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NEUTRON DIFFRACTION STUDY OF THE COMMENSURATE AND INCOMMENSURATE MAGNETIC STRUCTURES OF $NiBr_2$

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Abstract

Neutron diffraction experiments on powder and single crystal have shown that below T_{IC} = 22.8 K $NiBr_2$ orders with a helimagnetic structure in the basal plane, with a propagation vector $\vec{k}$ = [0.027, 0.027, 3/2] at T = 4.2 K. At T_{IC} a first order transition towards an antiferromagnetic structure occurs. This structure is similar to that of $NiCl_2$ and remains stable up to T_N = 52 ± 1 K.

At 4.2 K the moment value of Ni^{2+} is found to be 2.0 ± 0.15 μ_B.

Résumé

Des mesures de diffraction des neutrons sur poudre et sur monocristaux ont montré qu'au-dessous de T_{IC} = 22,8 K le composé $NiBr_2$ présente un ordre hélimagnétique dans le plan de base, à 4,2 K le vecteur de propagation vaut $\vec{k}$ = [0,027, 0,027, 3/2]. A T_{IC} a lieu une transition du premier ordre vers une structure antiferromagnétique. Cette structure est similaire à celle obtenue pour $NiCl_2$ et subsiste jusqu'à T_N = 5,2 ± 1 K.

A 4,2 K la valeur du moment magnétique est de 2,0 ± 0,15 μ_B.

1. Introduction

$NiBr_2$ is known to order antiferromagnetically below T_N = 52 K [1] with a magnetic structure similar to that of $NiCl_2$ [2]. Magnetization and antiferromagnetic résonance measurements have shown that below a temperature $T_{IC} \sim 20$ K a modification of the magnetic structure may occur in $NiBr_2$: a helical [3] or a triangular [4] order has been proposed. Later, a neutron diffraction study on powder and single crystal has been reported by P. Day and al. [1]. At $T_{IC} \simeq 22.5$ K a transition has been observed. They proposed that the low temperature structure consists of ferromagnetic (a-b) planes stacked antiferromagnetically as for the high temperature phase, but below T_{IC} the magnetic moments tilt out of the basal plane and make an angle of about 36° with the c-axis. This result seems to us rather unusual because it cannot be explained by one ion anisotropy.

In order to investigate more precisely the low temperature phase we have performed neutron diffraction experiments on powder and single crystal samples. Our results presented in this paper are not in agreement with those reported by P. Day et al. [1].

Sample

Anhydrous nickel bromide is difficult to prepare in single phase because the "wechselstruktur" occurs [5,6]. The high temperature phase, in which all samples have been obtained, crystallizes in the $CdCl_2$ structure of rhombohedral space group $R\bar{3}m$. The nickel ions are on a single Bravais lattice.

The powder sample of $NiBr_2$ has been prepared by reacting HBr on NiO [7]. The dehydratation has been obtained by putting the compound first under vacuum up to 130° C and then in a stream of dry HBr until the sublimation temperature.

Single crystals have been grown by melting the $NiBr_2$ powder in a sealed silica tube by slowly cooling it in a temperature gradient.

2. Magnetic measurements

Susceptibility and magnetization have been measured on a single crystal for a magnetic field applied both along the c-axis and in the basal plane. More complete results will be published elsewhere, but in figure 1 we report the magnetization measured in a magnetic field of 600 Oe. A maximum occurs at T = 52 K. Along the c-axis no anomaly is observed until the lowest temperatures. This behaviour is typical of a perpendicular susceptibility. When the magnetic field is applied in the basal plane a discontinuity takes place at T = 22 K. Thus the phase transition must consist in a moment rearrangement within the basal plane and has nothing to do with a canting of the moment along the c-axis.

