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A NEUTRON DIFFRACTION STUDY OF THE $GdAlO_3$ MAGNETIC STRUCTURE

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Abstract

Neutron diffraction experiments have permitted to determine the magnetic order in the $GdAlO_3$ perovskite compound. $GdAlO_3$ is a simple two-sublattice antiferromagnet well described by the Gx-mode. This ordering results from isotropic and negative next neighbours exchange interactions which are more important than dipolar interactions.

1. Introduction

Gadolinium ortho-aluminate belongs to the family of rare-earth-transition metal oxides which crystallize in a slightly distorted perovskite structure (Pbnm - D_{2h}^{16}) [1]. Its magnetic behaviour has been extensively investigated by many authors, in particular at Clarendon Laboratory at Oxford by J.F.B. HAWKES et al. by magnetization, magnetic susceptibility, specific heat and optical absorption. They deduced that the ordered state is a simple two-sublattice structure with the antiferromagnetic direction along the orthorhombic b-axis [2,3]. Then, D.C. COOK et al. [4], using both X-ray diffraction and Mössbaüer spectroscopy, indicated that the a-axis can be the magnetic moment axis, the ordering being predominantly of Gx-type in BERTAUT's notation [5], according to M. MERCIER [6]. Simultaneously, A.H. COOKE et al. [7], analysing the magneto-electric susceptibility, the magnetic susceptibility, and the X-rays results, confirm that the antiferromagnetic direction is along the a-axis, in contradiction with their previous work. H. ROHRER et al. [8] investigating the phase diagram near the spin-flop multicritical point, established that it appears as bicritical in the $H_{//}$- T plane, but tetracritical in the $H_{\perp}$- T plane. R.M. HORNREICH et al. [9] have measured again the magneto-electric susceptibilities in the critical range. But, all their interpretations are based upon the strong uniaxial character of the magnetic order of Gd Al O_3

Therefore, in order to clarify the situation, a neutron investigation of the magnetic structure of Gd Al O_3 has been undertaken.

2. Experimental

The neutron experiments have been performed on powder sample that we have prepared starting from gadolinium oxide enriched with 98.7 % in ^{160}Gd (the absoption cross section is 1.400 barns, in regards to 46.000 for the natural gadolinium).

Neutron diffraction patterns were recorded at the Siloe reactor of the CEN Grenoble, using both a conventional and a multidetector spectrometers ; a neutron wavelenght of 2.4 Å was used. The investigations were carried out at T = 1.5 K, the sample being placed into a vanadium container of 6 mm in diameter in a variable temperature cryostat. A complementary experiment has been performed at the Laüe-Langevin Institut at Grenoble, on the IN 12 spectrometer with a larger neutron wave-length of 5.984 Å.

3. Crystal structure

Gd AlO_3 has a distorted perovskite structure. The space group is Pbnm - D_{2h}^{16} and the unit cell contains four formula (figure 1). The orthorhombic lattice parameters are a = 5.251 Å, b = 5.301 Å, c = 7.444 Å ± 0.005 Å ; the distorsion of the pseudo-cubic cell is very small ($a = b = c\sqrt{2} = 5.264$ Å).

Magnetic ions are located on four Bravais lattices (site 4c) defined by :
$\vec{r}_1 = (x, y, \frac{1}{4})$. $\vec{r}_2 = (\bar{x}, \bar{y}, \frac{3}{4})$
$\vec{r}_3 = (\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{4})$. $\vec{r}_4 = (\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{4})$
4b site is occupied by Al ions ; the oxygen atoms are displaced from their ideal position as explained in figure 1. An accurate determination of these parameters, resulting from the refinement of our neutron data at 1.5 K or 4.2 K is reported in table 1 ; they are in good agreement with previously determined values [1].

