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Electron Spin Resonance in Single Crystals of Anhydrous Copper Sulfate

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The magnetic resonance of synthetic anhydrous copper sulfate has been investigated at 23.3 GHz at temperatures between 77°K and 4.1°K. In the paramagnetic region, the observed resonance consists of two lines. One of these is relatively narrow and remains essentially fixed even down to 4.1°K. The second line is unusually broad and its behavior indicates that it is due to the copper ions in the anhydrous crystal. The g values and corresponding linewidths have been measured for the broad line at 77°K. As the temperature drops to the Néel point, this broad line increases in width, then shifts, and disappears rather rapidly, indicating that it is associated with the antiferromagnetic phase.

I. INTRODUCTION

Anhydrous copper sulfate is currently of interest due to its antiferromagnetic properties below a Néel temperature[1] of 35°K. It is an orthorhombic crystal (Pbnm) and hence is expected to be a biaxial antiferromagnet. The symmetry of this crystal permits canted antiferromagnetism[2] which is sometimes accompanied by a weak ferromagnetic moment. Some investigators have reported a possible observation of weak ferromagnetism in powdered samples.[3] Kreines,[4] however, did not detect this in his single-crystal measurements of the susceptibility. The data from the latter work, together with the neutron-diffraction investigation by Almodovar *et al.*,[5] in polycrystalline samples have been used to determine the antiferromagnetic structure of $CuSO_4$. Recent developments in crystal growing techniques[6] have facilitated the growth of single crystals sufficiently large for neutron diffraction experiments. Recently Menzinger *et al.*[7] have reported a diffraction experiment on single crystals using polarized neutrons. Of particular interest was the detection of an unpaired spin density (between the copper ions lying along the c axis), which they believe may be involved in the super exchange. The pertinent results of these investigations are summarized in the caption for Fig. 1. We report here the results of our measurements on the electron spin resonance at low temperatures. Since our investigation was limited to 23 GHz, the main quantitative information pertains to the paramagnetic region. The behavior of the resonance below the Néel temperature allows us to make an estimate of the lower bound for the lower-mode zero-field resonance in the antiferromagnetic state.

II. EXPERIMENTAL

The single crystals used in this experiment were grown from $CuSO_4 \cdot 5H_2O$ in a solvent of $(NH_4)_2SO_4$ and H_2SO_4, then dehydrated at 350°C for 24 h. A subsequent spectrographic analysis indicated impurities of Ca, Fe, Mg, Si, Na, and V which are present in very small amounts. None of these elements could be detected, however, by the resonance techniques. X-rav techniques were used to orient the crystals.

Our experiments were carried out in a conventional K-band spectrometer operating at about 23.3 GHz. An AFC circuit locked the klystron to the sample cavity frequency, which was measured with a cavity wavemeter. The magnetic field was modulated at 100 kHz and the output from the bridge was phase detected. The derivative signal was displayed on an X–Y plotter, which had its axis coupled to the field sweep drive. A nuclear resonance flux meter and frequency counter were used to determine the magnetic field strength.

The temperatures between 77° and 20°K were obtained with the aid of the device sketched in Fig. 2. Copper cold fingers connected a liquid-helium reservoir to a K-band waveguide flange. A connecting copper waveguide then served to conduct the heat away from the sample cavity. The sample was cooled by the sample holder and helium exchange gas in the cavity. The spiral-walled epoxy cavity previously described[8] was modified by electroforming the threaded section of the cavity to permit sealing the cavity with Woods metal in order to contain the exchange gas. A heater coil located just above the cavity was used for additional heat input.

