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On the incommensurate phase in $BaMnF_4$: sample dependence of the order parameter

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Résumé. — Nous présentons des résultats sur la dépendance en fonction des échantillons, du vecteur d'onde de la modulation, et de l'amplitude du paramètre d'ordre qui décrit la transition N ($A2_1am$) → incommensurable dans $BaMnF_4$: des mesures de diffraction de rayons X, de C_p (« DSC »), et de biréfringence, ont été effectuées sur un large éventail de cristaux synthétisés par les méthodes de Bridgman, de Czochralski, et hydrothermale. Nous proposons l'existence d'un point tricritique pouvant être atteint sous contrainte σ_{yz}, et donnons une nouvelle interprétation de l'anomalie de C_p qui avait été observée en 1982 par Scott, Habbal et Hidaka.

Abstract. — We present results concerning sample dependence of not only the modulation wave vector, but also of the amplitude of the order parameter describing the N ($A2_1am$) → incommensurate phase transition in $BaMnF_4$: X-ray diffraction, C_p (« DSC »), and birefringence measurements were performed on a wide set of crystals which were synthetized by Bridgman, Czochralski, and hydrothermal methods. The existence of a tricritical point which can be reached under a σ_{yz} stress is proposed, and a new interpretation of the C_p anomaly observed in 1982 by Scott, Habbal and Hidaka, is given.

1. Introduction.

Barium manganese fluoride has attracted the interest of physicists since its discovery, in 1967 [1]. At room temperature, the symmetry of this compound is orthorhombic (space group $A2_1am$-C_{2v}^{12}), and the structure consists of puckered sheets of MnF_6 octahedra, which share corners [2]. The arrangement of Mn^{2+} ions ($S = 5/2$) gives the system 2D magnetic properties, which have been the subject of numerous investigations [3]. Besides, a magnetoelectric effect was discovered below room temperature [3], which implied a change of the symmetry [4, 5]. Since the evidence of a structural phase transition at 250 K by a sharp anomaly in ultrasonic attenuation, the low temperature phase has been intensively investigated [3], but a number of questions still remains unclear. Indeed, the low temperature phase is incommensurate [6], and has unusual features : there is no lock-in (commensurate) phase at a lower temperature, and the modulation wave vector $\mathbf{K} = \pm \xi \mathbf{a}^* \pm (\mathbf{b}^* \pm \mathbf{c}^*)/2$ has only a weak temperature dependence, which was determined to vary from one sample to another. These characteristics are attributed [7] to a pinning of the modulation by defects of the crystal lattice. However the nature of active defects has not yet been established. Another striking feature for an incommensurate system is that the phase transition between the normal ($A2_1am$) and the modulated phase has a first order character. This is evident from the existence of a thermal hysteresis [8] and a jump in the birefringence [9] and refractive index [10] variation *versus* T. Experimental data from crystals of various origins suggest a slight sample dependence of not only ξ, but also of the order parameter (O.P.) amplitude ρ (birefringence and indices are sensitive to the thermal variation of ρ^2 [11]), since the observed jumps at T_i seem to differ.

Within the last years a new problem appeared : on the basis of specific heat data and piezoelectric measurements [12, 13], it was claimed that there were in fact two phase transitions in this compound. However, these results were contradicted afterwards [14] and no additional anomaly could be observed in birefringence [9] or indices [10] variation. Other

experiments recently exhibited 4 or 5 anomalies, as determined by piezoelectric resonance data [15], and two of these correspond to visible anomalies of thermal diffusivity. The authors of reference [15] suggested that these « transitions » represent a devil's staircase of discrete jumps in the modulation wavevector (see also Ref. [16]).

The aim of this paper is to try to clarify the situation concerning experimental data by showing new results. We present data which were obtained on samples from different origins (grown from the melt) during a period which spread over several years. Recently, $BaMnF_4$ samples were synthetized by the hydrothermal method, and these crystals have unexpectedly strongly differing properties. We shall see that they permit a better understanding of sample dependences.

Besides the thermal behaviour of **k**, the specific heat C_p and the linear birefringence are studied. The results are presented in the next paragraph, and discussed in section 3 where theoretical results concerning phase diagram are taken into account.

