Magnetic Structure of β-CoSO₄†

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Recently the present authors reported the antiferromagnetic structure of CoSO₄, and a qualitative explanation was offered for the susceptibility and field-induced transition measurements of Borovik-Romanov and Kreines. It was assumed that the latter were made on the modification which is stable at ordinary temperatures. Subsequent study of a paper by Kreines, however, indicated that the single crystals used for these measurements were of the high-temperature modification (stable above 600°C). The present paper describes the determination of the antiferromagnetic structure of this modification. There are four different (but symmetry related) spin directions in a magnetic cell of the same size as the chemical unit cell. The observed moment per Co²⁺ ion is found to be (3.22±0.32)μ_B. While the structure accounts for the observation that none of the principal susceptibilities approaches zero at 0°K, in other respects the structure is rather different from what one might expect from the magnetic measurements.

$\mathbf{I}$N a recent paper[1] the present authors have reported the antiferromagnetic structure of the low-temperature form of CoSO₄, and this structure was used in an attempt to explain the magnetic susceptibility and field-induced transition measurements made by Borovik-Romanov and Kreines.[2,3] At the time of writing it was assumed that these measurements had been made on a single modification of CoSO₄; however, subsequent study of a paper by Kreines,[4] in which the transition from the antiferromagnetic to the weakly ferromagnetic state is discussed in more detail, indicated to us that the single crystals used for the susceptibility measurements were of the high-temperature modification. The present note describes the determination of the magnetic structure of the high-temperature form from neutron diffraction measurements.

The two forms of cobalt sulfate were described first by Hocart and Serres[5] and subsequently by Coing-Boyat,[6] who determined the space groups and structure types of the two forms. The low-temperature form, α-CoSO₄, is stable at temperatures below 600°C, has space group *Cmcm*, and is isostructural with CrVO₄ (Brandt[7]). At temperatures above 600°C β-CoSO₄ is stable. β-CoSO₄ has space group *Pnma*, or alternatively *Pbnm*, and is isostructural with CuSO₄ and ZnSO₄ (Kokkoros and Rentzeperis[8]). The two forms are readily distinguishable from one another by their x-ray powder photographs; their lattice constants are given in Table I.

We have tried to prepare single crystals of CoSO₄ using the method described by Kreines[9,10]; invariably when crystals were formed they were found to be β-CoSO₄ and after keeping for some weeks in dry air at room temperature they transformed gradually to polycrystals of α-CoSO₄. The β-CoSO₄ used in the present study was prepared in the form of small crystals by heating a mixture of one part anhydrous cobalt sulfate and four parts ammonium sulfate by weight at 500°C for 24 h. X-ray diffraction patterns showed that the resulting material was β-CoSO₄; no evidence of any contamination with the α form was detected. Neutron diffraction patterns were obtained from about 50 g of these crystals contained in a cylindrical sample holder at liquid-nitrogen temperature and at liquid-helium temperature. The patterns are shown in Fig. 1. The liquid-helium patterns can be seen to possess a number of peaks not present in the liquid-nitrogen pattern, and in addition several of the peaks in the liquid-helium pattern are increased in magnitude over the corresponding peaks in the liquid-nitrogen pattern. As in the case of the anhydrous sulfates described previously,[1] these peaks, which arise from the magnetic ordering, can all be indexed on the original chemical unit cell. The intensities of the magnetic reflections were determined by integrating the areas under the peaks and subtracting the liquid-nitrogen values from the

TABLE I. Lattice parameters and space groups of the two forms of CoSO₄.[a]

Lattice parameter (A)	Space group	α-CoSO₄	β-CoSO₄	
		Cmcm	*Pbnm*	*Pnma*
a		5.195	4.739	8.616
b		7.872	8.616	6.702
c		6.523	6.702	4.739

[a] M. J. Coing-Boyat, Compt. Rend. **248**, 2109 (1959).

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[2] A. S. Borovik-Romanov and N. M. Kreines, Zh. Eksp. i Teoret. Fiz. **35**, 1053 (1958) [translation: Soviet Phys.—JETP **8**, 734 (1959)].

[3] A. S. Borovik-Romanov, V. R. Karasik, and N. M. Kreines, Zh. Eksp. i Teoret. Fiz. **31**, 18 (1956) [translation: Soviet Phys.—JETP **4**, 109 (1957)].

[4] N. M. Kreines, Zh. Eksp. i Teoret. Fiz. **40**, 762 (1961) [translation: Soviet Phys.—JETP **13**, 534 (1961)].

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[7] K. Brandt, Arkiv Kemi **17A**, 1 (1943).

[8] P. A. Kokkoros and P. J. Rentzeperis, Acta Cryst. **11**, 361 (1958).

[9] A. S. Borovik-Romanov and N. M. Kreines, Zh. Eksp. i Teoret. Fiz. **33**, 119 (1957) [translation: Soviet Phys.—JETP **6**, 862 (1958)].