4. Neutrons results

It has been established experimentally [2,3] that $GdAlO_3$ orders, antiferromagnetically at T_N = 3.87 K without any parasitic ferromagnetism, and the magnetic moment direction lies within the (a - b) plane, near either the $\vec{a}$ or the $\vec{b}$ baxis. The neutron diffraction pattern recorded at 1.5 K (figure 2) exhibits a number of additional Braggs peaks which can be indexed on the basis of the cristallographic unit cell. Therefore the magnetic ordering can be described by the wave vector $\vec{k}$=(000). Moreover only magnetic

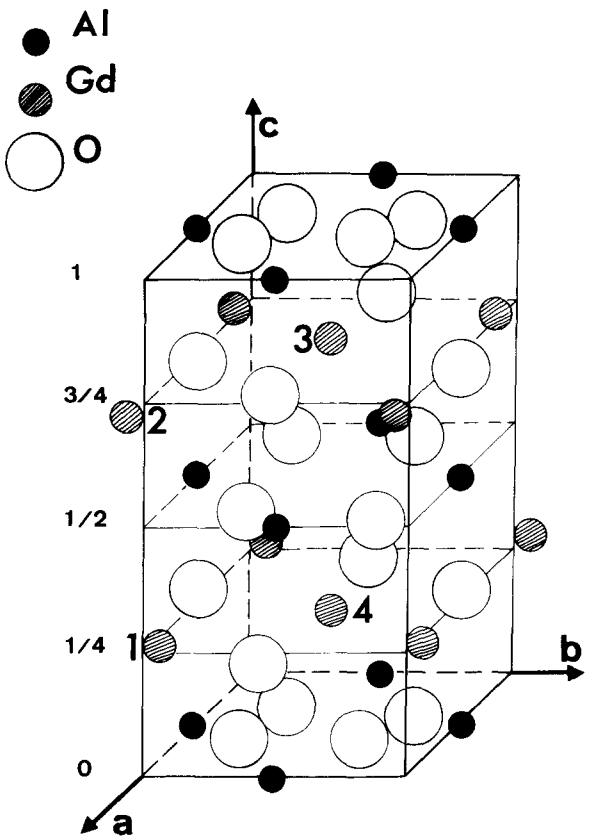

Figure 1 : Crystallographic structure of $GdAlO_3$.

According to group theory considerations developed by Bertaut [5], there exist four kinds of magnetic coupling. The magnetic structure factor for reflexions with h + k = 2n + 1 and l = 2n + 1 can be written as :

$\vec{F}(\vec{h}) = 4\vec{m}_1$ [sin2πhx . cos2πky] when $\vec{m}_1 = +\vec{m}_2 = +\vec{m}_3 = +\vec{m}_4$ (F-mode).

$\vec{F}(\vec{h}) = 4i\vec{m}_1$ [cos2πhx . cos2πky] when $\vec{m}_1 = -\vec{m}_2 = +\vec{m}_3 = -\vec{m}_4$ (G-mode).

$\vec{F}(\vec{h}) = 4\vec{m}_1$ [cos2πhx . sin2πky] when $\vec{m}_1 = +\vec{m}_2 = -\vec{m}_3 = -\vec{m}_4$ (C-mode).

$\vec{F}(\vec{h}) = 4i\vec{m}_1$ [-sin2πhx . sin2πky] when $\vec{m}_1 = -\vec{m}_2 = -\vec{m}_3 = +\vec{m}_4$ (A-mode).

x and y being small, $\vec{F}(\vec{h})$ is maximum for the G-mode and minimum for the A-mode. Therefore the observation of intenses peaks with h + k = 2n and l = 2n + 1 lead unambigously to a magnetic ordering corresponding to the G-mode.

In the case of $GdAlO_3$ where the magnetic moments lie within the (a - b) plane two possibilities remain according to group theory : GyAx associated to Γ_8 irreductible representation or GxAy (Γ_5). If the A-mode exists, it will give rise to a very weak contribution to the observed peaks h + k = 2n + 1, l = 2n + 1, but to a large contribution to additional Bragg peaks such as h + k = 2n, l = 2n + 1. As no such a peak has been observed within the experimental accuracy, we can deduce that the A component, if it exists,

Table 1 : Atomic position parameters calculated for Gd AlO_3 from low temperature data (T = 1.5 K)

	^{160}Gd	Al	O_I	O_{II}
x	- 0.017 (1)	0.5	0.0775 (25)	- 0.3225 (75)
y	0.03425 (75)	0.	0.5125 (25)	0.290 (25)
z	0.25	0.	0.25	0.030 (25)
B ($Å^2$)	0.155 (5)	0.63 (3)	0.42 (6)	0.54 (6)
b = (10^{-12}cm)	0.915 (5)	0.3449 (9)	0.5803 (6)	0.5803 (6)

reflexions such as h + k = 2n + 1 and l = 2n + 1 have been detected. Then, the magnetic structure factors for these reflexions can be written as :

$$\vec{F}(\vec{h}) = \pm i \{\vec{m}_1 e^{2\pi i(hx + ky)} - \vec{m}_2 e^{-2\pi i(hx + ky)} + \vec{m}_3 e^{2\pi i(hx - ky)} - \vec{m}_4 e^{-2\pi i(hx - ky)}\}$$

where $\vec{m}_1$, $\vec{m}_2$, $\vec{m}_3$, $\vec{m}_4$ are the magnetic moments of gadolinium atoms labelled as defined before.