3. Neutron diffraction results on powder

The $NiBr_2$ powder has been sealed in a thin

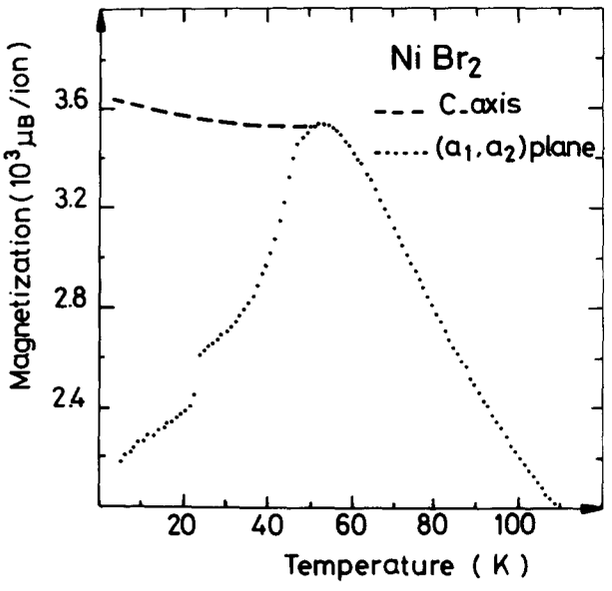

Fig. 1 : Magnetization for a magnetic field of 600 Oe applied along the $\vec{c}$-axis and within the basal plane.

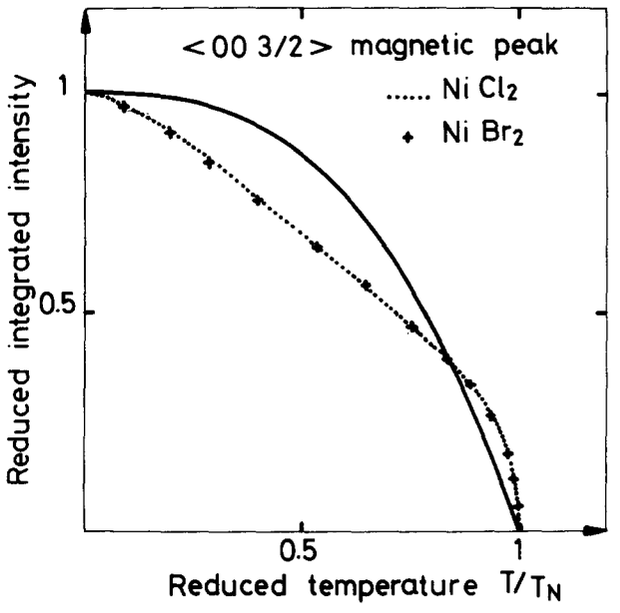

Fig. 2 : Thermal variation of the integrated intensity of the <003/2> magnetic peak of $NiBr_2$ in reduced units. A comparison is done with $NiCl_2$ and a S = 1 Brillouin function (full curve).

stainless steel tube under helium atmosphere. The experiments have been performed at different temperatures at the C.E.N./Saclay. They confirm that below T_N = 52 ± 1 K $NiBr_2$ orders antiferromagnetically with a magnetic structure similar to that of $NiCl_2$ [9]. The thermal variation of the most intense magnetic peak [003/2] is given in figure 2 in reduced units and is compared with $NiCl_2$. One sees that the two compounds have a similar behaviour, and no anomaly has been observed at 22 K. In $NiBr_2$ the magnetic moments remain in the basal plane at all temperatures as magnetization experiments let us suppose. The unusual strong decrease of the intensity of the [003/2] peak results from the weak coupling between the ferromagnetic sheets as in $NiCl_2$ [8] and from the two-dimensional character of magnetic excitations.

We normalize the magnetic intensity with the help of the nuclear peaks and get a value of the magnetic moment, of 2.0 ± 0.15 μ_B at 4.2 K, in good agreement with a spin S = 1 of the Ni^{2+} ion. A careful analysis (fig. 3) shows that the [003/2] peak shifts slightly in position between 30 K to 4.2 K (about 0.05° in 2θ for λ = 1.14 A) whereas the position of the [003] nuclear peak remains unchanged. The phase transition would consist of a change of the propagation vector. If we suppose that an incommensurate component appears in the basal plane [10,11], the observed shift will give $\tau \simeq 4.10^{-2}\ a^*$. In order to confirm this hypothesis a neutron diffraction experiment has been undertaken on a single crystal.

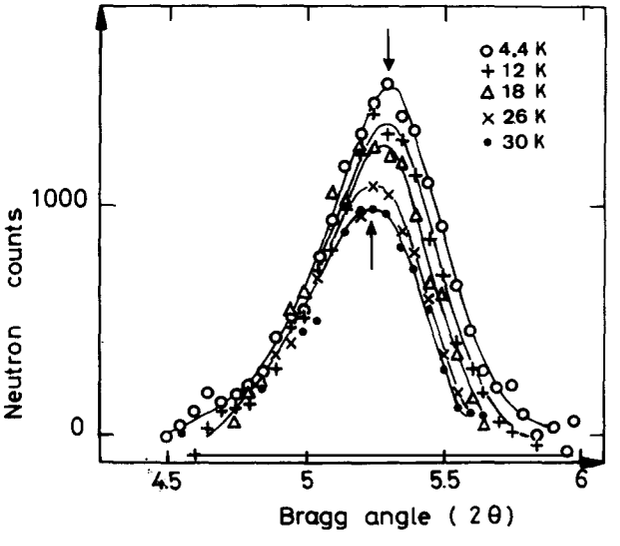

Fig. 3 : Profile of the <003/2> powder reflection at different temperatures, the background has been substracted.

