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Observation of forbidden Bragg reflections in BaMnF_4

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Résumé. — Des mesures aux R.X. et aux neutrons ont été utilisées pour mettre en évidence une faible tache de Bragg (100) dans BaMnF_4 , à température ambiante, dans le cas de cristaux présentant un certain volume (comparable à celui utilisé dans les expériences courantes : optique, infrarouge, Raman, neutrons, ...). L'intensité de cette réflexion croît à basse température. Cet effet n'est pas observé dans les petits cristaux ($\sim 0,02 \text{ mm}^3$). Au cours d'une brève discussion nous suggérons que le groupe d'espace $A_{2,1\text{am}}$ ne serait pas correct pour ces gros échantillons de BaMnF_4 .

Abstract. — Neutron and X-ray techniques have been used to show that a weak (100) Bragg reflection appears in BaMnF_4 at room temperature, in large samples, i.e. samples used in current experiments (optic, infrared, Raman, neutrons...). The intensity of this reflection increases at low temperature. This effect was not observed in small samples ($\sim 0.02 \text{ mm}^3$). In a brief discussion we suggest that the space group $A_{2,1\text{am}}$ would not be correct for these large samples of BaMnF_4 .

1. **Introduction.** — Extensive work has been done on magnetic, structural and dynamical properties of BaMnF_4 [1-4].

The two peculiarities of its incommensurate phase (below $T_c = 247 \text{ K}$) are that the wavelength of its deformation wave does not change with temperature and that no lock-in transition has been found as the temperature is lowered till 4 K. At our knowledge the atomic displacements of the incommensurate modulation wave have not been determined until now. Due to the richness of its properties, this compound still raises theoretical and experimental questions.

In the course of an experiment concerned with the magnetic properties of BaMnF_4 , where we used neutrons diffraction technic, we had the surprise of founding a weak (100) Bragg reflection : this reflection is normally forbidden by the selection rules of the $A_{2,1\text{am}}$ space group ($h = 2n$ for the $[h00]$ row). The present paper reports on this observation and on other observations performed later on by X-ray technics in order to confirm the neutron results.

2. **Experimental.** — 2.1 OBSERVATIONS ON A 3-AXIS SPECTROMETER (NEUTRONS). — The sample used, grown by one of us (J. N.) at Le Mans, has a parallelepipedic shape and a volume of $\sim 200 \text{ mm}^3$ (sample A). Although it looks perfectly transparent and clear, it contains several crystals (at least 2 and perhaps 3) the b axis of which are weakly disorientated of a small angle (a few degrees). The alignment of the sample on the 3-axis spectrometer IN2 at ILL has been done on the largest crystal. The experimental conditions are as followed : incoming neutron energy 5 meV, Be Filter, monochromator and analysor are PG(002), the diffusion plane is the $(01\bar{1})$ plane. On figure 1 is shown the variation with temperature of the intensity ratio $I(100)/I(200)$. It takes the value of 1.1 % at 300 K. Going down to the incommensurate phase it strongly increases from T_c although there is no real discontinuity at the structural transition. At 4.7 K, the intensity ratio gets the value of 3 %. A small anomaly is observed at $T_N = 26 \text{ K}$. Also is shown on figure 1 the intensity of the Bragg reflection (200). The jump at T_c is very small. Two anomalies are observed at low temperature : at T_N and at $\sim 50 \text{ K}$.

2.2 X-RAYS MEASUREMENTS. — As it has not been possible during the course of the neutrons experiment

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Fig. 1. — Temperature dependence of the ratio. a) $I(100)/I(200)$ (in %). The line is a guide for the eye. b) $I(200)$ (dashed line).

to ensure that the weak (100) reflection observed was not due (at least partly) to a double or a multiple scattering process, we decided to verify this point by using two different X-rays methods.

In the first experiment performed on a 3 circles diffractometer a sphere of diameter $\varnothing \sim 0.2$ mm (sample B-volume ~ 0.004 mm³) was cut from a larger crystal of the same origin as the previous one and mounted on a Lindeman capillary. The $\theta/2\theta$ scans carried out at room temperature and at ~ 100 K along the $[h00]$ row did not reveal any odd parity reflection, although the background over $I(200)$ ratio was better than 0.2 % in this case.

The experimental conditions used in the second method are as followed (Fig. 2a). The source is MoK α , $V = 28$ kV (the cut off is 35 kV for $\lambda_{\text{MoK}\alpha}/2$), the beam is focussed on a cylindrical film by a vertically bent PG(002) monochromator, the sample oscillates by 2° around a vertical (normal to the beam) axis. The angular widths of the beam are 0.14° for the horizontal and 2.0° for the vertical. Two different samples have been used. One is a plate normal to the **b** direction (sample C), of dimensions ($x \sim 5$, $y \sim 0.2$, $z \sim 3$ mm, $v = 3$ mm³), cut in a crystal grown at M.I.T. by D. Gabbe. The second sample (sample D) is also a plate of $x \sim 0.3$, $y \sim 0.1$, $z \sim 0.4$ mm ($v = 0.012$ mm³) of the same origin as samples A and B. It is comparable in size to sample B used on the diffractometer. Sample C has been mounted with a **a** axis horizontal. In a first stage the **c** axis was vertical and the (100) reflection appeared. Afterwards the sample was turned of $\sim 5^\circ$ around the scattering vector

(the horizontal **a** axis) in order to test if a multiple scattering process was not responsible for the observation of the forbidden (100) reflection.