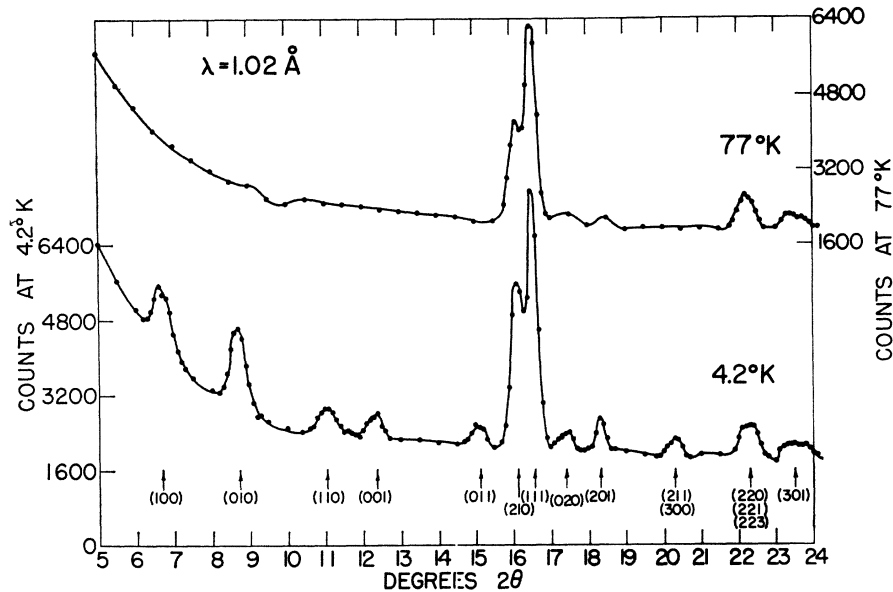[10] N. M. Kreines, Zh. Eksp. i Teoret. Fiz. **35**, 1391 (1958) [translation: Soviet Phys.—JETP **8**, 972 (1959)].

FIG. 1. Neutron diffraction patterns of β-CoSO$_4$ at liquid N$_2$ and He temperatures.

liquid-helium values where appropriate. The intensities of a number of the nuclear peaks were also measured to enable the magnetic intensities to be put on an absolute scale.

The cobalt ions in the structure of β-CoSO$_4$ are at the positions $(0,0,0)$, $(0,\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$, and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ in the unit cell. If we let $\mathbf{S}_1$, $\mathbf{S}_2$, $\mathbf{S}_3$, $\mathbf{S}_4$ be vectors giving the magnitude and direction of the spins on these four ions, respectively, then we have the conditions: $\mathbf{S}_1+\mathbf{S}_2+\mathbf{S}_3+\mathbf{S}_4=0$, since there is no net moment, and $S_1{}^2=S_2{}^2=S_3{}^2=S_4{}^2$, since the four ions are chemically identical. Under these conditions we can define three orthogonal vectors $\mathbf{L}_1$, $\mathbf{L}_2$, $\mathbf{L}_3$ such that

$$\mathbf{L}_1=\mathbf{S}_1-\mathbf{S}_2-\mathbf{S}_3+\mathbf{S}_4,$$
$$\mathbf{L}_2=\mathbf{S}_1-\mathbf{S}_2+\mathbf{S}_3-\mathbf{S}_4,$$
$$\mathbf{L}_3=\mathbf{S}_1+\mathbf{S}_2-\mathbf{S}_3-\mathbf{S}_4,$$

and these three vectors are identical with the three vectors $\mathbf{L}_1,\mathbf{L}_2$, $\mathbf{L}_3$ used by Kreines.[2] We can now write the modified structure factor for magnetic scattering used previously,[1]

$$\mathbf{F}(hkl)=\sum_{j=1}^{j=4}[\mathbf{e}(\mathbf{e}\cdot\mathbf{S}_j)-\mathbf{S}_j]\exp[2\pi i(hx_j+ky_j+lz_j)],$$

as

$$\mathbf{F}(hkl)=4[\mathbf{e}(\mathbf{e}\cdot\mathbf{L}_j)-\mathbf{L}_j],$$

where $j=1$ for reflections with $h+l$ odd, k odd; $j=2$ for reflections with $h+l$ even, k odd; and $j=3$ for reflections with $h+l$ odd, k even.

Examination of the pattern shown in Fig. 1 shows that magnetic reflections characteristic of each of these types of reflections occur, so that none of the vectors $\mathbf{L}_j$ is zero. This shows that the spins on all four ions in the unit cell are differently oriented.

The magnetic intensities were put on an absolute scale by comparing the intensity of the nuclear reflections with the calculated values based on the CuSO$_4$ parameters and processed to give the experimental $F(hkl)^2$ values. The cobalt form factor assumed was the same as that used in the analysis of the α-CoSO$_4$ structure.[1] A least-squares analysis for the vectors $\mathbf{L}_j$ was carried out taking each of the three sets of reflections separately. The components $L_{jx}L_{jy}L_{jz}$ were derived from the relation:

$$F_{hkl}{}^2=16d_{hkl}{}^2\left[L_{jx}{}^2\left(\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)\right.$$
$$\left.+L_{jy}{}^2\left(\frac{h^2}{a^2}+\frac{l^2}{c^2}\right)+L_{jz}{}^2\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}\right)\right],$$

where

$$d_{hkl}{}^2=\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)^{-1}.$$

The best agreement was obtained with $\mathbf{L}_1$ parallel to x,

TABLE II. Observed and calculated structure amplitudes.