The temperature was measured with a germanium resistance thermometer positioned about 0.010 in. above the top wall of the cavity. By using a sufficiently low helium pressure in the waveguide-cavity system,

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[2] R. R. Birss, *Symmetry and Magnetism* (John Wiley & Sons, Inc., New York, 1964), Vol. 3.
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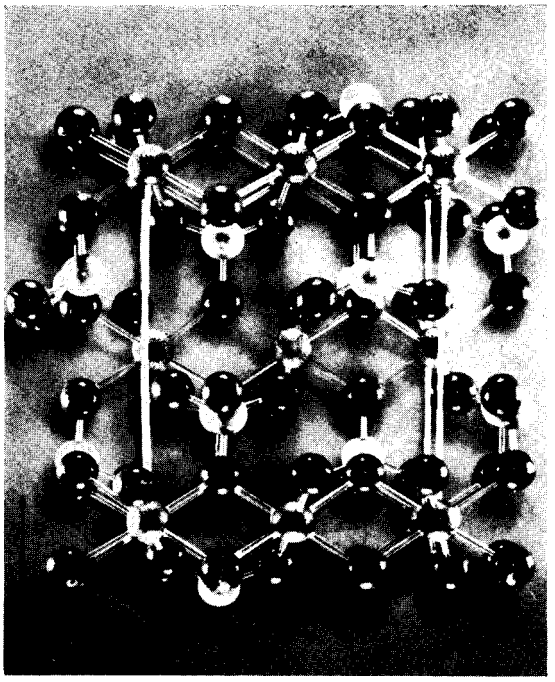

FIG. 1. Photograph of a model of $CuSO_4$. The light colored spheres represent sulfur atoms and the intermediate shaded spheres represent copper atoms. The dark spheres representing the oxygen atoms form distorted octahedra about the copper atoms. We have adopted the notation where the lattice constants are $a=4.79$ Å, $b=8.39$ Å, and $c=6.81$ Å. The b and c axes are indicated in the figure. The preferred spin direction in the AFM state is along the a axis. Copper–oxygen chains forming the superexchange path along the c axis are clearly visible. The two sublattices are comprised of copper atoms lying in alternate planes perpendicular to the c axis.

the temperature of the sample could be made to vary more slowly than that of the cavity. While it was not possible to determine the temperature accurately under these conditions, the qualitative AFM behavior indicated in Figs. 4 and 5 was observed by this technique.

Measurements were made on single crystals and on powdered samples. The paramagnetic resonance in both cases consisted of a superposition of two lines. One of these is a structured line about 750 Oe wide centered at $g=2.28$. This line has the same general appearance in both the single crystal and the powdered material, i.e., it is isotropic. While this line appears to be associated with a surface deterioration, i.e., hydration, we have not been able to eliminate it completely even by using freshly annealed samples with no visible surface contamination. However, the relative amplitude of this line as compared to the broad line is much smaller in newly prepared samples. This narrower structured line persists at helium temperatures, hence we conclude that it is not due to the copper ions in the anhydrous crystal.

The electron spin resonance in single crystals of $CuSO_4$ was measured at 77°K and examined at temperatures in the vicinity of the Néel point. At 77°K, the broad line varies in intensity and width depending upon the orientation of the crystal with respect to the magnetic field. The relative intensities of the EPR signals are shown in Fig. 3. The broad line is characterized by the following parameters:

$$g_a=2.15\pm0.05, \qquad \Delta H_a=4.00\pm0.35 \text{ kOe},$$
$$g_b=2.2\pm0.1, \qquad \Delta H_b=6.7\pm0.70 \text{ kOe},$$
$$g_c=2.14\pm0.05, \qquad \Delta H_c=3.37\pm0.35 \text{ kOe},$$

where the subscripts a, b, and c refer to the crystal axes and ΔH is the width between the extrema of the derivative. The uncertainties in these g values are due mainly to the obscuring effect of the narrow line. The uncertainties in the linewidths are due to the breadth of the lines and consequent subjective error in locating the extrema.

Experiments were also conducted at varying temperatures with the applied field parallel to the a axis, the most favorable orientation for observation of AFMR. As the sample was cooled to 34.5°K and below, the following qualitative behavior was observed. The broad line starts increasing in width and shifts to lower field. The shape of the line in the vicinity of the Néel point does not depend on whether the temperature is decreasing or increasing in that the high-field side of the line distorts before the low-field side. This behavior is shown in Fig. 4. As the temperature was further decreased, the derivative of only the narrow line was visible. At slightly lower temperatures, a very broad, ill-defined signal was observed to shift to high fields as the temperature decreased. This latter behavior (shown in Fig. 5) was observed only a few times since it was very difficult to reproduce the slowly varying conditions necessary for its observation. Since quantitative information was not obtained, it was not felt worthwhile to continue measurements at this frequency.

