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Magnetic Structure of $CuSO_4$†

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The antiferromagnetic structure of anhydrous cupric sulfate, $CuSO_4$, has been determined from neutron-diffraction powder data and by use of the single-crystal susceptibility results of Kreines. A least-squares refinement of the crystal structure was also carried out in order to obtain a good absolute scale factor for the neutron analysis. The original x-ray data of Kokkoros and Rentzeperis were used in these calculations. The magnetic structure is collinear, with $+--+-$ ordering on the 000, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ sites in the *Pbnm* orthorhombic cell. The Cu^{2+} moment was found to be 0.83 ± 0.10 Bohr magnetons with the spin-axis orientation parallel to the *a* axis of the unit cell.

INTRODUCTION

ANHYDROUS cupric sulfate, $CuSO_4$, is antiferromagnetic below about 34.5°K.[1–6] Some of the reported magnetic measurements on polycrystalline specimens have also been suggestive of weak ferromagnetism[7,8]; however, in single-crystal measurements by Kreines[5] no residual moment could be detected. Nor was the susceptibility field-dependent at liquid-hydrogen temperature, as had been reported,[7,8] although field dependence was observed for $\chi_\perp$ near the Néel temperature. Watanabe[6] reports that the magnetic behavior of polycrystalline $CuSO_4$ is not reproducible if the conditions of preparation from the pentahydrate salt are varied. It seems likely that incomplete dehydration is the explanation for most of the unusual properties that have been reported for $CuSO_4$, although Watanabe does offer an interesting suggestion that both the ambiguous susceptibility data and the weak, or parasitic, ferromagnetism are to be attributed to crystal imperfections.

In the present note we report the results of a neutron-diffraction study of this salt. Because of the low Cu^{2+} moment, and because of unfortunate overlapping of peaks in the neutron powder pattern, the magnetic structure should be investigated using single crystals, but $CuSO_4$ crystals of suitable size for neutrons are not easily grown. A complete determination of the magnetic structure is possible with powder data, however, if the single crystal magnetic measurements of Kreines[5] are taken into consideration.

SAMPLE PREPARATION

The polycrystalline sample was prepared from the pentahydrate by heating four hours in air at 500°C. This resulted in a 36.28% weight loss as compared to a calculated loss of 36.06%, and no extraneous lines were observable in either x-ray or neutron diffraction patterns. It is of interest that several attempts were made to prepare samples at lower temperatures in air (in the 200 to 350°C range), and in no case was a pure single-phase material obtainable. It was possible, however, to prepare a pure sample at 300°C by heating *in vacuo* for 24 h with a P_2O_5 trap. The Leiden samples were prepared *in vacuo* at 250°C.[1,7,8] Watanabe's samples were prepared at 270°C and 300°C under several different firing conditions (in air, *in vacuo*, with sulfuric acid, and with ammonium sulfate).[6]

CRYSTAL STRUCTURE

$CuSO_4$ crystallizes in the orthorhombic space group *Pbnm* (D_{2h}^{16}). Cell dimensions[9] are: $a=4.791\pm0.008$ Å, $b=8.391\pm0.013$ Å, $c=6.811\pm0.010$ Å. Atomic positions are 4 Cu in (a), 4 S in (c), 4 O_I in (c), 4 O_{II} in (c), and 8 O_{III} in (d). Kokkoros and Rentzeperis[10] (KR) carried out an analysis of the crystal structure by trial-and-error in a single-crystal x-ray study. Subsequently the structure was refined by Rama Rao using Fourier methods.[11] The structure is shown in Fig. 1.

Intensity calculations based on these x-ray studies showed only fair agreement with neutron data, and

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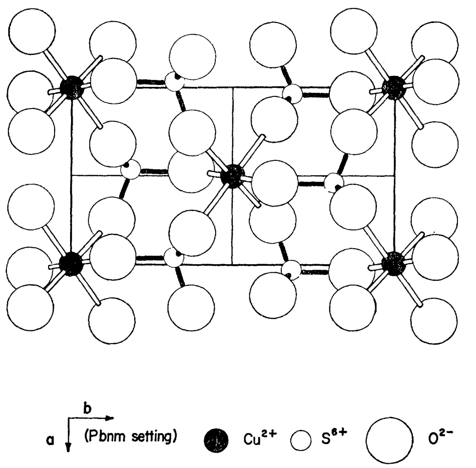

