

PARAMAGNETIC RESONANCE IN SOME CUPRIC SALTS

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1. INTRODUCTION

By reason of their interesting magnetic properties, the cupric salts have been studied for their paramagnetic resonance spectra in some detail by many workers. In fact, of the ions of the iron group of elements, Cu^{2+} , with electronic configuration $3d^9$ occurs with spin $S = \frac{1}{2}$ only, when the orbital momentum is quenched and is therefore the simplest. The quenching of the orbital moment takes place in all the salts of copper as revealed by the extensive susceptibility data available. In order to explain the magnetic properties of the cupric salts, the predominance of exchange forces between the ions is invoked in addition to various types of internal electric fields which contribute to the quenching of the orbital moment. The general character of the results show that these two effects predominate but a quantitative understanding of the many interesting features exhibited by the cupric salts await the collection of more data. The study of the paramagnetic resonance spectra of the salts of copper affords a better understanding of the nature of magnetic and electrical interactions in crystals. In the present work the study has been extended to eleven more cupric salts.

2. EXPERIMENTAL

The experimental set up used in the present study is of the conventional type. It consisted of a 3 cm. Klystron (723 A/B) operated from batteries to ensure high stability of the output. Power from the Klystron was fed by means of a long wave-guide to a cavity resonator, resonating in the H_1 mode, between the polepieces of an electromagnet. The electromagnet was capable of maintaining a field of 4,500 oersteds in a gap of $1\frac{1}{2}$ " and cross-section 3" square. The output of the cavity resonator was fed to a 1 N 23 crystal rectifier and the rectified current was measured by means of a galvanometer. The galvanometer deflections were reduced to absorption in arbitrary units by means of the familiar formula

$$\sqrt{\frac{\delta_0}{\delta}} - 1 = \text{absorption,}$$

where δ_0 is the deflection of the galvanometer when the cavity is tuned to resonance and the magnetic field is far higher than the resonance value. δ is the deflection at any particular magnetic field at which it is desired to know the relative paramagnetic absorption. The magnetic field was found by using manganous salts whose g values are very close to that of a free electron. In the case of single crystals, the crystals were mounted on the lower choke of the cavity, the choke being capable of rotation about the cavity axis through known angles. In the case of deliquescent crystals it is necessary to imbed the crystals in paraffin wax after proper desiccation, because even small amounts of water will lower the cavity Q enormously. Paraffin wax has low loss at these frequencies and the dielectric constant is also not large and it has a low melting point. Hence it is highly suitable for imbedding the crystals when necessary.

3. SUBSTANCES INVESTIGATED

Paramagnetic resonance was sought in the following cupric salts, cupric nitrate, cupric ammino-nitrate, cupric ammonium chloride, basic fluoride of copper, cupric acetate, azurite, cupric carbonate, cupric cyanide and cupric oxide.

TABLE I

| Substance | g . | $\Delta H_{\frac{1}{2}}$ | $[\Delta H^2]_{AV}^{\frac{1}{2}}$ | $[\Delta H^4]_{AV}^{\frac{1}{4}}$ | Ratio | Remarks |
|-----------------------------|-------|--------------------------|-----------------------------------|-----------------------------------|-------|--|
| Cupric ammonium chloride | 2.25 | | 220 | 290 | 1.38 | Anisotropy measurements in single crystals have been made |
| Cupric nitrate | 2.2 | 390 | 215 | 383 | 1.78 | Slight asymmetry in absorption |
| Cupric ammino nitrate | 2.1 | 320 | 215 | 303 | 1.41 | Anisotropy measurements also made |
| Cupric fluoride, basic | 2.08 | 410 | 215 | 370 | 1.71 | Asymmetric absorption |
| Cupric acetate } azurite | | | | | | Do not show any absorption in the magnetic field range 0-4500 oersteds |
| Cupric carbonate | | | | | | |
| Cupric phosphate | | | | | | |
| Cupric arsenate | | | | | | |
| Cupric cyanide | | | | | | |
| Cupric oxide | | | | | | |

Of these the acetate, azurite, carbonate, phosphate, arsenate, cyanide and oxide did not show any paramagnetic resonance absorption in the range of magnetic fields (0-4,500 oersteds) employed in this investigation. The other compounds showed easily detectable adsorption. The g values, root mean square moment, fourth root of mean fourth moment, their ratios and half-breadths are given in Table I. Only fairly narrow lines are found and it is usual to ascribe the effect to the influence of exchange interaction. The basic fluoride and the nitrate show asymmetric absorption peaks. Another smaller line seems to occur on the lower magnetic field side of the main resonance peak, in these substances. However, it must be remembered that most paramagnetic resonance curves are not truly symmetrical. There is always a small amount of absorption persisting even far below resonance some times up to zero field. This is perhaps due to some non-resonant process. As remarked later, only the data pertaining to the high magnetic field side of the resonance were used in calculating the second and fourth moments. In the case of the acetate, Gordy and Lancaster (1951), Bleaney and Bowers (1951) have reported a field dependent g value and structure of the resonance spectrum by working at frequencies up to 50,000 Mc/s. The case of the oxide seemed of interest at first as the first sample used showed broad resonance effects like those of some antiferromagnetic substances. However, other samples from various sources and degrees of purity were tried but they failed to show any noticeable effect. The nature of the impurity in the first case is not known. As already remarked, the basic fluoride exhibits some structure in its resonance line. The curve for the basic fluoride is given in Fig. 1.