2. Experimental situation in various samples.

2.1 Description of the crystals and experimental procedure.

2.1.1 *Samples.* — Most of the $BaMnF_4$ crystals were obtained from the melt, by the Bridgman or Czochralski method. Among them, two are particularly well known, as they were studied by neutron diffraction : we label them in the same way as in [7], namely « B » (for Bridgman) and « C » (for Czochralski) sample. Other Bridgman (resp. Czochralski) samples will be labelled as B_i (resp. C_i). Sample C was obtained after 2 crystallizations, and is expected to contain less impurities than B. Moreover, the dislocation density in C is much lower than in B, as can be seen from X-ray topography [17]. All crystals are transparent and optically homogeneous.

The samples obtained by the hydrothermal method (diffusion technique in sealed teflon tube) were synthetized from MnF_2, BaF_2, HF, and H_2O, under the following conditions : temperature about 495 K, and pressure of the order of 2.5×10^6 Pa. They are typically plates of small size ($0.2\ mm^3$). In this paper, they will be denoted as « H » samples.

2.1.2 *Measurements.* — For the study of the satellite position as a function of temperature in the H crystals, we used a four circle diffractometer Enraf-Nonius CAD 4. The sample was cooled by a nitrogen jet maintained at a temperature kept constant to within 1 K, which was determined by means of a Ni-Cr thermocouple. Measurements were performed with a Mo source, and the value of **k** determined from scans on 8 satellites.

Specific heat measurements were performed using the differential scanning calorimetry method, with a DSC 4 Perkin-Elmer apparatus. In the case of B and C samples, we used a single crystal (typical weight : 20 mg) whereas for the study of H crystals, the cap was filled with several small crystals. For this reason, data obtained with H's are less precise than the others.

The method for the determination of birefringence variation and the way of treating the results are described in [9]. Exactly the same procedure (measurements under microscope, with sodium light source, and Babinet-Soleil compensation) is applied here.

2.2 Data on the modulation wave vector. — The summary of all the results obtained up to now is presented in figure 1. Curve « A » refers to the study of reference [14], performed by means of X-Ray diffraction. Curves « B » and « C » refer to the neutron diffraction data of [7]. In all these cases, a slight increase of the ξ value occurs on cooling, and a thermal hysteresis is evident. At low temperatures, the ξ value becomes constant. In the best quality sample (« C »), the thermal variation is more pronounced, and ξ changes from about 0.39 at T_i to 0.399 below 80 K. It is noteworthy that the value at the transition is, within experimental accuracy, sample independent. This feature is not contradicted by data from H crystals. However, in the last samples, no thermal variation of ξ can be evidenced : down to 120 K, ξ keeps a value close to 0.39 (curve « H »). In order to check a possible influence of dislocations on the thermal variation of ξ, we annealed the H crystal at 600 K : the sample was

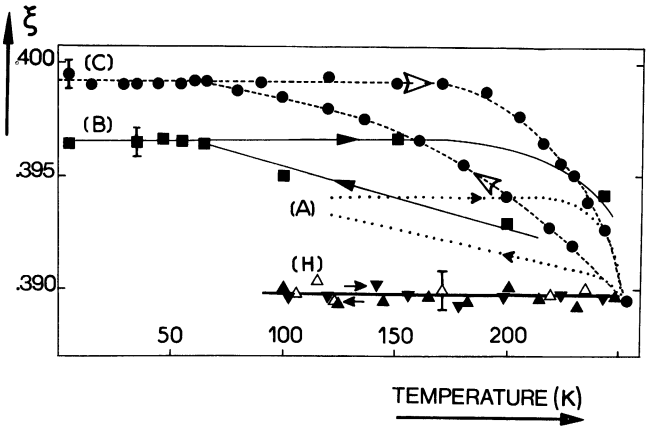

Fig. 1. — Thermal variation of the incommensurability in various samples. ξ is the wave vector component along **a*** ($\mathbf{k} = \pm \xi \mathbf{a}^* \pm (\mathbf{b}^* \pm \mathbf{c}^*)/2$). Curve A is from reference [13], B (Bridgman sample) and C (Czochralski) from reference [7]. Curve H is obtained with crystals grown by the hydrothermal method, and black and white triangles refer respectively to cooling and heating runs.

slowly heated up to this temperature, and carefully cooled again. The curve $\xi(T)$ remains however unchanged after this thermal treatment.