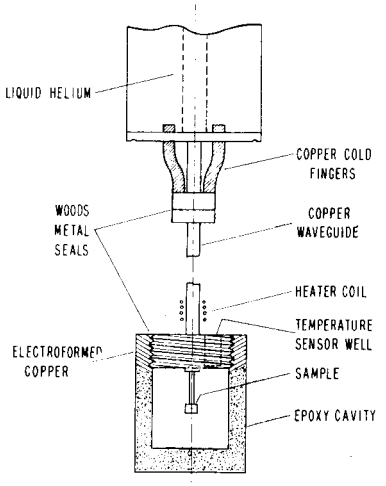

FIG. 2. Sketch of apparatus used to obtain variable temperatures. The tail of the Dewar into which this fits is about 1 in. diam and the cavity is about 12 in. below the bottom of the helium reservoir.

III. DISCUSSION

The observed resonance in the paramagnetic region is so broad that it could easily be mistaken for a baseline drift, especially when the b axis of the crystal is parallel to H_0. This extreme linewidth, coupled with the former difficulty in crystal growth, may account for the prior absence of published resonance data for $CuSO_4$.

Several different approaches were taken to explain this unusual width, but none were successful. A dipolar linewidth calculation using Van Vleck's formula,

$$h^2(\Delta\nu)^2=\tfrac{3}{4}S(S+1)g^4\beta^4\sum_R\left[\frac{(1-3\cos^2\theta)}{r_{jk}^3}\right]^2, \quad (1)$$

taking sums out to ions within 25 Å, yields a linewidth

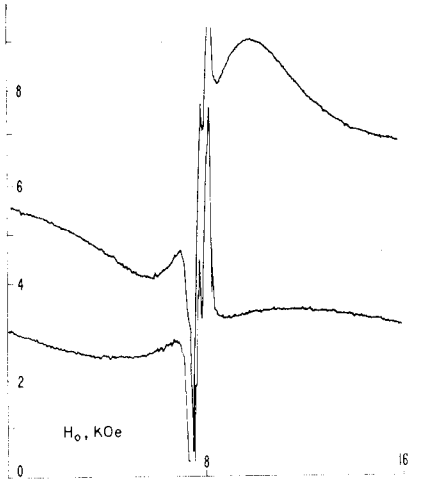

FIG. 3. Tracings of derivatives of the absorption in arbitrary units indicating the relative intensities and linewidths of the broad Cu^{2+} resonance. H_0 is parallel to the c axis of the $CuSO_4$ single crystal for the upper trace, and parallel to the b axis for the lower trace. The range of H_0 here is 0 to 16 kOe.

of 470 Oe, which is nearly an order of magnitude smaller than that which is observed. Since there are four inequivalent copper ion sites in the crystal, the possibility exists that the linewidth is due to an anisotropic g tensor whose principal axes are oriented differently for the four sites. Assuming the maximum difference possible in orientation and representative g values from other experiments, one might get a linewidth of 1400 Oe; however, these assumptions are not very realistic. The effects of an exchange term[9] for the paramagnetic region have also been considered, but this approach did not improve the situation. The possible role of exchange effects should be more apparent at higher frequencies and magnetic fields. A spectrometer is being constructed to utilize some available pulsed magnetic-field apparatus to examine some of these considerations.

[9] K. Yosida, Progr. Theoret. Phys. (Kyoto) **5**, 1047 (1950).

