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Optical study of the structural phase transition of BaMnF₄

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Résumé. — Le dichroïsme linéaire de la bande d'absorption à 3950-4000 Å dans BaMnF₄ a été étudié dans un domaine de température voisin de la transition de phase structurale. Au premier ordre, le dichroïsme linéaire, comme la biréfringence, est proportionnel au carré du paramètre d'ordre. La valeur ainsi obtenue pour β , l'exposant critique du paramètre d'ordre est en accord avec les résultats récents de diffusion de neutrons et en désaccord avec les prédictions de la théorie de Landau.

Abstract. — We present here a study of the linear dichroism of the optical absorption band at 3950-4000 Å in BaMnF₄ in a temperature range neighbouring the structural phase transition. In first approximation, the linear dichroism, as the linear birefringence is proportional to the square of the order parameter. So we obtain a determination of β , the critical exponent of the order parameter, in good agreement with the last value obtained from neutrons scattering and in disagreement with prediction of Landau theory.

BaMnF₄ has been shown to possess some interesting magnetic and electric properties and has been the subject of numerous investigations [1]. It exhibits a structural phase transition at about $T_c = 250$ K and neutrons studies have shown that below this temperature, the crystal structure is incommensurate along the polar *a* axis [2]. For temperature less than $T_N = 26$ K, three-dimensional antiferromagnetic order appears, with a spin-flop transition at about 10 kOe [3], two-dimensional magnetic order still exists up to 50 or 70 K [4].

Some questions concerning the incommensurate phase are still unresolved. Below T_c , the crystallographic structure is not completely known. It was not possible to find a *good physical picture of the atomic displacements necessary to produce the incommensurability* [5]. On the other hand, the non-commensurate phase is stable at all temperatures below T_c , and the wave vector of the distortion does not depend on temperature. The experimentally deduced values of the critical exponent β , of the temperature dependence of the order parameter below T_c , were first $2\beta = 0.45$ [5] and then $\beta = 0.31 \pm 0.05$ [2]. The value expected from Landau theory was $\beta = 0.5$.

No discontinuity was observed at T_c [2], however it is expected that the structural phase transition may be slightly discontinuous.

Optical methods have proved to be useful in many cases to measure static properties of magnetic insulators [6] as well as some critical parameters at magne-

tic or structural phase transitions [7, 8]. In the case of BaMnF₄, the study of the birefringence and the low temperature spectroscopy of the Mn²⁺ ion absorption bands can provide much new information on the magnetic energy, the possible existence of an intermediate magnetic phase and the behaviour near T_c .

In this preliminary report, we present only some results of linear dichroism measurements around T_c . Optical investigations between 2 K and 300 K, with and without magnetic field up to 30 kOe are now underway.

The linear dichroism

$$\Delta D = \frac{k_c(T) - k_a(T)}{k_c(T) + k_a(T)}$$

(in which k are the absorption coefficients) in the foot of the absorption band corresponding to the ${}^6A_1({}^6S) \rightarrow {}^4A_1g, {}^4E_g({}^4G)$ transition of the Mn²⁺ ions, is measured as a function of temperature. The temperature dependence of ΔD is expected to be the same as those of the birefringence $\Delta n = n_c - n_a$, n and k being related by Kramers-Kronig relations. (It was easier to measure ΔD than Δn , for technical reasons due to our experimental apparatus.)

In the usual linear approximation [7, 8], the change of Δn (or ΔD), representing the change of the optical anisotropy, at a phase transition, is, to a first order, proportional to the lattice distortions x_i .

In Landau theory for a second order phase transition in BaMnF_4 , it was demonstrated [9] that spontaneous lattice distortions are created at T_c , with a magnitude proportional to the square of the order parameter φ . So Δn (or ΔD) is expected to be proportional to φ^2 , as was observed in many other cases of structural phase transitions in commensurate systems (SrTiO_3 , NH_4Br , etc...).

But the Fritz's model did not take into account the incommensurability, which was discovered later.

A Landau expansion of the free-energy, involving the four primary order parameters Q_i used in [2] and including interaction terms allowed by symmetry is :

$$F = F_L + \frac{1}{2} \sum_{i=1}^6 \sum_{j=1}^6 C_{ij} x_i x_j + \sum_{i=1}^3 \beta_i x_i (Q_1 Q_2 + Q_3 Q_4) + \beta_6 x_6 (Q_1 Q_4 + Q_2 Q_3)$$

F_L depends on only Q_i (eq. (4) in Ref. [2]). The following terms describe the purely elastic part of the free energy and the interactions between the symmetrized strains x_i and the Q_i . In this model, the compressional strains and the ab shear strain couple to the soft mode.

The minimization of F with respect to the strain variables shows that spontaneous strains are induced, proportional to the product $Q_i Q_j$. In solutions given in [2], deduced from minimizing F_L , all the non-vanishing Q_i have the same amplitude φ , so the approximation $x_i \sim \varphi^2$ is still good (if we assume that β_6 is small). Thus, neglecting the fluctuations, the exponent of the temperature dependence of ΔD should be of the order of 2β .

Moreover, G. Gehring [10] has demonstrated that in the case of cubic systems undergoing structural phase transitions in which the n -dimensional order parameter corresponds to distinct points in the Brill-

Fig. 1. — Temperature dependence of the linear dichroism

$$\Delta D = \frac{k_c - k_a}{k_c + k_a}$$

in the foot of the ${}^6\text{A}_1({}^6\text{S}) \rightarrow {}^4\text{A}_1, {}^4\text{E}_g({}^4\text{G})$ transition of Mn^{2+} ions in BaMnF_4 .

louin zone, the form of the birefringence change below T_c is proportional to $\langle \varphi \rangle^2$. This relation was also experimentally checked in non-cubic layers compounds [11]. It is reasonable to expect that this relation still holds in the case of BaMnF_4 .

In our experiments, ΔD was measured in the ac plane, the light propagating along the b axis. This geometry is expected to be the most sensitive to the structural phase transition because a is the direction of the incommensurability. Experiments at three different wavelengths in the same absorption band, were performed, all gave the same temperature dependence for ΔD .

The temperature dependence of ΔD is shown in figure 1. The temperature of the sample was deter-

Fig. 2. — Linear dichroism of the whole band at three different temperatures.

Fig. 3. — Log-Log plot of the linear dichroism dependence versus the reduced temperature below T_c .

mined to within 0.1 K and the precision on ΔD is about 0.7 %.

The dichroism of the whole band is shown in figure 2 at three different temperatures around T_c . A log-log plot of ΔD as a function of the reduced temperature $\frac{T_c - T}{T_c}$ is presented in figure 3. ΔD obeys the law

$$\Delta D \sim \left(\frac{T_c - T}{T_c} \right)^{0.69 \pm 0.04}$$

This exponent is, within the experimental error limit, in good agreement with the value reported in [2], $\beta = 0.31 \pm 0.05$.

This value, smaller than the value expected from the Landau theory for second order phase transition, indicates that the order parameter decreases more

quickly than is normally found. (The Landau theory for weakly discontinuous phase transitions predicts a temperature dependence : $\varphi^2 \sim (T_0 - T)^{1/2}$ [12, 13] in which T_0 is a fictitious transition temperature which cannot be directly measured.)

A possible explanation for this intermediate value of β [2] is that the critical fluctuations are expected to drive the phase transition slightly first order. In our experiment, within the limit of experimental errors, the transition temperature is associated with a small kink in the ΔD curve (Fig. 1). This is not in contradiction with a slight first order character of the transition predicted by R. A. Cowley and A. D. Bruce [14], but further more precise investigations will be necessary to check this point.

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