AIP | Journal of Applied Physics

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Citation: J. Appl. Phys. **37**, 1038 (1966); doi: 10.1063/1.1708325
View online: http://dx.doi.org/10.1063/1.1708325
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v37/i3
Published by the American Institute of Physics.

JOURNAL OF APPLIED PHYSICS VOLUME 37, NUMBER 3 1 MARCH 1966

Some Neutron-Diffraction Investigations at the Nuclear Center of Grenoble

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In orthorhombic $CrRO_3$ (R = rare earth and Y), Cr spins are ordered in a G mode between T_N 282°K for R = La, to 112°K for R = Lu. The rare-earth ordering is coupled to the Cr-spin ordering, with the exception of terbium. In the magnetoelectric compound $Fe_{1.15}Ga_{0.85}O_3$, four sites are available for cations, one of these mainly occupied by Ga. Neutron-diffraction and magnetic-susceptibility measurements give evidence of a ferrimagnetic ordering. Tetragonal FeS shows no evidence for magnetic ordering by neutron diffraction and Mössbauer effect down to 1.7°K. The CrS–MnS solid solution has NaCl type. First kind of face-centered magnetic ordering is observed.

$CrRO_3$ (REF. 1)

PRECISE parameter values a,b,c of the complete $CrRO_3$ series (R = rare earth and Y, space group *Pbnm*) have been given in Ref. 2. The ordering temperatures T_{N1} of the Cr spins decrease regularly with the radius of R. Rare-earth spin ordering is observed at temperatures T_{N2} above 4.2°K for Ho, Er, Pr, Nd, and Tm; below 4.2°K for Tb, Dy (we have not yet investigated by neutron diffraction the highly absorbing compounds with R = Gd, Sm, Eu, and with R = Ce which is difficult to prepare in large quantities).

In all cases reported here the rare-earth ordering is coupled to the Cr spin ordering[3] with the exception of Tb where the major part of the spin component orders in a mode which requires doubling of the unit cell along b. Very weak coupling of the Tb and Cr spins is also indicated by the form of the susceptibility plot which decomposes into two straight lines. The analogy of the $CrHoO_3$ and $CrErO_3$ structure with the known magnetic structures[4] of $FeHoO_3$ and $FeErO_3$, respectively, is quite remarkable and will be further investigated for the other partners of the series. The results are tabulated in Table I.[5]

In a G mode all six nearest neighbors are antiparallel. For notations see Ref. 6. G without a lower index means that in the pseudotetragonal unit cell the spin direction in the Oxy plane cannot be specified. The angles in the second and third column are those between Ox and the spin direction. The X mode in Tb will be fully described in Ref. 1.

$Fe_{1.15}Ga_{0.85}O_3$ (REFS. 7, 8)

The complex structure has been already published[9] and group theoretical arguments have shown that the magnetization along Oz must be coupled with an electric polarization along Oy in accord with Rado's findings.[10] Mössbauer studies confirm the presence of four different crystallographic sites, the fourth one being only weakly occupied by Fe. This last site is identified with the tetrahedral site Ga_{II}. Neutron-diffraction studies at room, liquid-nitrogen, and helium temperatures show that the four unequivalent crystallographic sites labeled Fe_I, Fe_{II}, Ga_I (all octahedral) and Ga_{II} (tetrahedral) in Ref. 8 contain respective proportions of iron of 0.89, 0.87, 0.50, and 0.04. The spin directions along Oz of the four corresponding Néel sublattices are $+--++$ or $+-+-$, the former arrangement giving a slightly better intensity agreement. No noticeable antiferromagnetic component could be detected by neutron diffraction in power diagrams.

