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Neutron diffraction study of HoMo_6S_8 single crystal

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Résumé. — Nous rapportons les premiers résultats de diffraction de neutrons obtenus sur des monocristaux du composé HoMo_6S_8 . Au-dessous de $T_m = 0,65$ K, le composé HoMo_6S_8 présente un ordre magnétique à longue période ; les moments magnétiques, alignés selon la direction [111], sont perpendiculaires au vecteur d'onde de la modulation $\mathbf{k} = [k, -k, 0]$ (maille rhomboédrique). Cette phase modulée peut être trempée à $T = 0,1$ K ($k = 0,008$). Par contre, lors d'un refroidissement lent, la phase modulée se transforme en un ordre ferromagnétique avec des microdomaines de dimension 1 000 Å à 1 500 Å.

Abstract. — The first neutron diffraction results obtained on single crystals of HoMo_6S_8 are reported. At temperatures below $T_m = 0.65$ K, HoMo_6S_8 develops a magnetic ordering of long period ; the magnetic moments, aligned along the [111] direction, are perpendicular to the modulation wave vector $\mathbf{k} = [k, -k, 0]$ (rhombohedral cell). This modulated phase can be quenched at $T = 0.1$ K ($k = 0.008$). However, by slow cooling, the modulated phase transforms into a ferromagnetic ordering with microdomains of size 1 000 Å to 1 500 Å.

1. Introduction.

The study of magnetic superconductors has had a very important development since the discovery of the ternary or pseudo-ternary compounds of the lanthanides, in which a long-range magnetic order is found below the superconducting ordering temperature, T_c . A great number of theoretical and experimental works have been subsequently devoted to the problem of coexistence of superconductivity and magnetism [1], especially in the Chevrel phases LnMo_6S_8 and LnMo_6Se_8 and in the compounds LnRh_4B_4 (Ln = lanthanide).

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The neutron diffraction experiments are particularly important [2-4], since they allow the nature of the magnetic order, coexisting with the superconductivity to be determined. Not only the coexistence of superconductivity and antiferromagnetic ordering has been confirmed, but it has been shown that a long-period magnetic ordering sets in before the destruction of the superconducting state by the ferromagnetic order [4, 5]. An interesting problem concerns the long-period magnetic ordering. Is it due to the modification of the indirect interactions of RKKY-type by the superconductivity, thereby leading to a cryptoferromagnetic order [6], or is it a result of the super currents which build up in the superconductor in order to screen the induction, produced by the magnetization [7, 8] ?

Such a long-period magnetic order was actually found in HoMo_6S_8 [5] and ErRh_4B_4 [4]. In the compound ErRh_4B_4 , Sinha *et al.* [4] carried out a detailed study on a single crystal in order to characterize this phase. For the compound HoMo_6S_8 the study was done by Lynn *et al.* [5] only on polycrystalline samples.

A close collaboration between the Université de Rennes and the Centre d'Etudes Nucléaires de Grenoble was initiated to prepare single crystals of the LnMo_6S_8 compounds. The first crystals obtained for the compound HoMo_6S_8 were quite small, of the order of 1 mm^3 ; however, we were able to perform neutron diffraction experiments on them. The first results are reported in this paper, and they should be considered preliminary.

2. Experimental.

The powder samples of HoMo_6S_8 were prepared by the common procedure, avoiding as much as possible the formation of parasitic phases. The preparation of single crystals required a great effort. The method used [9] consists of melting the compound in a sealed molybdenum crucible, followed by a slow cooling. A crystal of very good quality, about 6 mg in weight, has been extracted for the neutron diffraction study. X-ray diffraction measurements confirmed the good stoichiometry of the compound.

The neutron diffraction experiments on the HoMo_6S_8 single crystal were carried out on the diffractometer with a lifting detector DN3, the Siloe reactor at Grenoble. We used thermal neutrons with a wavelength of $\lambda = 2.402 \text{ \AA}$, permitting good filtering. At this wavelength we had to work around the [100] Bragg peak, and because of this we used a tight collimation of $10'$ before and after the sample, in order to simultaneously reduce the vertical and horizontal divergencies. This reduction, together with the small volume of the crystal (less than 1 mm^3), resulted in a weak signal, which did not enable us to obtain conclusions as accurate as we would have wished. The crystal, placed in a ^3He - ^4He dilution cryostat, was oriented with a [100] axis vertical.