FIG. 1. The crystal structure of $CuSO_4$. The Cu^{2+} ions are at $z=0, \frac{1}{2}$ at each location in the figure. The CuO_6 octahedra share edges to form chains in the c direction. One of the oxygens of each SO_4 tetrahedron cannot be seen because of exact superposition on another oxygen.

since a reliable scale factor was needed in evaluating the Cu^{2+} moment, we have carried out a further refinement by least squares. The KR x-ray data were used in the calculations. Cu^{2+}, S^{2+}, and O^- scattering curves, interpolated where necessary and corrected for dispersion, were taken from the International Tables.[12]

Final parameters are listed in Table I and compared with earlier results. These were obtained by assuming a fixed over-all temperature factor of zero. Other calculations were carried out with variable isotropic atomic temperature factors, but they all took on negative values, indicating perhaps some sort of systematic error in the data. There appears to be a typographical error in the KR paper in the case of (002), since it is off by a factor of about two regardless of which set of parameters in Table I is used [listed as (020) in the KR paper because of the *Pnma* cell orientation]. It was omitted in final calculations.

The values of the structure factor reliability index $R=\sum||F_o|-|F_c||\div\sum|F_o|$, obtained were 0.142 and 0.128 with zero observations included and omitted, respectively. KR obtained 0.168 with zeros included. Rama Rao did not use all of the KR data, but he reports R values of 0.143 and 0.165 for the [001] and [100] zones, respectively. The neutron data provide an independent check on the relative accuracies of the three sets of parameters. The Rama Rao set yields a slightly better fit than that of KR, but the ***intensity R*** value (I used instead of F) is 0.338, which is much higher than the value of 0.139 obtained in the present refinement. Calculated and observed neutron intensities are compared in Table II.

TABLE I. $CuSO_4$ coordinate parameters.

Atom	Parameter	KR[a]	Rama Rao[b]	*AFHCB*
S	x	0.444	0.445	0.447
	y	0.186	0.185	0.185
O_I	x	0.736	0.755	0.755
	y	0.130	0.141	0.132
O_{II}	x	0.444	0.439	0.436
	y	0.367	0.375	0.369
O_{III}	x	0.305	0.307	0.310
	y	0.130	0.129	0.128
	z	0.053	0.069	0.064

[a] See Ref. 10.
[b] See Ref. 11.

TABLE II. Calculated and observed nuclear neutron intensities for $CuSO_4$.

hkl	2θ	I_{calc}		I_{obs} (77°K)	σ (I_{obs})
020	14.4°	199	1344	1123	11
110	14.5	1145			
101	15.4		52	91	9
021	16.9	686	2415	2619	13
111	17.0	1729			
002	17.8		11	51	9
120	19.2		141	169	7
121	21.2		5	25	6
022	23.0	728	906	990	7
112	23.0	178			
103	25.2	1083	1083	888	73
200	25.4	0			

MAGNETIC STRUCTURE

If the magnetic cell is identical with the chemical cell, the possible collinear spin configurations for anti-

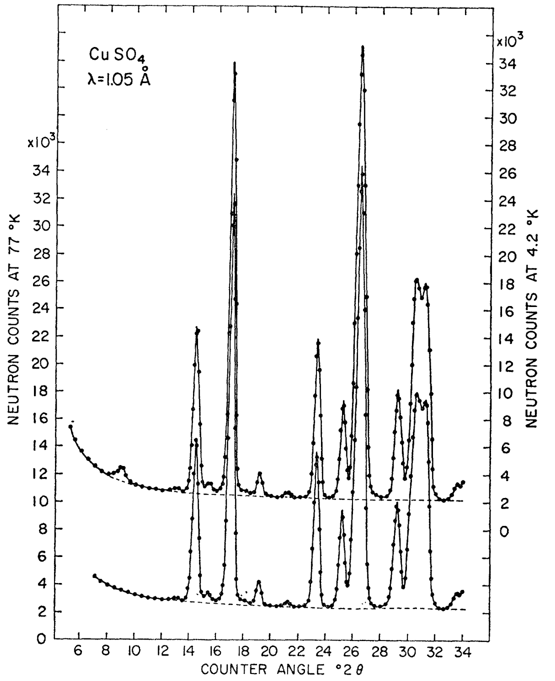

FIG. 2. Neutron diffraction patterns of polycrystalline $CuSO_4$ at liquid N_2 and He temperatures.

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[12] *International Tables for X-Ray Crystallography*, edited by C. H. MacGillvary and G. D. Rieck (Kynoch Press, Birmingham, England, 1962), Vol. III.

