

Ligand hyperfine spectra of  $\text{Cu}^{2+}$  in AgClW. B. Paul,\* S.-E. Wang,<sup>†</sup> and L. G. Rowan*Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27514*

(Received 1 July 1985)

Electron-paramagnetic-resonance studies of crystals of AgCl doped with  $\text{Cu}^{2+}$  show a rich hyperfine structure. The hyperfine structure is a sum of the hyperfine interaction from the Cu nucleus and the superhyperfine interaction with the four Cl ligand nuclei in the plane perpendicular to the  $z$  axis of the crystal. The superhyperfine constants arising from the wave function transferred to the  $\text{Cu}^{2+}$  ( $3d^9$ ) hole, through the bonding with the Cl ions in the lattice, are found to be  $A = 20$  gauss and  $B = 3$  gauss.

## I. INTRODUCTION

Copper-doped silver chloride has been used in the study of the photographic process in silver chloride. In the  $\text{Cu}^{2+}$  state, the copper ion will release a hole upon blue-light irradiation. The hole then can be self-trapped around an  $\text{Ag}^+$  ion.<sup>1</sup> Electron paramagnetic resonance (EPR) is used to identify the  $\text{Cu}^{2+}$  center and the  $\text{Ag}^{2+}$  center and to monitor their concentrations upon irradiation and temperature

change. We have observed some previously unresolved ligand hyperfine structure on the  $\text{Cu}^{2+}$  EPR lines, which has allowed us to evaluate bonding of the copper ion in the silver chloride lattice.

## II. EXPERIMENTAL PROCEDURES

EPR experiments were performed on a single crystal of AgCl from a boule grown by Mr. C. B. Childs of the