In this paper we adopt the rhombohedral description of the crystallographic structure of the LnMo_6S_8 compounds. Indeed, this description is simpler since the rhombohedral cell contains only one formula unit of LnMo_6S_8 , and, moreover, it is close to a cubic cell since the rhombohedral angle is almost a right angle ($\alpha_r = 89.35^\circ$ for HoMo_6S_8 , with $a = 6.448 \text{ \AA}$). As the elementary cell contains only one magnetic atom, the determination of the magnetic order involves only the knowledge of the wave vector and of the direction of the magnetic moment with respect to the crystallographic axes.

3. Results.

The study of HoMo_6S_8 single crystal showed that for temperatures $T < T_m = 0.65 \text{ K}$ a magnetic ordering of long-period set in, as in the case of HoMo_6S_8 powder [5]. However, to our great surprise, we found that this magnetic ordering remained at low temperature, when the crystal was cooled rapidly (a few minutes). It is therefore possible to quench the long-period magnetic phase. In order to determine the direction of the modulation wave vector at $T = 0.1 \text{ K}$, the reciprocal space around the centre of the [100] Brillouin zone was checked by performing scans along $[0k0]$

and $[00/]$; for example, one of these scans is reported in figure 1. The results are summarized in figure 2, where we have shown the variation of the intensity, starting with the scattering vectors

Fig. 1. — Reciprocal-space scans along the $[1, k, 0]$ direction in the magnetic phase quenched at $T = 0.1 \text{ K}$.

Fig. 2. — Reciprocal-space scans along $[h00]$ showing the value of the wave vector $\mathbf{k} = [0.008, -0.008, 0]$ in the phase quenched at $T = 0.10 \text{ K}$.

$Q = [1, \pm 0.008, 0]$ and moving along the $[h00]$ direction (these values were chosen to eliminate the nuclear contribution). The observation of maxima at the points $[1 + 0.008, -0.008, 0]$ and $[1 - 0.008, +0.008, 0]$ indicates, without any doubt, that the wave vector is directed along $[1, \bar{1}, 0]$, and it is $\mathbf{k} = [k, -k, 0]$ with $k = 0.008$ at $T = 0.1$ K. In spite of this, as the unit cell is rhombohedral, the trigonal axis directed along $[111]$ generates three wave vectors: $\mathbf{k}_1 = [k, -k, 0]$, $\mathbf{k}_2 = [0, k, -k]$, and $\mathbf{k}_3 = [-k, 0, k]$, equivalent by symmetry. Then, around each zone centre, there are six superlattice peaks.

The absence of magnetic diffraction around the centre of the $[111]$ zone proves that the magnetic moments are aligned along the rhombohedral axis $[111]$. The magnetic ordering corresponds therefore to a transverse modulation of the moment value, propagating along a $[1\bar{1}0]$ direction with a wavelength $\lambda = a/k\sqrt{2} = 570 \text{ \AA}$ ($k = 0.008$). Indeed, at low temperature the magnetic moments of the Ho^{3+} ions have nearly their full value ($m_0 \simeq 9.5 \mu_B$), corresponding to a doublet $|J_z = \pm 8\rangle$, implying that the modulation is actually a square modulation. Such a modulation generates harmonics of the order 3, 5, 7, ... etc., but with intensities 9, 25, 49, ..., etc. times weaker than that of the fundamental component. Taking into account the small size of the crystal, these different harmonics could not be measured. Thus the magnetic ordering certainly corresponds to a series of $N/2$ ferromagnetic $(1\bar{1}0)$ planes, magnetized along $[111]$, followed by $N/2$ planes, magnetized along $[\bar{1}11]$ ($N = 1/k \simeq 124$). This order is just a structure with domains containing $N/2 = 62$ planes, i.e. with a width of about $285 \text{ \AA}$.

On the other hand, when the crystal is cooled slowly (typical rate $10 \text{ mK}/10 \text{ min}$) the modulated structure is observed only in a small temperature range of 50 mK below $T_m = 0.65 \text{ K}$ (i.e. $0.60 \text{ K} < T < 0.65 \text{ K}$).

The value of the wave vector decreases with temperature from $k = 0.012 \pm 0.002$ at T_m to $k = 0.008 \pm 0.001$ at $T = 0.60 \text{ K}$ (see Fig. 3). It is quite surprising to find that at T_m , the wave

Fig. 3. — Reciprocal-space scans along $[1, k, 0]$ showing the dependence on temperature of the long-period modulated phase in the case of slow cooling.

length of the modulation, of about $380 \text{ \AA}$ ($\sqrt{2} k \frac{2\pi}{a} \simeq 0.016 \text{ \AA}^{-1}$) is twice the value observed with powders by Lynn *et al.* [5] ($Q = 0.03 \text{ \AA}^{-1}$ leading to $\lambda \simeq 200 \text{ \AA}$). We do not have an explanation for this notable difference between the powder and crystal results. It is, no doubt, connected to the greater purity of the crystal, but also to the modification of the transverse component of the Fourier transform $J(\mathbf{k})$ of the exchange integral by the superconductivity which leads to a very flat maximum of $J(\mathbf{k})$. Then, close to T_m , the modulation must indeed be closer to a sine-wave modulation than to a square-wave modulation.