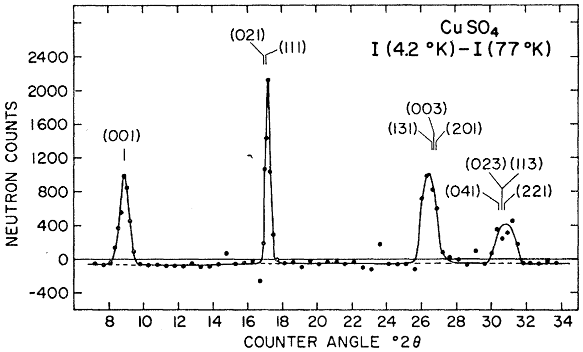


FIG. 3. Difference pattern showing magnetic peaks for $CuSO_4$. Obtained by subtracting neutron data collected at 77°K from that collected at 4.2°K.

ferromagnetic ordering are $+--+$, $++--$, and $+-+-$ on the Cu^{2+} sites (000, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$). In the Wollan-Koehler-Bertaut notation these arrangements are labeled G, C, and A, respectively.[13]

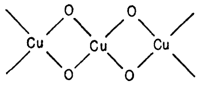
In comparing neutron diffraction patterns taken at 4.2 and 77°K (see Fig. 2), only one clearly resolved new peak was found in the low-temperature pattern. This indexed as the (001) reflection, which is characteristic of type A ordering. A change of intensity was also found for the combination (021), (111) peak, again characteristic of structure type A. The magnetic peaks can be seen more clearly in the difference pattern shown in Fig. 3. The two high-angle peaks cannot be used quantitatively due to a large uncertainty in residual aluminum contributions from the cryostat at 26.0° and 30.1°, but permissible reflections for A type ordering have been indicated in the figure.

Trial intensity calculations, assuming an A type collinear spin structure and a Cu^{2+} moment of one Bohr magneton, lead very quickly to an a-axis orientation for the spin direction. A c-axis orientation can be eliminated immediately because of the presence of the (001) reflection, and a b-axis orientation does not yield good intensity agreement. The a-axis orientation

TABLE III. Calculated and observed magnetic neutron intensities for $CuSO_4$.

hkl	2θ	I_{calc}	I_{obs} (4.2°K)	σ (I_{obs})
001	8.9°	123	115	5
021	16.9	56 } 105	118	13
111	17.0	49		

FIG. 4. Copper-oxygen chains in $CuSO_4$.



and the spin collinearity, are in complete agreement with the magnetic measurements of Kreines.[5] Kreines used small single crystals which were oriented by morphology and x rays. While the setting is not specified in her paper, it can be identified from the cell dimensions as *Pcmn*.[14] Transforming to *Pbnm*, the susceptibility measurements give $\chi_\perp=\chi_b=\chi_c$, and $\chi_{\parallel}=\chi_a$. This suggests a collinear spin structure with the spin axis parallel to the a axis of the crystal. With this confirmation, the Cu^{2+} moment may be calculated from the neutron diffraction data and we obtain 0.83±0.10 Bohr magnetons. The magnetic intensity agreement is shown in Table III.

CONCLUSIONS

The antiferromagnetic structure of $CuSO_4$ is a simple one of the $CrVO_4$ type[15] with collinear $+-+-$ ordering on the Cu^{2+} sites: 000, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Thus, in agreement with the model proposed by Kreines, we find an antiferromagnetic interaction between Cu nearest neighbors. This occurs in the c-oriented chains of Fig. 4. In other respects, however, the ordering scheme differs from that in her tentative model.

The spin axis, identified from the susceptibility data of Kreines, is parallel to the a axis of the *Pbnm* oriented cell. The Cu^{2+} moment is then calculated from the neutron data to be 0.83±0.10 Bohr magnetons.

The crystal structure refinement, in addition to providing an accurate scale factor for the magnetic intensities, supports the conclusion reached by Rama Rao on the coordination polyhedron about copper. In the original KR study it appeared that copper might have the rare type of octahedral coordination with two nearest neighbors and four coplanar neighbors at significantly greater distances. In the more usual case, the oxygen octahedron is distorted in the opposite way; i.e., the four coplanar neighbors are closer to copper than the other two. In agreement with Rama Rao, the present refinement favors this "normal" distortion. We find two O_{II}'s at 2.03 Å and two O_{III}'s at 1.89 Å, for the four nearest coplanar neighbors, and there are two O_I's at 2.33 Å.

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[14] Figure 4 in Kreines' paper is drawn incorrectly, since the Cu sites are improperly assigned for this setting, but this does not affect the conclusions which may be drawn from the measurements.

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