4. Neutron diffraction results on single crystal

The experiments have been performed at the C.E.N./Grenoble on the spectrometer DN_3 in the Siloe reactor which is equipped with a counter moving out of the equatorial plane. The crystal of 8 x 4 x 1 mm^3 size was oriented with a ($\vec{a}^*$, $\vec{c}^*$) plane horizontal. As the value of the incommensurate component is expected to be small, special attention has been paid to increase the resolution of the spectrometer. Thus we have used a high wave length of 2.4 A reflected by a pyrolytic graphite monochromator, horizontal slits, in order to decrease the vertical divergence and graphite filters to remove the λ/2 contamination.

Determination of the propagation vector

The propagation vector at T = 4.2 K was determined by scanning the reciprocal space around the [003/2] point which corresponds to the most intense Bragg peak observed in the powder experiments.

In order to identify the direction of the wave vector, scans [h, k, 3/2] along [100] direction have been performed with k varying from 0 to -0.045. These scans show that the component of the propagation vector along the c-axis remains commensurate with a value $k_z = 3/2$. However an incommensurate component exists in the basal plane and is oriented along a <110> direction. We have reported in figure 4a few

ture is drawn in figure 5. Along a <100> and <010> direction the moment direction rotates progressively by an angle ϕ, 2ϕ, 3ϕ, ... with $\phi = 9.72°$. From one plane to another the moment direction can be deduced by performing successive antitranslations -1/3, 1/3, 1/3.

Temperature dependence of the wave vector

From 4.2 K to 22.8 K the propagation, vector has been found to be temperature dependent. The k_z-component remains commensurate to a value 3/2. The in-plane component is always along a <110> direction by the k_x-value decreases from 0.027 at 4.2 K to 0.09 at 22.8 K (fig. 6). k_x does not go to zero continuously and in fact a first order transition occurs at

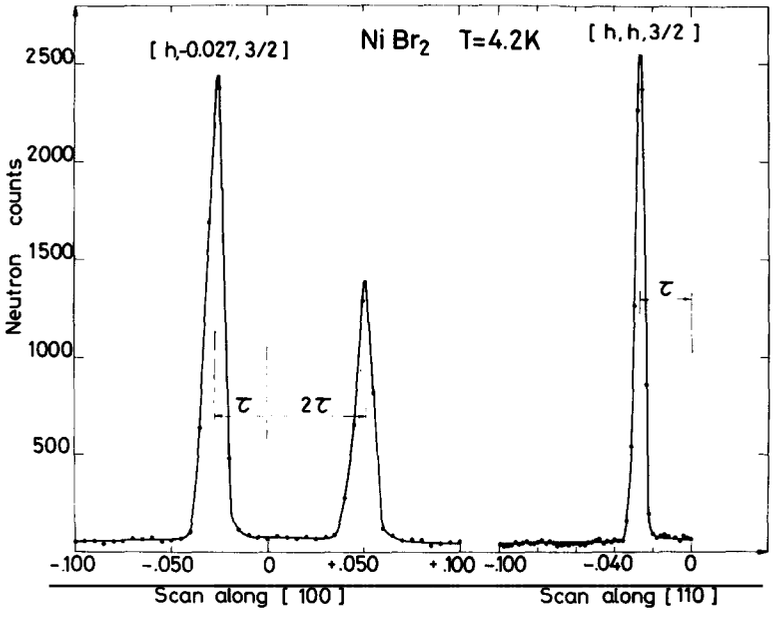

Figure 4 : Scans along [100] and [110] at T = 4.2 K.