2.3 SPECIFIC HEAT DATA. — Figure 2 shows a set of DSC signals obtained with various samples grown from the melt. In a DSC experiment, one measures the heat quantity per time unit, necessary to keep constant the temperature variation of the sample, dT/dt, at a constant heating or cooling rate : $dQ/dt = mC_p\, dT/dt$ (m is the mass of the sample).

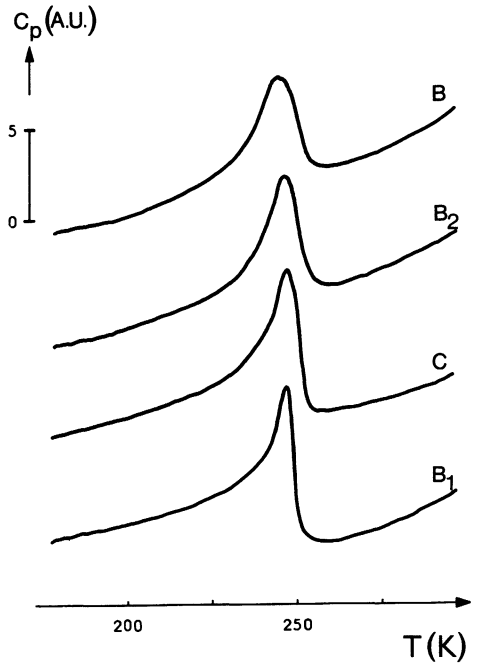

Fig. 2. — C_p thermal change in various crystals grown from the melt, labelled as B, B_1, B_2, and C respectively (see text). The units which are indicated correspond roughly to mcal/gK.

It therefore provides the specific heat (C_p) variation. In the present experiments, a sharp increase of C_p is observed at the phase transition point (towards low temperatures) and, below T_i, C_p progressively decreases again. The range of C_p variation in the incommensurate phase extends over several tens of degrees, and the anomaly is of the λ-shape type. From one crystal to another, only slight changes in the specific heat anomaly can be observed, which occur close to T_i. Indeed, in some samples, as in C and B_1, the first-order character of the transition is clear, and evidenced by the presence of a small peak corresponding to a weak latent heat associated with the structural change. On the contrary, in other crystals, as in B or B_2, the latent heat seems to be zero, and no additional peak can be detected.

In the samples grown hydrothermally, the C_p anomaly is less marked and the variation in the incommensurate phase is weaker (Fig. 3, curve a).

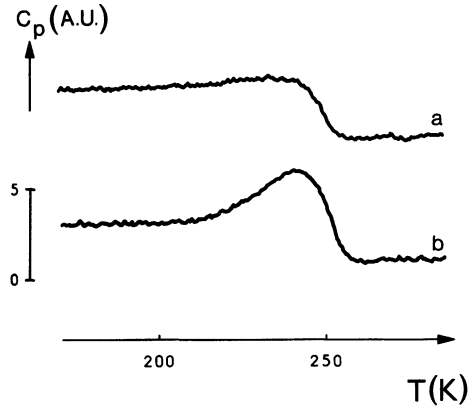

Fig. 3. — C_p anomaly in H samples. a) as-grown samples. b) after annealing at 600 K. (same arbitrary units than in Fig. 2).

As in B or B_2 samples, no latent heat at T_i can be evidenced. The C_p anomaly in these crystals is sensitive to the thermal history of the sample, and after a heating at 600 K, the signal observed on H samples is closer to the preceding ones, as it becomes λ-shaped (Fig. 3, curve b).

Let us note that, in all samples, only one anomaly is evident. In particular, we were unable to observe the second small peak reported in [12].

2.4 BIREFRINGENCE. — Figure 4 shows the thermal dependence of Δn in various samples grown from the melt. Consistently with C_p data, the difference that occurs among the various curves concerns the magni-