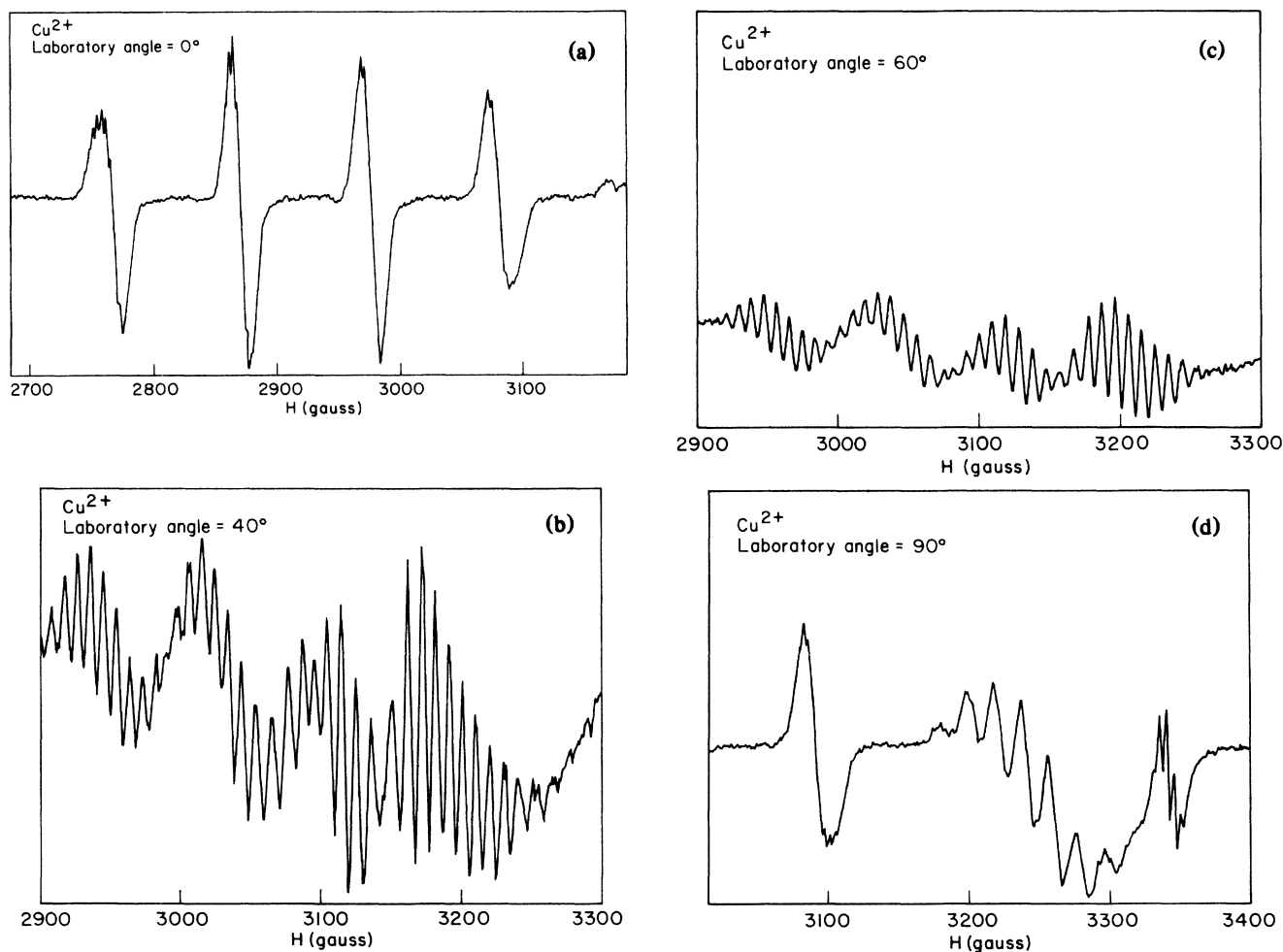


FIG. 1. Experimental EPR spectra of  $\text{Cu}^{2+}$  in AgCl. The graphs show the derivative of the power absorption. (a)  $H$  field along the  $\langle 001 \rangle$  axis. (b)  $H$  field  $40^\circ$  to the  $\langle 001 \rangle$  axis. (c)  $H$  field  $60^\circ$  to the  $\langle 001 \rangle$  axis. (d)  $H$  field  $90^\circ$  to the  $\langle 001 \rangle$  axis. [At about 3100 gauss is shown the lowest hyperfine line of the spectra shown in (a).] Also shown at about 3340 is the spectra of the self-trapped hole in AgCl.

Department of Physics and Astronomy, University of North Carolina, prepared in the form of a rectangular parallelepiped with a  $\langle 110 \rangle$  axis, and doped by solid-state diffusion with approximately 100 ppm of copper. The crystal was annealed in 1 atm of chlorine at 325 °C to convert a portion of the cuprous ion  $\text{Cu}^+$  to cupric  $\text{Cu}^{2+}$ , and then cooled slowly to room temperature. After removal from the capsule, the crystal was quickly cooled to liquid-nitrogen temperatures in order not to lose all of the  $\text{Cu}^{2+}$ . The EPR experiments were performed at temperatures of from 10–40 K on a Bruker ER200tt spectrometer. Figure 1 shows typical examples of the EPR spectra. Note that for the magnetic field along a  $\langle 100 \rangle$  direction (laboratory angle of 0°), the superhyperfine splitting from the ligand Cl ions is resolved.

This splitting is not resolved if the crystal has too many strains.

### III. EPR DISCUSSION

The ground state of the  $\text{Cu}^{2+}$  ion has a  $3d^9$  electronic configuration, which is a hole in a closed  $3d^{10}$  shell. In an octahedral crystal field, the  $\Gamma_3$  doublet of the orbital  $D$  state is lowest. The octahedral symmetry is reduced to tetragonal symmetry by a static Jahn-Teller distortion, with distortions along the  $\langle 100 \rangle$  directions.