(hkl)	Nuclear structure amplitudes		Magnetic structure amplitudes	
	F_0	F_c	F_0	F_c
(100)	0	0	1.52	1.75
(010)	0	0	2.39	2.36
(110)	0	0	1.23	1.20
(001)	0	0	1.66	1.64
(011)	0	...	1.25	1.43
(210)	2.93	2.44	2.21	2.16
(111)	2.82	3.22	1.37	1.43
(201)	0.90	1.55	1.66	1.50
(310)	0	0	0.47	0.45
(301)	2.06	1.54	0	0

L_2 parallel to z, and L_3 parallel to y. The magnitudes of the vectors are:

$$L_1 = 3.00 \pm 0.32, \quad L_2 = 4.62 \pm 0.46, \quad L_3 = 3.32 \pm 0.36.$$

The spin vectors can be determined from these values by use of the following relations:

$$4S_1 = L_1 + L_2 + L_3, \quad 4S_3 = L_2 - L_1 - L_3,$$
$$4S_2 = L_3 - L_1 - L_2, \quad 4S_4 = L_1 - L_2 - L_3.$$

This is shown diagrammatically in Fig. 2. Using the L values cited above, one finds for the orientation angles of S_1 relative to the x, y, and z directions: $\varphi_{11} = 62.2°$, $\varphi_{12} = 59.0°$, and $\varphi_{13} = 44.2°$, respectively. The total moment on each cobalt ion is $(3.22 \pm 0.32)\mu_B$.

The observed and calculated structure factors are compared in Table II. The structure factor agreement is somewhat better for the magnetic data than for the nuclear, indicating that the CuSO₄ positional parameters can give only a fair approximation for β-CoSO₄. The effect on the results reported here is that a scale factor error is introduced which appears in the Co⁺² moment. This was considered in calculating the standard error of the moment.

The orientation of the vectors L_1, L_2, L_3 is in accordance with the requirements of the symmetry of the space group $Pnma$ as given by Kreines[4] and by Bertaut.[11] It is clear from the magnetic structure why none of the three principal susceptibilities tend to zero at zero temperature. It is however difficult to reconcile the susceptibility measurements of Borovik and Kreines[2-4] with the magnetic structure in detail. For example, we would expect the largest value of the 0°K inverse susceptibility to occur in the direction of the c axis, since this would correspond most closely to the $\chi_{||}$ case, but Kreines finds it to be in the a direction. Also, if one attempts to use an argument similar to that developed in our earlier paper,[1] in which the weakly ferromagnetic state is accounted for by simple reversal of half the spins in the structure, best agreement with the observed moment of about $1.1\mu_B$ is obtained by reversal of S_2
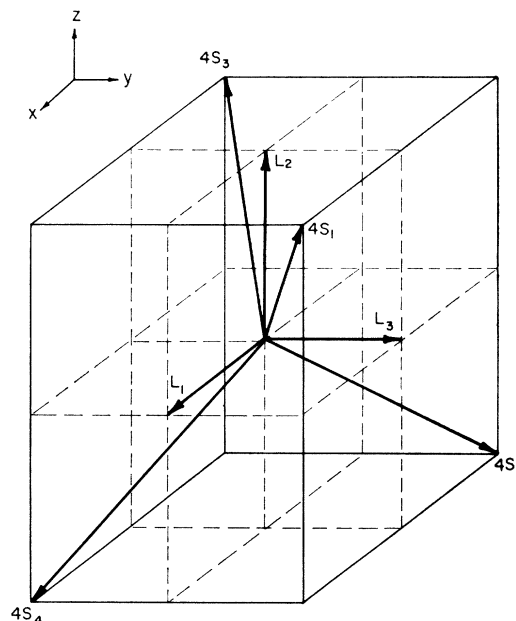
[11] E. F. Bertaut, J. Phys. Radium **22**, 839 (1961).

FIG. 2. The four spin orientations in β-CoSO₄.

and S_3, yielding a net moment per cobalt ion of $1.5\mu_B$ in the a direction. According to Kreines, however, the ferromagnetic direction is along the c axis, and simple reversals for a moment in this direction (involving S_2 and S_4) would result in a net moment of $2.3\mu_B$. Thus, it appears that further elucidation of the field-induced transition must await neutron diffraction measurements in high fields.

Note added in proof. When the galley proof of the present paper was being prepared, it came to the authors attention that a very similar study of β-CoSO₄ had just been completed by Dr. J. Coing-Boyat and Dr. E. F. Bertaut. We are grateful to them for allowing us to compare results prior to publication. A preliminary account of their work appeared in the program abstracts of the Eighth Annual Conference on Magnetism and Magnetic Materials (Pittsburgh, Pennsylvania, November 1962), and a full account is to be published soon.