of these scans. They indicate that at $T_c = 4.2$ K the wave vector $\vec{k} = k_x \vec{a}_1^* + k_y \vec{a}_2^* + k_z \vec{c}^*$ has the following component values : $k_x = k_y = 0.027$ and $k_z = 3/2$. The magnetic cell is incommensurate with the nuclear cell along both the $\vec{a}_1$ and $\vec{a}_2$ direction. The absence of any second, third or higher harmonics (§ fig. 4b) proves that $NiBr_2$ orders with a helical structure within the basal plane in zero field at T = 4.2 K. The planes remain coupled antiferromagnetically. The structure is described by only one $\vec{k}$-vector and there are three domains associated to the three equivalent wave vectors $\vec{k}$. $\vec{k}_1 = [\tau, \tau, 3/2]$, $\vec{k}_2 = [-2\tau, \tau, 3/2]$ and $\vec{k}_3 = [\tau, -2\tau, 3/2]$ (§ fig. 4b). Taking into account that the Ni^{2+} ions are located in a Bravais lattice the arrangement of the magnetic moments associated to the wave vector $\vec{k}_1$ is defined by :

$$\vec{m}_n = m_o[\hat{u} \cos(2\pi \vec{k}_1 \vec{R}_n) + \hat{v} \sin(2\pi \vec{k}_1 \vec{R}_n)]$$

where $\vec{R}_n$ is a lattice translation, m_o is the moment value, and $\hat{u}$ and $\hat{v}$ are two orthogonal unit vectors of the basal plane.

Within the basal plane the magnetic structure is drawn in figure 5. Along a <100> and <010> direction the moment direction rotates progressively by an angle ϕ, 2ϕ, 3ϕ, ... with $\phi = 9.72°$. From one plane to another the moment direction can be deduced by performing successive antitranslations -1/3, 1/3, 1/3.

about $T_{IC} = 22.8$ K which drives the system to a commensurate state ($k_x = k_y = 0$ and $k_z = 3/2$). This first order transition is well demonstrated by scans reported in figure 7 which shows over

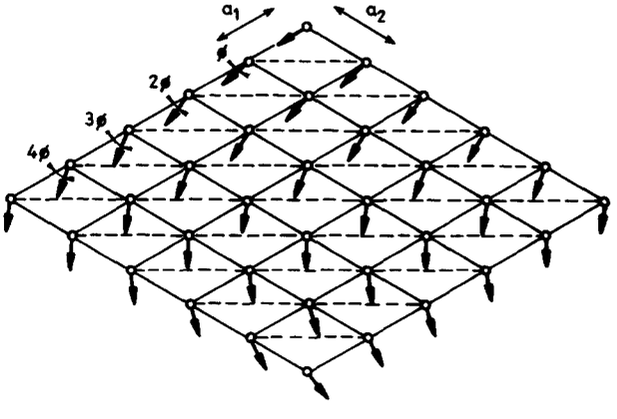

Fig. 5 : Helimagnetic ordering within the basal plane for $NiBr_2$ at T = 4.2 K.

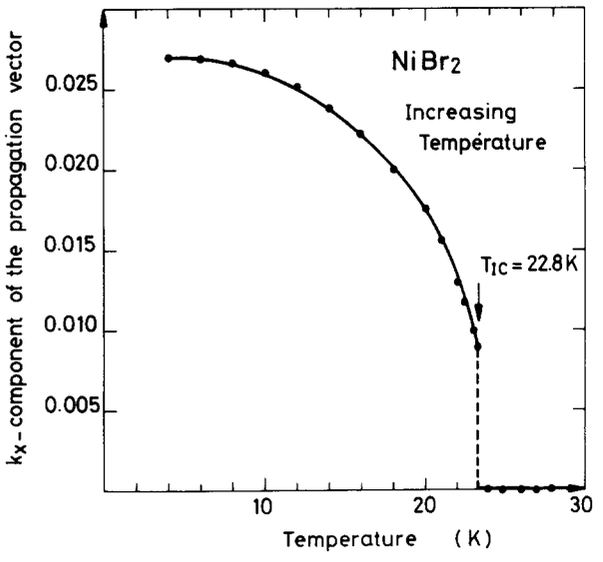

Fig. 6 : Thermal variation of the k_x-component of the propagation vector.

one degree the coexistence of the commensurate and incommensurate phases. Hysteresis effects have also been observed. Above T_{IC} the magnetic structure is the same as for $NiCl_2$ ($\vec{k}$ = [0, 0, 3/2]) and consists of ferromagnetic sheets coupled antiferromagnetically. The [003/2] peak disappears at T_N = 44 K with a second order phase transition. It is rather surprising that the Neel temperature is not the same for a powder or a single crystal sample. The value obtained with a single crystal corresponds in fact to the inflexion point of the susceptibility curve and not to the maximum.