The EPR spectra of the  $\text{Cu}^{2+}$  ion can be represented by the following axial spin Hamiltonian:<sup>2</sup>

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A I_z S_z + B(I_x S_x + I_y S_y) + Q[I_z^2 - \frac{1}{3}I(I+1)] \\ + A_1 I_x^1 S_x + B_1 I_y^1 S_y + B_1 I_z^1 S_z + B_1 I_x^2 S_x + A_1 I_y^2 S_y + B_1 I_z^2 S_z + B_2 I_x^3 S_x + B_2 I_y^3 S_y + A_2 I_z^3 S_z \\ + A_1 I_x^4 S_x + B_1 I_y^4 S_y + B_1 I_z^4 S_z + B_1 I_x^5 S_x + A_1 I_y^5 S_y + B_1 I_z^5 S_z + B_2 I_x^6 S_x + B_2 I_y^6 S_y + A_2 I_z^6 S_z,$$

where the electron spin  $S = \frac{1}{2}$ , the Cu nuclear spin  $I = \frac{3}{2}$ , the Cl nuclear spins along the  $+X$  and  $-X$  axes are  $I^1$  and  $I^4$ , respectively, the Cl nuclear spins along the  $+Y$  and  $-Y$  axes are  $I^2$  and  $I^5$ , respectively, and the Cl nuclear spins along the  $+Z$  and  $-Z$  axes are  $I^3$  and  $I^6$ , respectively. The Cl nuclear spin is  $\frac{3}{2}$ .