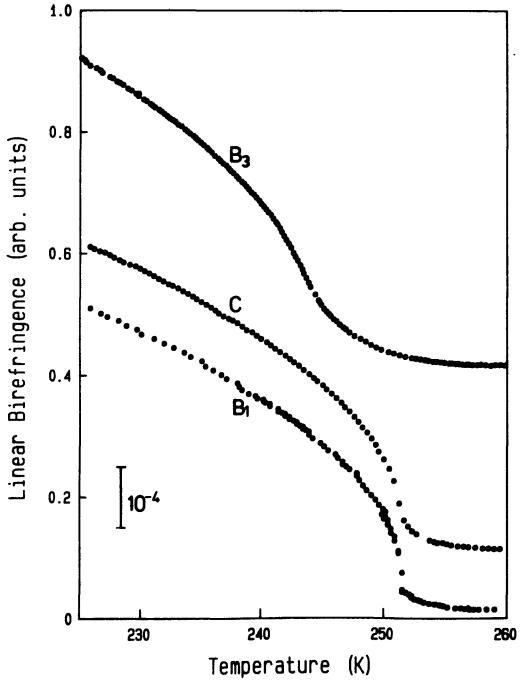

Fig. 4. — Thermal dependence of the ac plane birefringence in various samples grown from the melt, labelled as B_3, C, and B_1 respectively (see text).

tude of the jump at T_i. In some crystals, such as B_3, there is no jump at all and in C, a clear and sharp discontinuity is present. Intermediate cases were observed ; in particular, in the Δn study of reference [8], performed with the B sample, there exists a small hysteresis (close to T_i, Δn is slightly higher on heating than on cooling), but the jump is very discrete.

H samples have a strongly differing behaviour : whereas in the preceding cases, the birefringence curve is convex within the modulated phase, curve (a) of figure 5 practically shows a linear temperature dependence below T_i for as-grown H's.

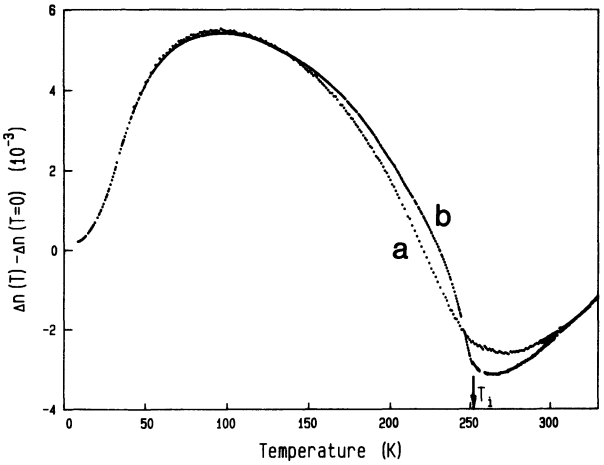

Fig. 5. — Birefringence evolution *versus* temperature in the ac plane of an H crystal of $BaMnF_4$. a) as-grown sample. b) after annealing at 600 K.

As the transition is almost continuous in $BaMnF_4$, previous studies presented fits by power laws, since the anomalous part of Δn is expected to follow the thermal variation of ρ^2 ($\delta\ \Delta n \sim \rho^2 \sim (T_i - T)^{2\beta}$). The same method applied here shows that slight differences occur among the samples grown from the melt, but the β-value lies within the range 0.27-0.28. After correction for « fluctuations » (see Ref. [9]) the anomalous part of Δn, measured in H samples, appears to be linear below T_i. The β-exponent is very close to 1/2, and its exact determination performed by least-squares fits within the range 200-250 K is $\beta = 0.495$.

The influence of annealing the H samples is of particular interest. After slowly heating up to 600 K and cooling again, the birefringence curve appears to have changed (Fig. 5, curve b) : it now presents a convexity ; this means that β significantly decreased. Indeed, fitting as described above now yields the value $\beta = 0.345$. Observation of the samples under a polarizing microscope allows us to establish that annealing removes internal strains, appearing under white light illumination as zones with different interference colors. The change in the behaviour of H's can be attributed therefore to internal strains, and annealing induces the Δn *versus* T variation to become closer to that observed on samples grown from the melt.

3. Discussion.

In this study, it is confirmed that there is a sample dependence of both the amplitude and the phase (the modulation wave vector) of the order parameter. Influence of annealing on these quantities has been investigated, and data were obtained with very different samples.

Let us first give general comments. Since it is predicted (within the framework of the theory of symmetry) that $\delta\ \Delta n$ could depend on $\mathbf{k}$ [18], one could think of the sample dependence of the modulation wave vector, in order to explain that of $\delta\ \Delta n$. This, however, is evidently contradicted by our data. Indeed, in H samples, the $\mathbf{k}$ thermal behaviour is unchanged after annealing (Fig. 1) whereas $\delta\ \Delta n$ is drastically modified (Fig. 5). Moreover, hysteresis phenomena were investigated in all crystals within the incommensurate phase : there is a hysteresis of $\mathbf{k}$ in a temperature range between about 70 K and T_i (in the samples where $\mathbf{k}$ does change), but only very small hysteresis, if any, is observed in the birefringence. The present study shows therefore that the $\mathbf{k}$-dependence of $\delta\ \Delta n$, if present, is rather weak.