For $T < 0.60 \text{ K}$, with slow cooling, a ferromagnetic phase appears instead of the modulated phase obtained with fast cooling (Fig. 3). The magnetic intensity increases and afterwards saturates at about $T = 0.40 \text{ K}$ (Fig. 3), indicating that below this temperature the thermal fluctuations are small. However, the magnetic contribution to the $[100]$ Bragg peak has a width ($\Delta k \simeq 12 \times 10^{-3}$), which is clearly above the experimental resolution ($\Delta k \simeq 6 \times 10^{-3}$) given by the nuclear contribution. This width can be interpreted by the existence of ferromagnetic microdomains of the order of $1\,000 \text{ \AA}$ to $1\,500 \text{ \AA}$. In this case, the ordering is not different from a structure with a square-wave modulation with a wavelength of $2\,000$ to $3\,000 \text{ \AA}$, which is 4 to 5 times larger than that obtained by quenching.

When the temperature increases (Fig. 4), the ferromagnetic phase in the microdomains remains to $T_m = 0.65 \text{ K}$, where the ferromagnetic state goes directly to the superconducting state, by a second order transition. The modulated phase is not observed, a result analog to that obtained with powders. Indeed, when a quenched modulated phase is obtained by fast cooling of the crystal, this modulated phase disappears in heating at about $T = 0.4 \text{ K}$ (Fig. 4), and transforms into the ferromagnetic phase in microdomains, which remains as before to $T_m = 0.65 \text{ K}$. The quenched modulated phase disappears by « annealing » when the fluctuations become sufficiently important, above $T = 0.40 \text{ K}$.

Fig. 4. — Temperature dependence of the height of the ferromagnetic $[100]$ peak and the modulated component.

Finally at $T = 0.1 \text{ K}$, measurements of the integrated intensity indicate that the Ho^{3+} ion has practically the full magnetic moment ($m_0 = 9.5 \pm 0.3 \mu_B$). This shows that the entire crystal is ordered magnetically in both the quenched long-period phase and in the ferromagnetic phase in microdomains. Also, the large value of m_0 , indicates that the anisotropy is very large, with the easy

axis along [111]. But due to the pseudo-cubic symmetry of the lanthanide site, the other $\langle 111 \rangle$ directions of the pseudo-cubic cell must also be easy directions.

The ground state of the Ho^{3+} ion is therefore not an isolated doublet $|J_z = \pm 8\rangle$, but is formed by a crystal field level band with a eight fold degeneracy.

4. Conclusion.

The neutron diffraction experiments on HoMo_6S_8 single crystal, in spite of being not very accurate due to the small size of the crystal, have yielded important results, which are different from those obtained on powder samples : the wavelength of the modulated phase is twice as large in the single crystal and the possibility exists to quench this phase at $T = 0.1$ K. The long-period modulated phase is of the transverse type, with the moments oriented along the [111] direction while the wave vector is along $[1\bar{1}0]$, which is in good agreement with the theoretical predictions that show the transversal component of $J(\mathbf{k})$ to have a maximum for finite $\mathbf{k}$. The large value of the period (~ 570 Å at $T = 0.1$ K) and the existence of a ferromagnetic phase in microdomains of the order of 1 000 to 1 500 Å, indicate that the modulated phase is actually induced by the electromagnetic interaction between the persistent current and the magnetic moments, as shown by Blount and Varma [7] and by Matsumoto *et al.* [8]. In fact, Tachiki [11] has recently proposed a model that describes quite well the experimental results. In the frame of an Ising model, Tachiki has shown that the modulated phase disappears to be replaced by an antiphase structure with a wave vector 5 to 6 times greater. This antiphase structure is, in fact, none other than the ferromagnetic state in microdomains, that we have proposed. A first order transition between the long-period modulated structure and the antiphase structure is possible, as a result of the very flat form of the transversal component of $J(\mathbf{k})$ at small wave vectors resulting from electromagnetic interaction between the magnetic moments and the persistent currents.

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