corresponds to a magnetic moment value lower than 0.6 μ_B/Gd, and then to a canting angle smaller than 4° in the (a - b) plane. Therefore in the following we will suppose that the magnetic ordering is a four sub-lattice antiferromagnetic arrangement, which can be simplified to a two sub-lattice state Gx or Gy, because the canting angle is indeed very small or equal to zero. In these two cases, the refinement of the magnetic structure has been carried out, using

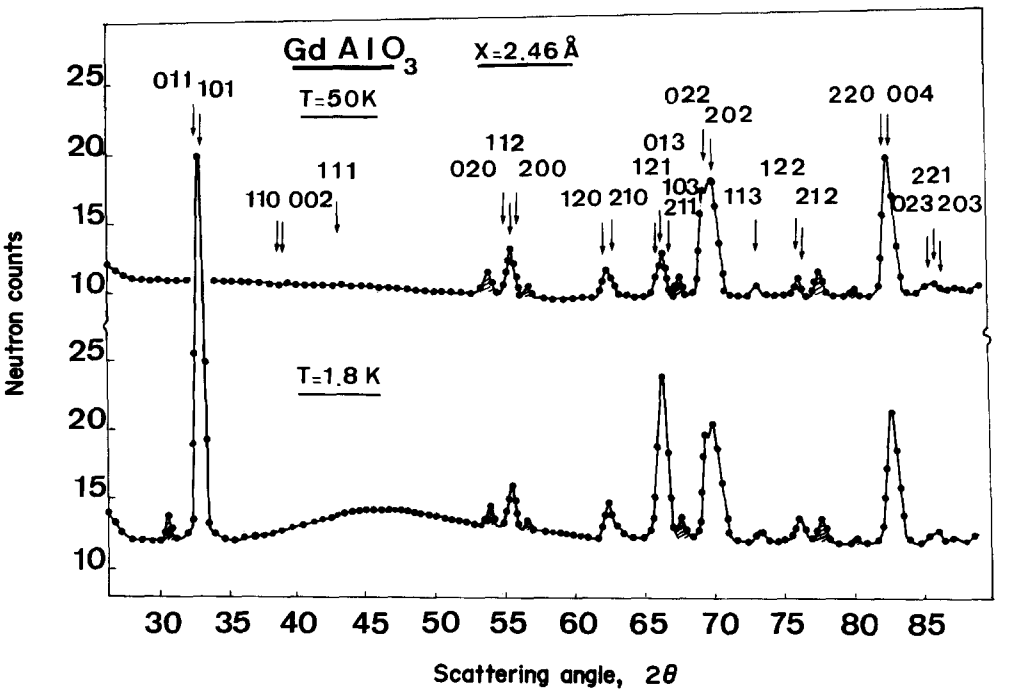

Figure 2 : Powder neutron diffraction patterns (T = 1.5 K and T = 50 K). Dashed peaks are due to Gd_2O_3 impurities.

Table 2 : Magnetic intensities and magnetic components calculated for both Gx and Gx Ay models.

	Gx model		Gx Ay model	
hkl	I_{obs}	I_{calc}	I_{obs}	I_{calc}
011, 101	4621	4588	4621	4588
121, 013, 103, 211	8477	8852	8477	8831
031, 123, 213, 301	6000	5818	6000	5810
231, 321, 015, 105, 033, 303	5085	5212	5085	5181
mx	0		0.4 μβ/at	
my	6.090μβ/at		6.08 μβ/at	
φ	0°		4°	
R %	2.96 %		2.78 %	

the Fermi length b = 0.915 barns of ^{160}Gd given by [10] for Gd_2O_3. In table 2 are reported the results for a Gx and a GxAy structure : the agreement is quite good nevertheless it is not possible to choose between a collinear or a canted model with an angle of 4° (figure 4). Thus, the main question concerning the magnetic moment direction in $GdAlO_3$ as a or b axis remains.