As we already noticed, the parameter which is important is the magnitude of internal strains ; it influences the thermal evolution of the O.P. amplitude, but does not seem to act significantly on $\mathbf{k}$-behaviour. More likely, the thermal change of this last quantity is determined by the amount, in the crystal, of impurities which pin the modulation. A hypothetic effect of dislocations on the curve $\mathbf{k} = \mathbf{k}(T)$ would be inconsistent with the observation that annealing does not change the situation significantly.

The strong influence of internal strains supports the conclusions of Lorenc [19] and the hypothesis issued in [20]. Let us show that a natural explanation of our results can be found within this framework. In $BaMnF_4$, the O.P. has four components $\eta(\mathbf{k}_1)$, $\eta(\mathbf{k}_2)$, $\eta(\mathbf{k}_3)$, $\eta(\mathbf{k}_4)$, where the $\mathbf{k}_i$ belong to the star of the modulation wave vector :

$$\mathbf{k}_1 = \xi\mathbf{a}^* + (\mathbf{b}^* + \mathbf{c}^*)/2\ ,$$
$$\mathbf{k}_2 = \xi\mathbf{a}^* + (-\mathbf{b}^* + \mathbf{c}^*)/2\ ,$$
$$\mathbf{k}_3 = -\mathbf{k}_1\ ,\quad \mathbf{k}_4 = -\mathbf{k}_2\ .$$

Depending on the amplitudes of the invariants in the free energy expansion, various situations can occur below T_i :

(i) $\eta(k_1) = \eta(k_2) \neq 0$

(ii) $\eta(k_1) \neq 0$, $\eta(k_2) = 0$ or $\eta(k_1) = 0$, $\eta(k_2) \neq 0$ (two domain states)

(iii) $\eta(k_1) \neq 0$, $\eta(k_2) \neq 0$, and $\eta(k_1) \neq \eta(k_2)$.

These cases differ by their macroscopic point symmetry [21]. Let us recall that the set of experimental data now available permits us to know which case applies to the real system. Indeed, it was shown in [14], that systematic extinctions in the reciprocal space occur at positions such as $\mathbf{k}_1 + \mathbf{k}_2$ (and symmetry related ones). This hinted at a spatial separation of the modulations with $\mathbf{k}_1$ and $\mathbf{k}_2$ vectors. Moreover, a γ-ray diffraction study [20], gave evidence to the (improper) ferroelastic character of the incommensurate phase, and the temperature dependence of u_{yz} strain was determined. Its spontaneous appearance below T_i is due to the invariant $u_{yz} \cdot \{(|\eta(\mathbf{k}_1)|^2 - |\eta(\mathbf{k}_2)|^2)\}$, which leads, after minimisation of the free energy expansion, to the relation : $u_{yz} \sim |\eta(k_1)|^2 - |\eta(k_2)|^2$. γ-ray diffraction data are well consistent with the existence of domains characterized by opposite values of u_{yz}, and another study evidenced more directly the domains and gave an estimate of their size [22]. All these data are clearly in agreement with case (ii) only. This conclusion is consistent with the theoretical analysis of magnetoelectric effect [5] and Raman data [3].

In reference [19], Lorenc showed that precisely in the case (ii) tricritical points can be expected in the (σ_{yz}, T) phase diagram. Other anisotropic stresses give merely rise to shifts of the critical temperature. In a stress-free crystal ($\sigma_{yz} = 0$), the transition would be discontinuous due to critical fluctuations (see alro Ref. [6]), whereas at large $|\sigma_{yz}|$, it is continuous. The corresponding phase diagram is presented in figure 6 (curve a).