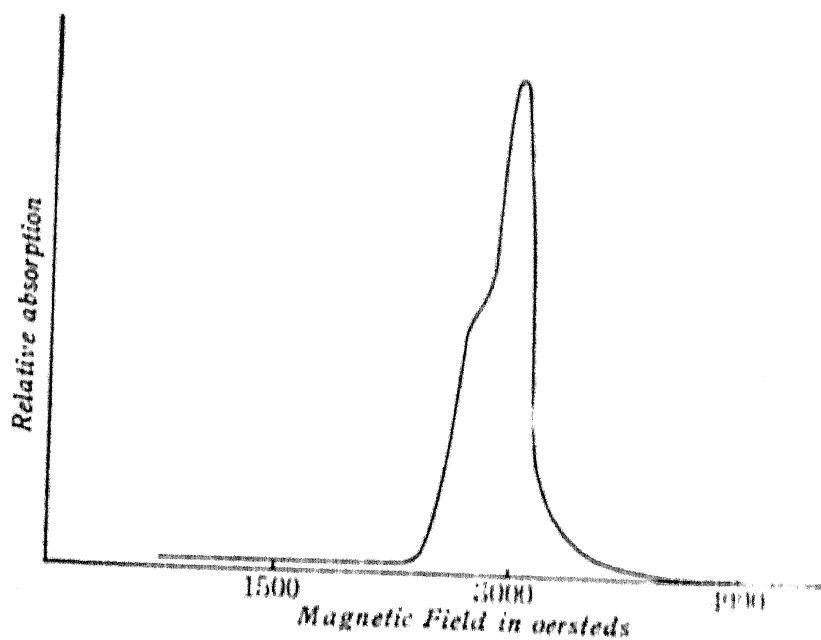


FIG. 1. Resonance curve for the Basic fluoride of Copper

4. ANISOTROPY OF g FACTOR AND LINE SHAPE

Single crystals of cupric ammonium chloride and cupric ammonium nitrate were studied in different orientations. Like other similar salts, these also show variation in g factor and line shape with orientation. The results are presented in Table II and Fig. 2 for line shape parameters and g factor respectively. In calculating the line shape parameters $[\Delta H^2]_{AV}^{\frac{1}{2}}$ and $[\Delta H^4]_{AV}^{\frac{1}{4}}$ the data pertaining to the higher magnetic field side of the resonance curve was alone used on the assumption that side of the

TABLE II

Anisotropy data on $CuCl_2 \cdot 2NH_4Cl$:— c -axis lying perpendicular to the cavity axis

| Angle | $[\Delta H^2]_{AV}^{\frac{1}{2}}$ | $[\Delta H^4]_{AV}^{\frac{1}{4}}$ | Ratio | g . |
|---------|-----------------------------------|-----------------------------------|-------|-------|
| 0° .. | 220 | 290 | 1.38 | 2.44 |
| 30° .. | 174 | 250 | 1.48 | 2.40 |
| 60° .. | 202 | 246 | 1.22 | 2.34 |
| 90° .. | 147 | 179 | 1.22 | 2.30 |
| 120° .. | 125 | 198 | 1.59 | 2.33 |
| 150° .. | 215 | 280 | 1.34 | 2.38 |
| 180° .. | 128 | 188 | 1.43 | 2.40 |

resonance curve will be free of complicating factors due to non-resonant absorption and structure due to unresolved lines. The lower side will contribute very much more particularly to the value of the fourth moment as the absorption might sometimes extend upto zero field. Of the copper compounds the chlorides are of interest because the chlorine atoms with their low energy d orbitals give scope for the exchange effects to predominate. The data for cupric ammonium chloride are given in curve (a) (Fig. 2) and in Table II. The variations with orientation when the crystal is rotated in the a - c plane are pronounced and a minimum exists at 120°. This line is very sharp and the exchange interaction seems to contribute a large amount to the fourth moment, whereas at neighbouring angles the line is quite broad and seems to be gaussian. This may be due to anisotropy of exchange interaction. Similar data are reported for the case of copper ammonium selenate by Bleaney, Penrose and Plumpton (1949). About other directions the anisotropy is not marked and the resonance lines are comparatively