5. Discussion

At low temperature $NiBr_2$ is in fact a helimagnet with the incommensurate component of the propagation vector directed along a <110> direction. At $T_{IC} \simeq 22.8$ K a first order transition occurs giving rise to a magnetic order described by an antiferromagnetic stacking of ferromagnetic sheets. At all temperatures the moment direction lies in the basal plane, and the Ni^{2+} ions behave like an X-Y system. Moreover the weak coupling between planes has been evidenced by the unusual thermal variation of the order parameter.

These results lead to several questions : why this incommensurate wave vector ? Why an antiferro-helimagnetic transition ? Why is this transition first order ? At low temperatures the direction of the propagation vector can be accounted for by introducing the first, second and third neighbour exchange integrals J_1, J_2 and J_3. Following Rastelli et al. [12] and defining the ratios $j_2 = J_2/J_1$ and $j_3 = J_3/J_1$ the stability of the structure is realized when $2j_3 < j_2 < -(1 + 4j_3)/3$. Thus J_2 and J_3 must have the same order of magnitude. By using a mean field approximation the helimagnetic-antiferromagnetic transition can be explained by a thermal variation of the exchange integral ratios j_2 and j_3 which induces a crossing of the separation line between the two phases. But in this case the k_x-component must go continuously to zero and a second order transition is expected. This behaviour does not correspond to the experimental situation and we think that it is not the driving mechanism.

Let us suppose now that the exchange integrals are temperature independent and that the ratios j_2 and j_3 are such that at the ordering

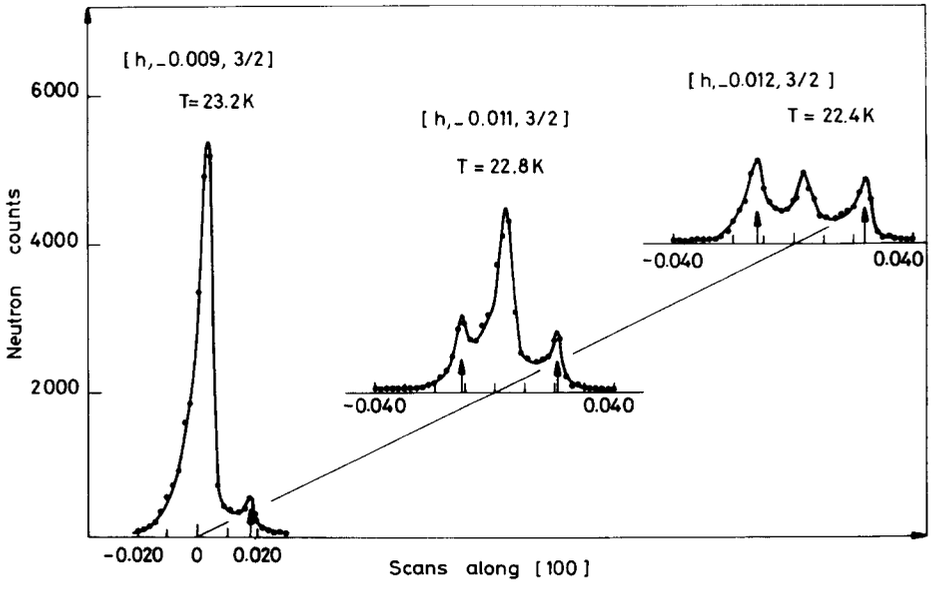

Figure 7 : Scans along [100] at the first order transition between the helimagnetic and the antiferromagnetic structures.

temperature the system is very close to the separation line between the antiferromagnetic and helimagnetic states (Lifshitz point). In a mean field theory the propagation vector $\vec{k}$ does not depend on T.J. Villain has shown [13], by using a self consistent harmonic approximation that a spin system described by an isotropic (Heisenberg or XY) temperature independent spin Hamiltonian and having a helimagnetic structure at low temperature may undergo a phase transition towards a ferromagnetic state (or antiferromagnetic) at higher temperature. This transition has been found to be second order for three dimensional systems, whereas it becomes first order for two dimensional systems. This theory explains quite well the behaviour of $NiBr_2$. At low temperature the exchange integral ratios j_2 and j_3 lead to a helimagnetic order within the basal plane but with a very small wave vector. As the planes are weakly coupled, strong fluctuations exist which introduce fluctuations between states of wave vectors $\pm \vec{k}$. This leads to a decrease of the wave vector value and when the fluctuations become too large compared to the potential barrier between the states $\pm \vec{k}$, a first order transition towards ferromagnetic planes occurs, due to the two dimensional character of the interactions.

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