In neutron experiments using a neutron wavelength of 2.4 Å the distorsion of the cubic cell is too small to get a splitting of the <011> and <101> magnetic peaks of which intensities would allow to choose between the Gx or Gy mode. The magnetic intensity ratios $\frac{I(011)}{I(101)}$ will be equal to 2.92 for a Gx-mode, and 0.32 for the Gy mode. To separate the <011> and <101> magnetic peaks a complementary neutron experiment has been performed at the HFR reactor of ILL on the IN 12 spectrometer using a neutron wavelength of λ = 5.984 Å. In figure 3 the splitting of the

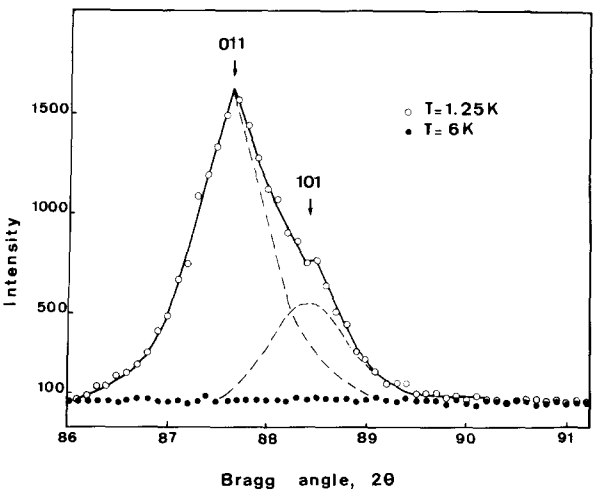

Figure 3 : Splitting of the two peaks <011> and <101> in Gd_3Al0_3. (λ = 5.984 A, T = 1.5 K).

two peaks can be clearly seen. The observed intensities give a ratio $\frac{Iobs(011)}{Iobs(101)}$ = 3.3 indicating that the magnetic ordering corresponds unambigously to a Gx-model. As in powder experiments, there is no possible ambiguity, we are able now to confirm that the magnetic structure of $GdAlO_3$ is well described by a Gx-mode. The calculation of the magnetic moment value for one Gd ion gives then 6.1 μB : this reduced moment comparatively to the theoretical value

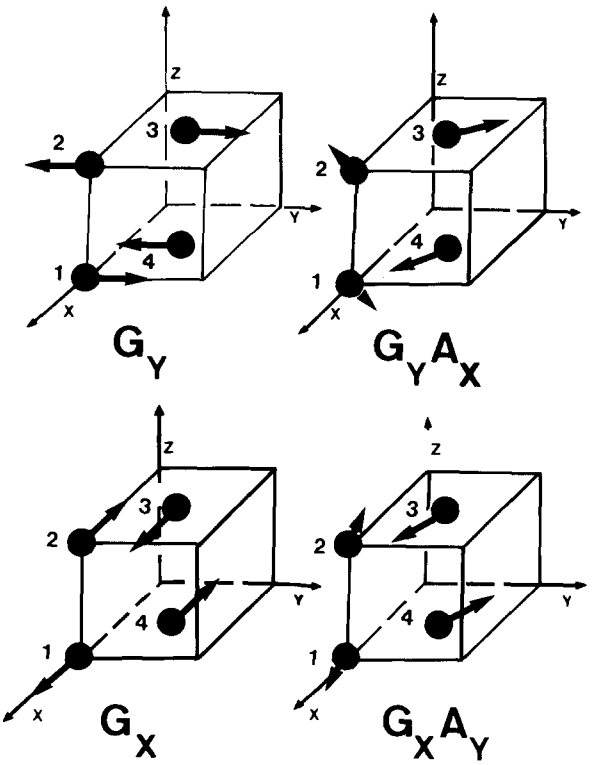

Figure 4 : G-models collinear or canted in perovskite type compounds.

at $T_N/2$ (about 6.4 μB/atom) is not yet well understood and may result from the high absorption of the sample.

5. Conclusion

Therefore $GdAlO_3$ is a simple two sub-lattice antiferromagnet with the antiferromagnetic direction along the a-axis. In the ordered state, there is a competition between isotropic and negative next neighbours exchange interactions which favour a G-mode, and dipolar magnetic interactions which induce an A-mode. Anisotropic exchange interactions leading to a canting angle are indeed very weak because Gd^{3+} ions are in a S-state, so, the magnetic structure is then determined mainly by next neighbour exchange interactions.

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