In the preceding part, we arrived at the conclusion that, due to internal strains (which are equivalent to the situation where one applies stresses since internal strains are expected to change only smoothly with temperature), the transition becomes continuous. This is evident from the shape of the C_p anomaly in H-crystals, and from the absence of birefringence discontinuities in crystals with internal strains. Moreover, the β exponent, in strongly stressed samples, can even reach the classical value for a second-order phase transition, $\beta = 1/2$. We can understand these data if we assume as can be expected by symmetry — that the active component of stress tensor is σ_{yz}. In reference [20], the thermal dependence of u_{yz} was determined, and fitted both by a Landau-Devonshire expression (for a first order phase transition) with spinodal lines very close to each other ($\delta T = 0.2$ K), and by a power law $(T_i - T)^{2\beta}$ with $\beta = 0.23 \pm 0.02$. From these data, it was concluded that the real system would lie close to a TCP.

The safe determination of the critical exponent β of the O.P. is a difficult task. γ-ray diffraction experiments, performed with the C sample, provide $\beta = 0.23 \pm 0.02$ whereas birefringence data from the same crystal yield $\beta = 0.28 \pm 0.02$. The origin of this discrepancy is not known, but it seems that the birefringence behaviour is more complicated than a simple law $\delta \Delta n \sim \rho^2$. Moreover, in the analysis of this quantity, it is necessary to estimate and to subtract the thermal background in order to obtain the anomalous part of Δn. In this respect, the value obtained from γ-data is presumably better, because no correction has to be performed since there is no « fluctuation » contribution in u_{yz}. In all cases, it appears that data can be well fitted (even if a small discontinuity is present) by a power law with an exponent β close to 1/4. This value is the classical value of β at the TCP, which is expected to be only

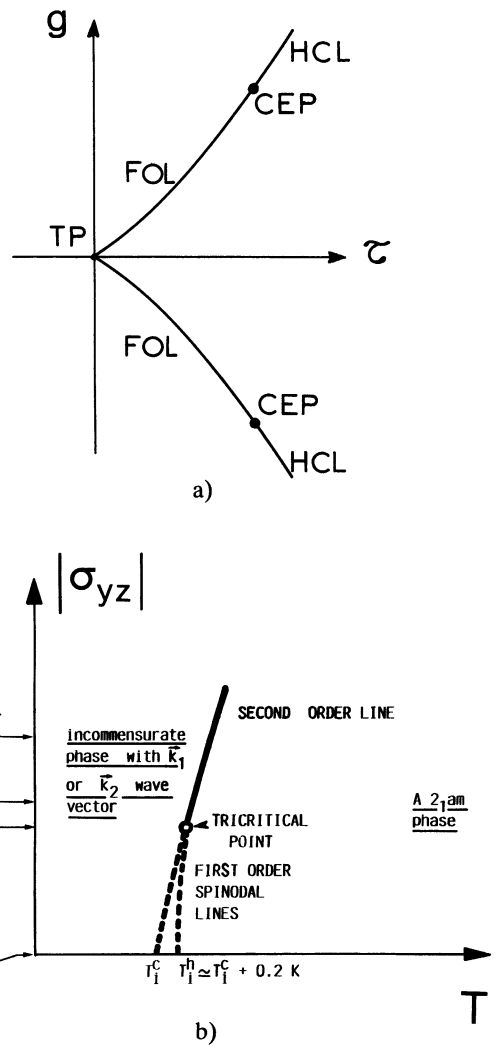

Fig. 6. — Phase diagram for anisotropically stressed $BaMnF_4$. a) Theoretical prediction (from Ref. [19]) ; note that $g \sim \sigma_{yz}$. b) as suggested from the present experiments. The hypothetical positions of the various samples presented in this paper are indicated on the ordinate axis.

slightly changed by critical fluctuations. More problematic is however the β value in highly internally stressed H samples. It seems surprising to find the classical value 1/2, whereas, according to theory, the properties of the system should be governed by an $n = 2$ Heisenberg fixed point, with a β value close to 0.35. One might first think of non-orientating stresses as invoked in the case of the similarly behaving orthorhombic-to-tetragonal structural phase transition of $RbAlF_4$ [23]. However, contrary to that case involving domains with birefringence of opposite signs in $BaMnF_4$ merely rigid shifts of Δn *versus* T along one or both coordinate axes are expected. Depending on the symmetry of the non-conjugate stress, change of Δn might refer to its absolute value or to rotations of the indicatrix. Then, assuming virtual temperature independence of these stresses, the observed exact coincidence of Δn *versus* T for as-grown and annealed H type samples in the limits $T < 100$ K and $T > 330$ K (Fig. 5) cannot be understood. Hence, a veritable modification of the critical behaviour seems, indeed, to prevail in $BaMnF_4$.