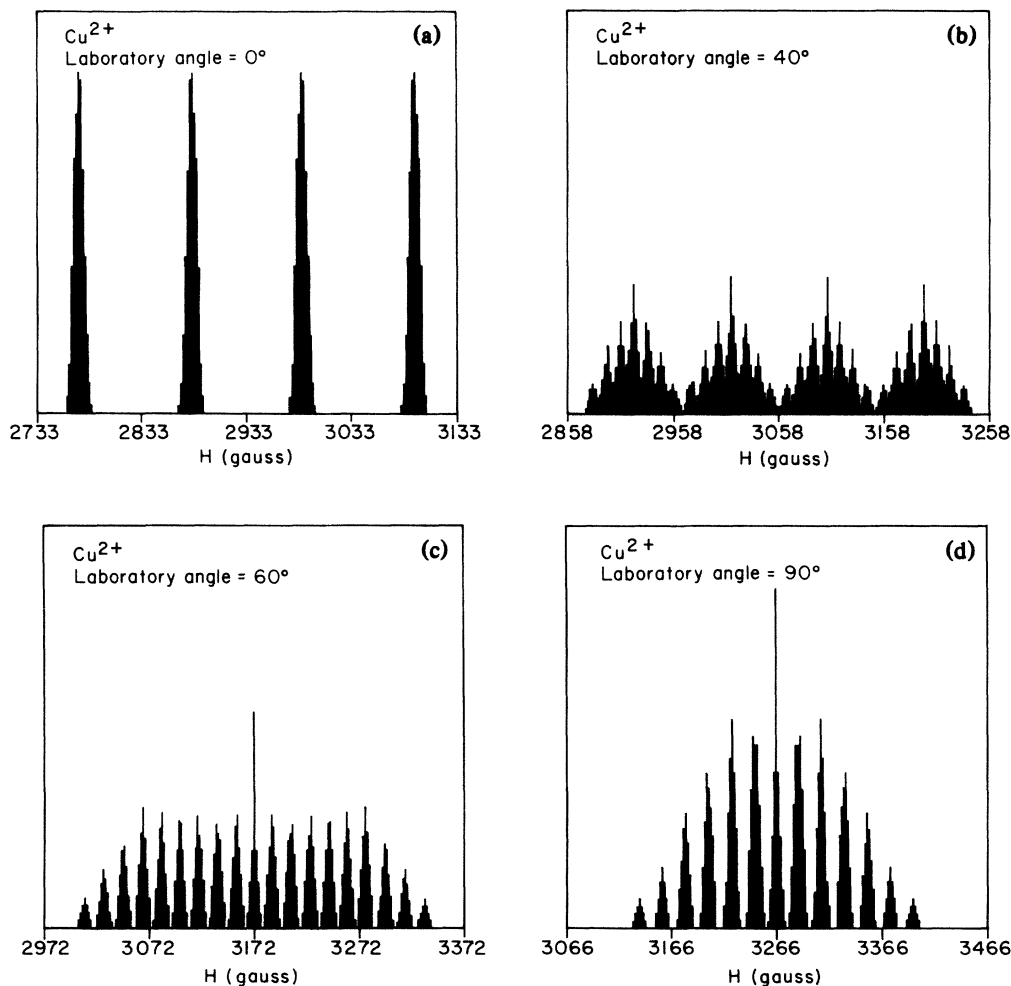


FIG. 2. Calculated EPR hyperfine spectra of  $\text{Cu}^{2+}$  in AgCl. The graphs show the absorption spectra of the hyperfine lines. (a)  $H$  along the  $\langle 001 \rangle$  axis. (b)  $H$  field 40° to the  $\langle 001 \rangle$  axis. (c)  $H$  field 60° to the  $\langle 001 \rangle$  axis. (d)  $H$  field 90° to the  $\langle 001 \rangle$  axis.

The hyperfine interaction with axial symmetry is defined by a constant  $A$  for the hyperfine coupling along the longitudinal axis and a constant  $B$  for the hyperfine coupling along the transverse axes. Therefore, in the above equation,  $A$  and  $B$  are the hyperfine coupling constants between the electron spin and Cu nuclear spin along the  $Z$  axis and the  $X$  and  $Y$  axes, respectively.  $Q$  is the quadrupole interaction of the Cu nucleus with the electric field gradient.

In the hyperfine interaction between the electron spin and the Cl nuclei of the lattice, the following system of notation is used. The hyperfine constant  $A$  is used for the interaction along the bond axis between the electron and a particular Cl nucleus and the  $B$  hyperfine constant is used for the interaction transverse to the bonding axis of the particular Cl nucleus of the lattice. For example, the interaction with the Cl nucleus along the  $+X$  axis is written as  $AI_xS_x + BI_yS_y + BI_zS_z$ . The interaction with the Cl nucleus along the  $+Y$  axis is written as  $AI_yS_y + BI_zS_z + BI_xS_x$ . Similar terms are written for Cl nuclei along the  $-X$  and  $-Y$  axes.

The interaction with the Cl nuclei along the  $Z$  axes is written in the same manner, but the  $A$  and  $B$  constants for these nuclei are of different values than the  $A$  and  $B$  values for the nuclei along the  $X$  and  $Y$  axes. Therefore, the  $A$  and  $B$  constants for the  $X$  and  $Y$  Cl nuclei are called  $A_1$  and  $B_1$ . The  $Z$  axes Cl nuclei are given  $A_z$  and  $B_z$ .

From the spin Hamiltonian shown above, the hyperfine spectra were calculated on an Apple IIe computer. Figure 2 shows the computer calculations. These are "stick" diagrams of the absorption spectra. The derivative of Fig. 2 should be compared with Fig. 1. The values of the various constants are given in Table I. The observation of the superhyperfine coupling with the ligand Cl ion for the laboratory angle of 0, or along the  $\langle 100 \rangle$  axis, allows us to determine the  $B^1$  constant [see Fig. 1(a)].

