theory by Dvorak and Fousek for the structural transition of BaMnF_4 [3], the spontaneous deformation u_{yz} is a second order parameter which couples to the primary order parameter ξ by a term (lowest order coupling term : $u_{yz}\xi\xi^*$).

This gives a temperature dependence of u_{yz} of the form $u_{yz} \sim |\xi|^2$, then $\eta \sim |\xi|^2$ i.e. proportional to the intensity of a first order satellite.

The change in the angular width can be directly compared to the intensity of the first order satellites obtained from neutron measurements. The curve of figure 4 reproduces the correctly calibrated curve $I(0.39, 3/2, 3/2) = f(T)$ given by Cox *et al.* The basic line is taken at 0.164° . The agreement with the experimental points is satisfactory. The values obtained for the η angle in this hypothesis are comparable to those found by Bastie and Bornarel in $\text{Th}(\text{MoO}_4)_3$ which presents a similar ferroelastic behaviour [9]. The occurrence of a u_{yz} strain is a proof that the solution for the incommensurate phase is not of the (i) type described in references 1 and 8, in agreement with the recent results of Cox *et al.* [5]. The angular width change is expected to exhibit some thermal hysteresis like the intensity of the satellite (Fig. 2). However, the error bars in figure 4 are too large to allow its observation.

Besides this, it is also worth noting that our X-ray data never indicated the existence of (0.4,

0, 0.5) reflections. Moreover, our DTA and DSC measurements reveal the existence of only one phase transition at about 250 K whatever the origin of the sample was (Czochralski, Bridgman on hydrothermal synthesis).

3. Discussion.

New information are provided by the comparison of the three data presented in figure 1 : it is now clear that q_0 is slightly temperature dependent and that a global hysteresis exists in the incommensurate phase down to about 65 K. This behaviour may be attributed to a significant influence of defects, as was observed in the case of BSN [7] and others substances [10]. The value of $\delta(T)$ is sample dependent even in the neighbourhood of the disordered-incommensurate phase transition. However, at T_0 , it seems that the three samples exhibit the same value, $\delta \simeq 0.389$. The maximum value of $\delta(T)$ below 65 K is also sample dependent. However, this temperature $T \simeq 65 \pm 5$ K at which the hysteresis disappears and at which $\delta(T)$ becomes constant, is certainly the same for the two samples B and C [11]. For the heating runs, the temperature at which δ begins to decrease is sample dependent (170-180 K in sample C ; around 220 K in Cox's sample).

Among these experimental facts, the sample dependent behaviour and the hysteresis may be qualitatively explained by the influence of lattice defects, in a description of the incommensurate phase consisting of commensurate domains bounded by discommensurations pinned by defects.

It is admitted [10] that, in a cooling run, the structure reached at a given temperature T is not that corresponding to the thermal equilibrium at T (realized in a defect free crystal), but rather that corresponding to a little higher temperature. On the contrary, the real structure in a heating run corresponds to the structure expected in a defect-free crystal for a lower temperature. This explains the sense of the variation of $\delta(T)$ in cooling and heating runs and also the hysteresis on the intensity of the satellite which would obey a power law $\left(\frac{T_0 - T}{T_0}\right)^{2\beta}$ in a defect-free crystal.

Fig. 5. — Summary of the results of different authors in the hypothesis of a low-temperature nearly-commensurate phase with a thermal hysteresis depending on the lattice defect concentration.

It is also worth noting that the sample « C », due to the crystal growth techniques, presumably contains less defects than the others and it reaches a nearly commensurate value for δ [11]. The temperature of about 65 K appears like a threshold below which the discommensurations become unable to move and thus the wave vector δ becomes constant [12]. This temperature can be considered as an activation energy for the diffusion of phase solitons. In contrast to the case of BSN, we have not observed any discontinuity on δ . So, it is impossible as yet to decide whether a true phase transition occurs or only a very smooth continuous change of δ .

However, the two temperatures (≈ 65 K on cooling and ≈ 170 K on heating on sample « C ») could appear like the limit of metastability of a nearly-commensurate phase. This suggestion is founded on the demonstration in [10] that the defects increase the range of thermal hysteresis at the « lock-in » transition.

Moreover, this suggestion of a nearly commensurate phase allows a tentative explanation for some of the discrepancies between the results from [1] and [2] : the specific heat measurements [2], given on heating two transition temperatures at 247 K and 255 K, would be consistent with the data of figure 1, accounting for the difference in defect concentration in different samples. This hypothesis is summarized on figure 5. On heating, the transition temperature between the δ constant to the δ variable regime would be different from sample to sample, depending on the lattice defect concentration.

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 - [12] It is interesting to point out, though this fact is unexplained, that this energy, corresponding to 65 K (i.e. ≈ 1.35 THz or 5.6 meV) has the same order of magnitude as the spin wave energy.
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