CC/NUMBER 42
OCTOBER 15, 1990

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Bleaney B & Bowers K D. Anomalous paramagnetism of copper acetate.
Proc. Roy. Soc. London Ser. A 214:451-65, 1952.
[Clarendon Laboratory, University of Oxford, England]

This paper reported electron spin resonance measurements on copper acetate, showing that it contained pairs of cupric ions interacting through antiferromagnetic exchange forces, with a ground singlet and an excited triplet state, but no cooperative phase. The novel hyperfine interaction, seven lines in the form of a "Christmas tree," confirmed the presence of such pairs of ions. [The *SCI*® indicates that this paper has been cited in over 845 publications.]

Anomalous Paramagnetism

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May 3, 1990

Our attention to this compound was attracted by the unusual results of B.C. Guha.[1] In a survey of magnetic anisotropy in many crystals of iron group compounds, he discovered that the susceptibility of copper acetate monohydrate passed through a maximum at about room temperature and then decreased so rapidly that it should approach zero at about 50 K. There was no sharp transition to an antiferromagnetic phase, and typical Néel temperatures of copper compounds of comparable dilution lie at liquid helium temperatures.

Single crystals were grown from aqueous solution by my colleague Klaus Bowers, recently retired (February 1990) from his position as a vice president of Bell Laboratories, US. Together we found that the paramagnetic resonance spectrum was quite different from that of normal copper compounds. At 90 K a line appeared in zero magnetic field at 3 centimetre wavelength; this disappeared at 20 K, but was stronger at room temperature. It therefore must arise from an excited level, and further measurements showed that this state had an apparent electron spin $S = 1$, with a small initial splitting, and an energy ca. 300 wave numbers greater than the ground state, a nonmagnetic singlet.

The presence of interacting pairs of copper ions was confirmed by the novel hyperfine interaction. Instead of a set of $(2I + 1) = 4$ lines of equal intensity expected for the nuclear spin $I = 3/2$ of each copper isotope, a set of seven lines was resolved at the lowest temperatures, corresponding to $[2(2I) + 1] = 7$ for two copper ions. Furthermore, the intensities were not equal, but had the form of a "Christmas tree" with ratios 1:2:3:4:3:2:1, corresponding to the number of ways in which a given sum $(m_1 + m_2)$ could be formed from the components of the two nuclear spins, each 3/2.

The hypothesis of two interacting copper ions was soon independently confirmed by X-ray crystallography[2] that gave an internuclear distance of only 0.264 nm. The electron paramagnetic resonance spectrum was also reported by Kumagai[3] and colleagues, followed by that of a crystal slightly diluted with zinc.[4]

Numerous examples of other copper dimeric compounds have been reported over the years (no less than 25 references in 1988). Our formula for the magnetic susceptibility is generally quoted, together with the unusual hyperfine structure. A cubic copper tetramer with four interacting ions has been measured[5] using electron spin resonance; it has $[2(4I) + 1] = 13$ hyperfine lines.

1. **Guha B C.** Magnetic properties of some paramagnetic crystals at low temperatures. *Proc. Roy. Soc. London Ser. A* 206:353-73, 1951. (Cited 105 times.)
2. **Van Niekerk J N & Schoenig F R L.** A new type of copper complex as found in the crystal structure of cupric acetate, $Cu_2(CH_3COO)_4.2H_2O$. *Acta Crystallogr.* 6:227-32, 1953. (Cited 530 times.)
3. **Kumagai H, Abe H & Shimada J.** Anomalous magnetic resonance absorption of copper acetate at 10 kMc/sec. *Phys. Rev.* 87:385-7, 1952. (Cited 5 times.)
4. **Kokoszka G F, Allen H C & Gordon G.** Electron paramagnetic resonance spectra of zinc-doped copper acetate monohydrate. *J. Chem. Phys.* 42:3693-7, 1965. (Cited 75 times.)
5. **Rubins R S, Black T D & Barak J.** Zeeman, hyperfine and magnetic dipolar effects on the EPR spectrum of a cubic copper tetramer. *J. Chem. Phys.* 85:3770-8, 1986.

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