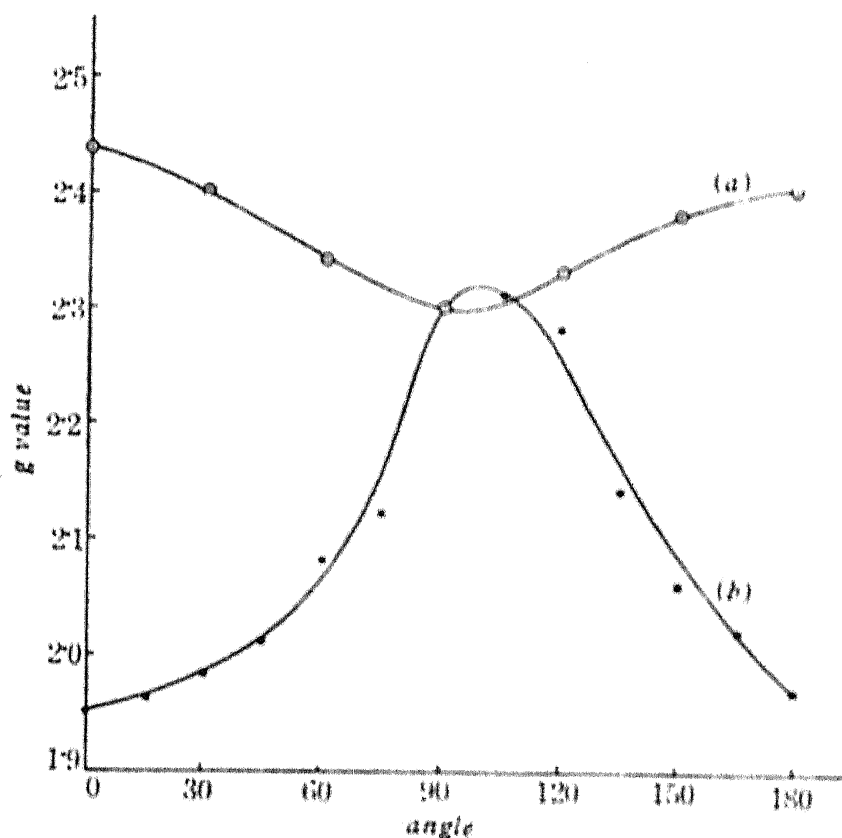


FIG. 2. (a) Variation of g factor with orientation for cupric ammonium chloride.
(b) Variation of g factor with orientation for cupric amino nitrate.

weak and broad. In these directions the g value is about 2.3. Some measurements on the potassium and ammonium chlorides of copper have been reported by Fujimoto and Itoh (1951) working in the 3,000 MC region. The g values given by them for the potassium salt range from 2.06 to 2.18. A g value determination in the case of powdered cupric ammonium chloride has been made by Gordy and Lancaster (1951) and their value is 2.21. The values in the present determination lie mostly about 2.2 to 2.3 but with 2.44 in some directions. The g values are thus higher in the ammonium than in the potassium salt.

Cupric amino-nitrate (monoclinic, prism about c -axis) was also investigated for anisotropy about three directions. It was found that sharp resonances could be obtained when the long or the c -axis of the crystal was along the magnetic field and the resonance became broader and weaker as the crystal was turned away from this position. The g value also varied with direction and the variation is presented in curve (b) in Fig. 2. When the crystal was mounted with the c -axis vertical, the resonances were weak and there was no variation in the g value. The g value in this case was found

to be 2.1 as contrasted with values ranging from 1.9 to 2.1 about a direction perpendicular to the planes containing the *c*-axis.

Several substances do not show paramagnetic resonance. One of the objects of this investigation was to find whether there was any compound intermediate between those which show paramagnetic resonance strongly and those which do not show any at all. None of the substances falls into this category. The following may be the reasons for the unobservability of the effect.

1. Relaxation times are too small or too large.
2. Magnetic interaction is very large so that the line is spread out.
3. Sufficiently low energy paths are not available for the electrons to contribute effectively to exchange interactions leading to sharpening of the resonance. It is difficult to say which or what combination of these operate in any particular instance. So further investigations of these salts at low temperatures are needed.

We wish to record our gratitude to Professor R. S. Krishnan for his kind interest and encouragement.

5. SUMMARY

Paramagnetic resonance absorption of 3 cm. wave in eleven copper salts has been studied. Of these four show paramagnetic absorption; *g* factors and half-widths obtained are given. Single crystals of cupric ammonium chloride and cupric ammino-nitrate have been studied for anisotropy in *g* factor and line-shape parameters. Results regarding cupric ammonium chloride indicate that exchange interaction may not be isotropic.

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