Figures 2b and 2c correspond to the turned position of sample C at 300 K and 100 K : the (100) reflection unambiguously appears. The (300) reflection has also been observed on this sample (Figs. 2d and 2e). Although this method does not warrant a quantitative comparison between the intensities of the Bragg spots, one quotes that at low temperature the (300) reflection becomes as intense or even more, than some first order satellites of the incommensurate phase. In figure 2f which corresponds to sample D at room temperature, the (100) reflection does not appear. A large increase of the exposure time in order to compensate for the decrease of the irradiated surface (~ 1.2 mm² for sample C whereas 0.12 mm² for sample D) did not reveal the (100) reflection.

3. Discussion. — Some explanations for the appearance of the forbidden $(2n+1, 0, 0)$ reflections can be tempted. As $1/a = 0.1671 \text{ \AA}^{-1}$, $1/b = 0.0662 \text{ \AA}^{-1}$, $1/c = 0.2369 \text{ \AA}^{-1}$, one can easily verify that the (100) spot observed at room temperature cannot be due to other Bragg reflections (hkl) produced by the other disorientated crystals. If a $\lambda/2$ contamination must be rejected in all cases, it was not sure at all, as was said before, that a double scattering process was not responsible for the observation of the (100) reflection by neutron scattering. The X-rays patterns obtained with the two orientations of sample C demonstrate that it is not the case. If the forbidden reflections unambiguously appear for the large samples (A and C) the size of which is that of samples used in current experiments (optic, neutrons, infrared, Raman...), they never appear on very small samples (B and D and probably on the sample used for the structure determination by Keve *et al.* [1], and in powder spectrum by Cox *et al.* [2]). Thus it seems that a size effect occurs for the appearance of these forbidden reflections. In these conditions an explanation by an anharmonic effect on the Debye-Waller factor as it was shown in the case of Si [5] (one could think to some relaxator to be present), would not be fully satisfactory for it would not explain the difference between large and small crystals. For the same reason one does not see how the fluor vacancies ($\sim 1\%$ as quoted by Scott, J. F. [6]) could give an explanation of this effect. Thus one is left to suppose that a very slight structure change occurs with respect to the structure given by Keve *et al.* [1], i.e. the space group is no longer $A_{2,1am}$ but a different one. However one must remind that if a « very small space group change » has no sense, i.e. the space group is either correct or wrong, the structural change remains certainly very weak : the (100) intensity at low temperature is only of order 0.2 % of the strongest lines given in the neutrons powder scans of reference [2]. Why this change is more pronounced in the case of large crystals is an open question. Weak reflections forbidden by

Fig. 2. — X-rays patterns for BaMnF_4 by the photographic method described in the text. a) View of the apparatus. b) The (100) reflection is in Bragg position (arrow) at 300 K. See g) for the labelling of the spots (sample C). c) The same as in b) at $T = 100$ K (sample C). First order ($q \# (0.39, 0.5, 0.5)$) and second order ($q \# (0.22, 0, 0)$) satellites are visible. The last ones are closed to the Bragg spots. d) The (300) reflection is in Bragg position (arrow) at 300 K (sample C). e) The same as in d) at $T = 100$ K (sample C). f) The (100) reflection is in Bragg position (arrow) at 300 K, but does not appear (sample D). g) Drawing of the « images » of the reciprocal planes (00l) and (h00) i.e. images of the intersection of these planes with the Ewald sphere. The third set of lines corresponding to the planes (0k0) is not shown. Labelling of the Bragg spots applied for the b), c) and f) cases. First order satellites are located on the horizontal $l = -1/2, 1/2$ and $3/2$ lines, whereas second order satellites appear on the horizontal $l = 0, l = -1, l = +1$ lines.

selection rules have also been observed in thiourea on diffuse scattering X-rays patterns but no similar sample size effect were mentioned [7]. Taking the subgroups of $A_{2,1am}$ for which the selection rule $h = 2n$ does not apply, i.e. $A_{1,1m}$ and $A_{1,11}$ (P_1), one encounters the difficulty that the 2-fold axis parallel to the **a** direction would disappear already at room temperature. This is in contradiction with the magnetic properties, for example, for which the only group which has been proposed for the magnetic structure below T_N has the $2'$ symmetry. If the symmetry is $A_{1,1m}$ the monoclinic distortion is presumably very weak : X-rays [8] and neutrons measurements indicate that the angles between the three-axis are, within the experimental accuracy, equal to $90^\circ \pm 0.1$. Finally let us remark that the existence of a (100) reflection at room temperature demonstrates that the planes perpendicular to

the **a** direction and separated by $a/2$ in direct space, are no longer equivalent and moreover that the violated selection rule is precisely those which is related to the incommensurate **a** axis.

We did not succeed to find any satisfactory interpretation to our observations except by a small change in the structure (at least concerning some regions of the crystal, for example in domain walls). If this hypothesis is correct, it would be very interesting to perform a structure determination of $BaMnF_4$ on a large sample (neutron).

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