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Rare Earths

A. ARROTT, *Chairman*

Magnetic Structure Investigations at the Nuclear Center

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The magnetic structure of the compounds UOS, β-$CoSO_4$, YCo_5, and $HoCo_5$ is briefly described.

UOS is antiferromagnetic. The Néel temperature is $T_n=55°K$. The magnetic cell is doubled in the c direction with a $++--$ sequence of U moments along c. The apparent spin is $S\sim1$. The negative interaction corresponds to U–O–U links.

In β-$CoSO_4$ (high-temperature modification, space group $Pbnm$), Co atoms are in 000, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$. Here three different antiferromagnetic spin modes, mutually perpendicular, $A_x(+--+)$, $G_y(+-+-)$, and $C_z(++--)$, in the Wollan–Koehler notation, are coupled. Direction cosines are 0.71, 0.50, and 0.50, respectively. The Co moment is about 3,84 μ_B at 4.2°K. A field-induced spin flip to the configuration F_x, C_y, G_z is predicted.

YCo_5 is ferromagnetic at room temperature with a moment value of Co practically equal to that of metallic Co and moment direction along c, which is conserved down to 4.2°K.

In $HoCo_5$ the moment of Ho is opposite to those of the Co atoms. When cooling from room to liquid helium temperature, the direction of easy magnetization changes from near c to a direction in the basal plane and the Ho moment increases from 4 to about 9 μ_B. The compensation temperature is 70°K.

UOS

THE structure of UOS has been established by Zachariasen[1] to be isomorphous with PbFCl. The space group is $P4/nmm$ and lattice parameters are $a=3.835kX$; $c=6.681kX$. U and S are in positions $2c)$ $00z$; $\frac{1}{2}\frac{1}{2}\bar{z}$ with $z(U)=0.200$; and $z(S)=0.65$.[1] 0 is in the parameterless position $2a)$ $\frac{1}{2}00$; $0\frac{1}{2}0$. Refinement of the z parameters by means of a neutron diffraction pattern, taken at room temperature leads to $z(U)=0.199$; $z(S)=0.643$. U has 4 0-neighbors at 2, $33kX$, $4S$ at 2.91, and $1S$ at $2.97kX$.

The compound is antiferromagnetic with a Néel temperature of $T_N=55°K$ and a Curie constant near to one ($C\sim1$; $S\sim1$) as if spin only was effective. A high uniaxial anisotropy energy ($\sim7.5\times10^7$ ergs/g) may be inferred from susceptibility measurements at low temperatures.

The magnetic lines of the neutron diffraction recording, observed at liquid helium temperature, can be indexed in a unit cell doubled along c. The absence of magnetic contributions to $(00l)$ reflections proves the spins to be along the c direction in agreement with the observed uniaxial anisotropy. The magnetic structure is described by double layers of uranium spins in the succession $++--$ at the levels $z_1=0.2c$; $z_2=0.8c$; $z_3=1.2c$; $z_4=1.8c$ of the chemical unit cell. The negative interactions correspond to U–O–U links. We are indebted to Dr. Brockhouse and Dr. Henshaw[2] for communicating their form factor data on UO_2 which allowed us to determine a magnetic moment of $1.9\pm0.11\mu_B$ per U atom, near to the value of paramagnetic measurements.

Crystalline field calculations for U^{4+} in a *cubic* environment and in the paramagnetic region[3] have shown that the "spin only" value is a numerical coincidence. Similar calculations are under way in the present tetragonal case.[4]

$CoSO_4$

$CoSO_4$ exists in 2 forms.[5] The low temperature or α form belongs to space group $Cmcm$ and has been studied by neutron diffraction.[6] The high temperature or β form belongs to space group $Pbnm(D_{2h}^{16})$. It has been studied magnetically by Kreines[7] and by neutron diffraction (present paper).

The interesting feature of β-$CoSO_4$ is its antiferromagnetic nature with $T_N=12°K$, accompanied by a field-induced ferromagnetism along the a axis of 6000 emu per mole, say of $1.07\mu_B$ per Co atom (maximum value at 4.2°K).

The Co atoms are in positions $4a)$ 000; $00\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$, and are numbered from one to four in the above sequence.