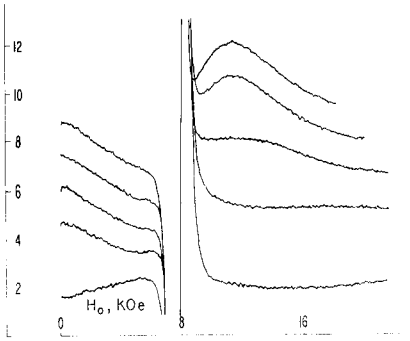

FIG. 4. Traces of derivatives of the Cu^{2+} resonance absorption (arbitrary units) for H_0 parallel to the a axis, which is the preferred spin direction in the antiferromagnetic state. The top trace was made at about 35°K. Each successively lower trace was made at a lower temperature than the preceding trace. The broad line broadens further, changes shape, and in the lower trace shifts toward lower fields.

To show that the behavior below the Néel temperature is qualitatively as one would expect, we review the resonance condition[10] for a biaxial antiferromagnet. When the applied field is parallel to the a axis, the resonance condition at $T=0$°K is

$$\omega^2/\gamma^2=\tfrac{1}{2}\{2H_0^2+2\lambda(K_1+K_2)\pm[16H_0^2\lambda(K_1+K_2)+4\lambda^2(K_1-K_2)^2]^{1/2}\}, \quad (2)$$

where ω is the circular frequency of the microwave radiation, γ is the gyromagnetic ratio, H_0 is the externally applied field, λ is the exchange constant, and K_1 and K_2 are the anisotropy constants. This is to be compared with the simpler uniaxial resonance condition,

$$\omega/\gamma=(2\lambda K)^{1/2}\pm H_0. \quad (3)$$

The essential differences are: (1) there is an energy gap between the two branches at $H_0=0$ in the biaxial case,

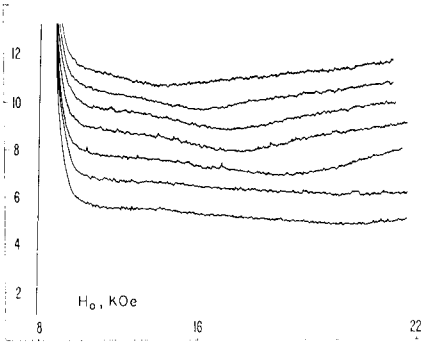

FIG. 5. Traces of absorption derivatives (arbitrary units) for same orientation as in Fig. 4. Successively lower traces are again at decreasing temperatures. A broad, rather ill-defined signal is seen moving to higher fields at successively lower temperatures. The nearly vertical line on the left is the positive going portion of the derivative of the extraneous narrow line.

[10] T. Nagamiya, K. Yosida, and R. Kubo, Adv. Phys. **4**, 1 (1955).

and (2) the branches are not linear functions of the field in the biaxial case. Upon cooling a biaxial antiferromagnet from above the Néel temperature and observing the resonance at a fixed frequency, one would expect to see the resonance first shift toward zero field, then disappear completely due to the presence of the gap, then reappear at zero field and shift in the high-field direction to a value determined by $(2\lambda K_1)$.

The above description seems to fit the qualitative behavior of the resonance observed in $CuSO_4$ below the Néel point. Since the linewidth, ΔH, may vary[11] in the antiferromagnetic region as

$$\Delta H=\frac{2H_A(0)}{n}\left\{\frac{1}{B_s(T/T_N)}-B_s\left(\frac{T}{T_N}\right)\right\}, \qquad (4)$$

where $H_A(0)$ is the anisotropy field, n the number of nearest neighbors, and B the Brillouin function, the temperature range over which we have attempted observations is the least favorable for the observation of AFMR. This temperature range is a consequence of the relatively low frequency to which we have been restricted. Experiments have been started for 70 GHz, and planned for 140 GHz. The use of the higher frequencies will permit one to work at lower temperatures, utilize the full range of the magnet, and hopefully provide an accurate base for extrapolation to $T=0$.

From the susceptibility data, we calculate the exchange field in $CuSO_4$ to be 2.5×10^5 Oe. Reasonable estimates of the temperature interval over which resonance was possibly observed indicate that the zero-field resonance frequency for the lower mode is a minimum of 112 GHz, which would correspond to an anisotropy field H_A, of at least 5 kOe.

[11] F. M. Johnson and A. H. Nethercot, Phys. Rev. **114**, 705 (1959).

ACKNOWLEDGMENTS

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