The wave function of the ground state under a Jahn-Teller distortion is described as follows:

$$\Psi = \cos(\frac{1}{2}\phi)|x^2 - y^2\rangle + \sin(\frac{1}{2}\phi)|3z^2 - r^2\rangle, \quad (1)$$

where  $\phi$  is the mixing parameter of the two wave functions. The equations for the  $g$  values under a rhombic distortion are given by Bleaney, Bowers, and Pryce<sup>3</sup> as

$$\begin{aligned} g_x &= 2.002 - (2\lambda/\Delta)[\cos(\frac{1}{2}\phi) - \sqrt{3}\sin(\frac{1}{2}\phi)]^2, \\ g_y &= 2.002 - (2\lambda/\Delta)[\cos(\frac{1}{2}\phi) + \sqrt{3}\sin(\frac{1}{2}\phi)]^2, \\ g_z &= 2.002 - (8\lambda/\Delta)[\cos(\frac{1}{2}\phi)]^2, \end{aligned} \quad (2)$$

TABLE I.  $g$  values and hyperfine constants for  $\text{Cu}^{+2}$  in  $\text{AgCl}$ . The units of the hyperfine constants are  $10^{-4} \text{ cm}^{-1}$ .

|                         | Cu          |              | Cl              |  |
|-------------------------|-------------|--------------|-----------------|--|
| $g_{\parallel} = 2.302$ | $A = 115.0$ | $A_1 = 21.0$ | $A_z \approx 0$ |  |
| $g_{\perp} = 2.067$     | $B = 41.5$  | $B_1 = 2.0$  | $B_z \approx 0$ |  |

where  $\lambda$  is the spin-orbit parameter and  $\Delta$  is the crystal-field splitting. The best fit of the  $g$  values is obtained at  $-\lambda/\Delta = 0.035$ ,  $\phi = 0^\circ$ . This implies that the Jahn-Teller distorted site wave function is predominately  $|x^2 - y^2\rangle$ . Thus the Cl molecular orbitals that couple with the electron include only the chloride ions in the  $x$ - $y$  plane. Hence we conclude that  $A_z$  and  $B_z$  should be zero, as shown in Table I.

The superhyperfine coupling of the Cl ions in the  $xy$  plane will lead to an  $A$  coefficient for the  $I_xS_x$  term for those ions along the  $x$  axes and a  $B$  coefficient for the  $I_yS_y$  and the  $I_zS_z$  terms of the spin-ligand interaction. This is also true for the ions along the  $y$  axes. Thus we obtain the spin-ligand interaction shown. The  $A$  and  $B$  values are given by  $A = A_s + 2(A_d + A_\sigma)$  and  $B = A_s - (A_d + A_\sigma)$ , where

$$\begin{aligned} A_s &= \frac{16}{3}\pi g_n \beta \beta_n |\psi(0)|_{\text{Cl}_s}^2 f_s, \\ A_\sigma &= \frac{4}{3}g_n \beta \beta_n \langle r^{-3} \rangle_{\text{Cl}_p} f_\sigma, \\ A_d &= g_e g_n \beta \beta_n R^{-3}. \end{aligned} \quad (3)$$

Using the values given by Schoemaker<sup>4</sup> for the above quantities, the amount of  $s$  and  $p$  character at the ligand ions on the  $xy$  plane are estimated to be 2% and 12%, respectively.

#### ACKNOWLEDGMENTS

This research was supported by the National Science Foundation (Solid State Chemistry Program), under Grant No. DMR-85-01059.

\*Present address: RCA, Princeton, NJ 08540.

†Present address: Institute of Photographic Chemistry, Academia Sinica, Bei Sha Tan, De Wai, Beijing, People's Republic of China.

<sup>1</sup>E. Laredo, W. B. Paul, L. G. Rowan, and L. Slifkin, Phys. Rev. B **27**, 2470 (1983).

<sup>2</sup>G. E. Pake and T. L. Estle, *The Physical Principles of Electron Paramagnetic Resonance*, 2nd ed. (Benjamin, New York, 1973).

<sup>3</sup>B. Bleaney, K. A. Bowers, and M. H. L. Pryce, Proc. R. Soc. London, Ser. A **228**, 166 (1955).

<sup>4</sup>D. Schoemaker, Phys. Rev. **149**, 693 (1966).