All magnetic lines appearing at 4.2°K may be indexed in the chemical cell. The four possible colinear

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[6] B. C. Frazer and P. J. Brown, Phys. Rev. **125**, 1283 (1962). Our magnetic measurements show α-$CoSO_4$ to be a "classical" antiferromagnet where the Néel-relation $\chi(0)=\frac{2}{3}\chi(T_n)=1/n$ is obeyed. The Néel temperature T_n is between 11° and 12°K. α-$CoSO_4$ does *not* show any metamagnetism for fields up to 20.000 Oe.
[7] N. M. Kreines, Soviet Phys.—JETP. **40**, 534 (1961) describes $CoSO_4$ in space group $Pnma$. The correspondence between his axes and ours is $a=c_K=4.739$; $b=a_K=8.616$; $c=b_K=6.702$ Å (parameters abc from reference 5).

TABLE I. Group *Pbnm*.

Γ_1	A_x	G_y	C_z
Γ_2	F_x	C_y	G_z
Γ_3	C_x	F_y	A_z
Γ_4	G_x	A_y	F_z

arrangements $++++$; $+-+-$; $++--$; $+--+$ are labeled F (ferromagnetic), G, C, and A arrangements, respectively. Each line of Table I contains those arrangements which may be associated two by two in a spin Hamiltonian of order two, respecting invariance under the space group symmetry *Pbnm*.[8] Our neutron diffraction data show that three spin modes A_x, G_y, and C_z (first line of Table I) are associated with the following "proportions" $|\gamma_x| = 0.71 \pm 0.01$; $|\gamma_y| = |\gamma_z| = 0.5 \pm 0.01$, where γ_x, γ_y, γ_z are the components of a unit vector along the spin direction ($\gamma_x^2+\gamma_y^2+\gamma_z^2=1$). Figure 1 shows the resultant canted spin model with the components of the spin indicated by broken lines along the axes. The apparent spin "S" per Co atom is found to be "S"$=1.92$ at $4.2°K$ (the spin only value is $S=\frac{3}{2}$) so that there is an orbital contribution.

From the existence of a field induced ferromagnetic mode F_x[7] and from line 2 of the table, we may predict that the ferromagnetic mode F_x will now be associated with the two antiferromagnetic modes C_y and G_z. Experiments are in progress to check this point.

It may also be expected that switching from configuration of line 1 to line 2 of the table is due to a mechanism proposed by Néel.[9]

YCo_5; $HoCo_5$

YCo_5 and $HoCo_5$ are AB_5 compounds isomorphous with $CoCu_5$.[10] The space group is *P6/mmm*. A is in (000), $2B_I$ in $\pm(\frac{1}{3}\frac{2}{3}0)$, $3B_{II}$ in $(\frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}\frac{1}{2}\frac{1}{2})$.

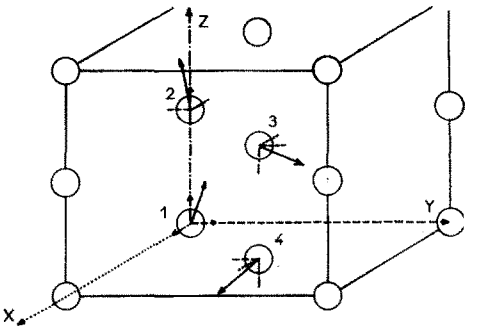

FIG. 1. Spin configuration in β-$CoSO_4$. Broken lines indicate the component modes A_x····, G_y– – – and C_z–·–·–.

Parameters are $a_0=4.928$ Å; $c_0=3.992$ A for YCo_5,[11] and $a_0=4.88$ Å; $c_0=3.96$ for $HoCo_5$.[12]

Neutron diffraction at room temperature shows YCo_5 to be ferromagnetic with spins aligned along the c axis and a moment value of 1, $74\mu_B$ per Co atom, near to the value in cobalt metal. The spin direction along c is conserved at 4.2°K, where no appreciable changes in the neutron diffraction diagram are found.

$HoCo_5$ has been studied by neutron diffraction at room and liquid helium temperature. The moment value of the Ho atom increases from $4\mu_B$ at room temperature to $9\mu_B$ at helium temperature and is opposite to the moment direction of the Co atoms so that there must be a compensation temperature above 4.2°K already indicated by experiment.[13] Our magnetic measurements show it to be at 70°K.

Best agreement with neutron diffraction intensities is obtained for a spin direction making an angle of 22° with the c direction at room temperature, whereas at 4.2°K the spins are in the basal plane.[14] Comparing with the YCo_5 data it is clear that Ho is responsible for the change in spin direction.

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