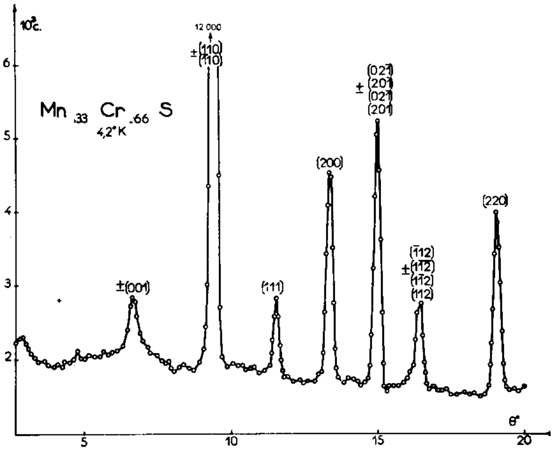

FIG. 1. Neutron-diffraction pattern of $Mn_{0.33}Cr_{0.66}S$.

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TABLE I. Spin configurations and transition temperatures in $CrRO_3$.

R	Spin mode of Cr^{3+}		Moment of Cr^{3+} (μ_B)		Spin mode of R^{3+}	Moment of R^{3+} (at 4.2°K)	T_{N1} (°K)	T_{N2} (°K)
	(80°K)	(4.2°K)	(80°K)	(4.2°K)				
La	G	G		2.45[5]			282	
Ce							257	
Pr	G	G_x	2.46	2.46	Fz	0.5 ± 0.4	239	
		G_x		2.52				
Nd	G	or	2.52		Cz	1.3	224	~10
		$G_{xy}60°$		2.55				
Sm							192	
Eu							181	
Gd							170	
Tb	G_z	G_z	2.55	2.85	Cz; X	1.4; 8.5	158	$1.5<T_{N2}<4.2$
Dy[a]	G_z	G_z			C; F		146	$1.5<T_{N2}<4.2$
Ho	$G_{xz}86°$	G_z	2.70	2.94	F_x; C_y	3.4; 7.0	141	~12
Er	G_x	$G_{xy}47°$	2.45	2.90	Cz	5.2	133	16.8
Tm	$G_{xz}62°$	G_x	2.24	2.58	Fz	0.8 ± 0.4	124	>4
Yb	$G_{xz}68°$	$G_{xz}68°$	2.44	2.80	not observed		118	
Lu	$G_{xz}63°$	$G_{xz}63°$	2.27	2.51			112	
Y	G_x	G_x	2.56	2.96			141	

[a] The calculation for the case of Dy is presently under way (Ref. 5).

The paramagnetic susceptibility above T_c is well represented by

$$1/\chi=\frac{T}{5.5}+215-\frac{13440}{T-272},$$

and thus shows the characteristic hyperbolic behavior of a Néel ferrimagnet. In the ferrimagnetic region where $\sigma_z=\sigma_{0z}+\chi H_z$ a nearly constant susceptibility is measured which might be due to a small (undetected) antiferromagnetic component perpendicular to Oz.

FeS (REF. 11)

The tetragonal variety of FeS prepared by the action of H_2S on a suspension of fine iron powder in water gives rise at room temperature, as well as at liquid-helium temperature, to identical neutron-diffraction patterns which are both in excellent agreement with the reported nuclear structure,[12] but show no evidence of a paramagnetic background. Mössbauer studies down to 1.7°K have not shown any ordering effect either. The short Fe–S distance of 2.33 Å in the FeS_4 tetrahedral is in favor of covalent (d^3s) bonding. By heating above 100°C the tetrahedral variety transforms exothermically to the B–8 structure type.

CrS–MnS (REF. 13)

α-MnS can dissolve considerable amounts of CrS in a (disordered) NaCl type structure. The solid solutions CrS·2MnS, CrS·MnS, and 2CrS·MnS studied by neutron diffraction show the progressive disappearance of the classical MnO ordering (propagation vector $k=[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$) and the appearance of the so-called first kind or ordering ($k=[001]$) in which ferromagnetic (001) planes alternate $+-+-$ in the Oz direction; the pattern for 2CrS·MnS is shown in Fig. 1. This is the first time that such an ordering is reported in a NaCl type structure. Stability conditions [6,14,15] require negative first-neighbor interactions $J_1(90°)$ and positive second-neighbor interactions $J_2(180°)$. It is gratifying to state that all superexchange mechanisms envisaged for 180° links of the kind Mn–S–Cr (simple transfer or double exchange) are conducive to ferromagnetic interactions.

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