The discrepancy between the measured value 1/2 and the theoretical prediction 0.35 leads to the important and difficult problem of determining the size of the critical region, which seems to be too narrow to be observable in $BaMnF_4$. Unfortunately, only a part of the coefficients entering the Levanyuk-Ginzburg criterion [24] is known, and a quantitative estimate is not possible now. Moreover, it should be pointed out that quadratic couplings of the O.P. (to polarization and strains) occur, and this is known to slightly reduce fluctuations [25]. Experimentally, we were unable to evidence a critical behaviour in C_p ; moreover, taking into account the performance of the temperature display and the birefringence data (which do not exhibit any change of behaviour on approaching T_i as much as possible), it comes out that the critical region should correspond to a temperature range defined by $\tau = (T_i - T)/T_i$ smaller than 10^{-4}. In this compound, it seems therefore that the exponents which are reported are measured in the classical region. This is in agreement with the idea that, for structural phase transitions, the critical region is often very narrow [26] (and in general non-classical values of exponents are more likely due to defects than to fluctuations [27]). In $BaMnF_4$, let us recall that the birefringence or refractive index curves present tails above T_i. Pretransitional effects are also clear from diffraction data, but do not fit with usual laws for critical fluctuations [28]. The experimental data do not therefore contradict the conclusion of narrowness of the critical region, the « fluctuation » tail in Δn and the diffuse X-ray scattering being attributed to defects.

In conclusion, the phase diagram that we propose is presented in figure 6b, where we indicate the approximate location of the samples in the (σ_{yz}, T) plane.

4. Conclusion.

In $BaMnF_4$, the study of the influence of defects is difficult, because one cannot start with a perfect crystal and introduce defects gradually. Even in the best samples, the properties of the incommensurate phase are determined by the crystalline imperfections. Because of this situation, we think that one has to pay attention to the method of synthesis, and to characterize the sample in detail when presenting data concerning this material.

We have seen in this paper that the thermal variation of the modulation wave vector **k**, is probably influenced by impurities. In the H samples, **k** is constant, whereas it varies in general in the samples melt-grown that we investigated. One can imagine that intermediate situations might exist in some particular samples, where **k** would remain constant some degrees below T_i, and that a depinning of the modulation thereafter occurs (such phenomena were observed for example in doped incommensurate systems [29] — see also Ref. [30]). This hypothesis could explain the observations described in references [12, 13, 15] : indeed a **k**-jump could induce a small peak in the specific heat temperature dependence (and an anomaly in some other quantity — see Ref. [13] and [15]). However, we saw in the present paper that the **k**-dependence of Δn is very weak, and this explains why no anomaly is observed in the birefringence curve. This interpretation differs from earlier ones, based on the possibility of a supplementary phase transition in the case of the perfect crystal [31, 32].

To our feeling, the eventual pinnings of **k** between jumps (which seem to be possible in some samples) have *a priori* no reason to occur on values which are commensurate with the underlying lattice, since the forces acting on the modulation are attributed to point defects, distributed at random. In all cases, it is not possible experimentally to make any difference between an incommensurate and a commensurate value with a high order of commensurability (in the case of $BaMnF_4$, the smallest order is 23 !).

In another paper, it was claimed that the phonon instability occurs not at (0.39 ; 0.5 ; 0.5) but at (0.39 ; 0 ; 0.5). In a theoretical model developed by Hardy [33], it was shown that the phonon branch is the softest at the former point, but that it is almost as soft as the latter. These results need attention, since both points have different symmetries in the Brillouin zone. However, among our samples, we had no evidence for an instability occurring at (0.39 ; 0 ; 0.5).

It is now established that the amount of internal stresses is an important parameter influencing the

thermal dependence of the O.P. amplitude. It is noteworthy that T_i is however only slightly shifted from one sample to another. This is expressed by the quasi-vertical orientation of transition lines in figure 6b. The T_i shift, given in reference [19] as a function of σ_{yz} and coefficients entering the free energy, is not necessarily expected to be important : here, σ_{yz} is not a field conjugated to the O.P., since the transition is of the improper ferroelastic type.

The explanation of the observed phenomena in terms of tricritical behaviour which can be controlled by applying σ_{yz} stress, will be checked in further experiments.

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