



Electron paramagnetic resonance of anilinium tetrachlorocuprate and ethylenediammonium tetrachlorocuprate
by Richard Allen Bergstrom

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Physics
Montana State University
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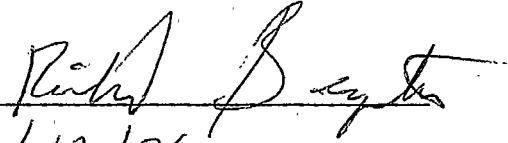
Abstract:

High and low field g-values and the angular and temperature dependence of the linewidths for both anilinium tetrachlorocuprate and ethylenediammonium tetrachlorocuprate were taken on a Varian E-3 spectrometer. The spin-orbit coupling constant λ was shown to lie between -200cm^{-1} and -600cm^{-1} . The data taken on the temperature dependence of linewidths was used as a further test of the model proposed by Zaspel which has been shown to agree with data taken on other 2-dimensional compounds.

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TETRACHLOROCUPRATE

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RICHARD ALLEN BERGSTROM

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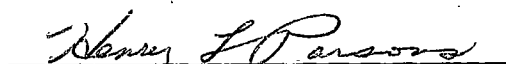
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Approved:


Chairperson, Graduate Committee


Head, Major Department


Graduate Dean

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ABSTRACT

High and low field g-values and the angular and temperature dependence of the linewidths for both anilinium tetrachlorocuprate and ethylenediammonium tetrachlorocuprate were taken on a Varian E-3 spectrometer. The spin-orbit coupling constant λ was shown to lie between -200cm^{-1} and -600cm^{-1} . The data taken on the temperature dependence of linewidths was used as a further test of the model proposed by Zaspel which has been shown to agree with data taken on other 2-dimensional compounds.

I. INTRODUCTION

The main information gained from electron paramagnetic resonance (EPR) spectra is an evaluation of the various terms in the spin hamiltonian. Although the crystal field and spin-orbit energies are independently evaluated from optical spectra, they can be correlated with EPR data. The most informative EPR data will be that which is recorded at more than one temperature, frequency, and microwave power. EPR data can be used to identify an unknown transition metal ion or lattice defect. It can distinguish between several valence sites of the same ion, and it can also frequently identify the lattice site and symmetry of the paramagnetic species. Much information can be extracted about diffusion constants and correlation times, and sometimes relaxation time data will detect long range effects.¹

In this thesis, the angular and temperature dependence of the g values for the Cu^{++} ion in anilinium tetrachlorocuprate (ALTC) and ethylenediammonium tetrachlorocuprate (EDTC) were measured. ALTC is a quasi-2-dimensional layered structure. There is a wide interest in structures of this type because they can be used to approximate a plane of magnetic atomic dipoles. For example, theoretically there should be no long range ordering in 2-dimensional crystal structures, but experiments have indicated

that some ordering does indeed exist.² Both ALTC and EDTC will be eventually studied by other techniques to see if there is any long range ordering. Also, the exchange energies can be estimated by comparison of the exchange-narrowed linewidths with calculated second moment widths, and other interesting information comes from the temperature dependence of the linewidths.

Once the g values and crystal field splitting are known, the spin-orbit coupling constant λ can be found. We will see that because of the structure, we will only be able to set limits on the values. The structure of EDTC is unknown but comparison of the g values indicates that it is much like the structure of ALTC.

Paramagnetic resonance is the spectroscopy of magnetic dipole transitions induced by an oscillating magnetic field between the energy levels of a system of paramagnets. The magnetic dipoles with which we are concerned are those on the atomic level. An atom may have a magnetic moment owing to nuclear spin, electron spin, or electron orbital angular momentum, but because of their greater order of magnitude, only that due to electron spin S and electron orbital angular momentum L will be considered. Resonance occurs in a static magnetic field H_0 when a small perturbing time dependent magnetic field H_1 causes transitions between the different atomic energy levels created by H_0 or quantum mechanically:

$$E = -\vec{\mu} \cdot \vec{H}_0$$

$$\Delta E = h\nu = g\beta H_0$$

where h is Planck's constant, ν is the frequency of H_1 and $\vec{\mu}$ is the magnetic moment which is $\vec{\mu} = -\beta(\vec{L} + g_e\vec{S})$ where β is the Bohr magneton, and g_e is the free electron g value. For a critical treatment of non-spherical symmetry, such as in a solid, it is convenient to define a g factor which relates the angular momentum to the dipole moment in general.

To measure the g values at resonance, one must have a source for the H_0 field and an r.f. source for the time-dependent H_1 field. The Varian E-3 EPR spectrometer provides both. The frequency of the H_1 field is kept constant and the H_0 field is slowly varied, so slowly that it can be considered constant compared to H_1 , through resonance. At resonance, energy is absorbed by the crystal from the r.f. field. The spectrometer will detect this energy absorption and because of phase detection will plot the derivative of the absorption with respect to the field H_0 . This curve is then used to compute the g values for the Cu^{++} ion.

II. THEORY

The Cu^{++} ion has a $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$ configuration in the ground state so we can consider the collective motion of the nine 3d electrons as a hole in a $3d^1$ configuration.

First we consider the perturbation produced in the crystal field due to cubic and tetragonal symmetry. Then we include the effect of spin-orbit coupling, and finally add the perturbation of the external field H_0 .

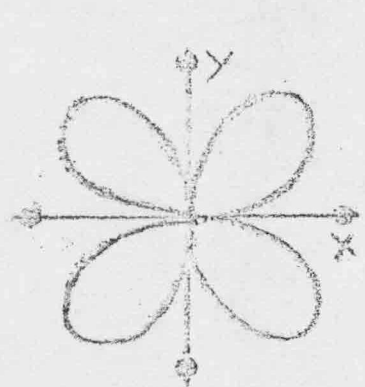
The free ion orbital can be represented by $\psi_l^{m_l}$. This is an eigenfunction of L_z . For a free ion, the hamiltonian will be invariant under rotation about the Z axis, and so it will commute with L_z . But for an ion in the crystal lattice, there isn't spherical symmetry so that this commutation no longer occurs. In the lower symmetry we can choose the proper linear combinations of the orbitals using a method developed by Bethe.³ This results in a change from running to standing waves and is done by forming:

$$\Psi_l^{\pm m_l} = \psi_l^{m_l} \pm \psi_l^{-m_l}$$

Then for a $3d^1$ state we have $\psi_l^{m_l} \pm \psi_l^{-m_l}$ (Fig. 1).

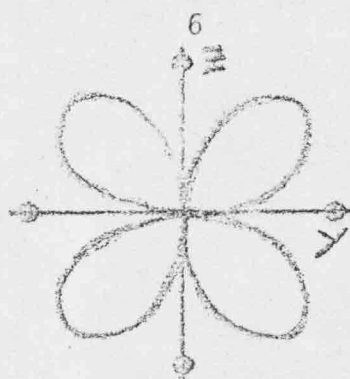
FIGURE I

Diagrams of d - electron orbitals at a site of octahedral symmetry in relation to six equivalent point charges, shown as dots.



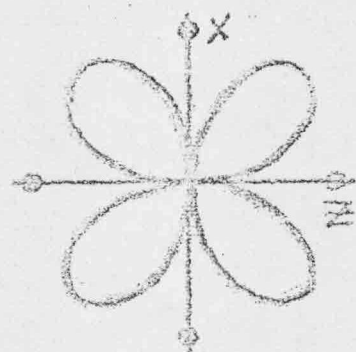
$$XY r^{-2}$$

$$\Psi_{12}^a - \Psi_{12}^{-a}$$



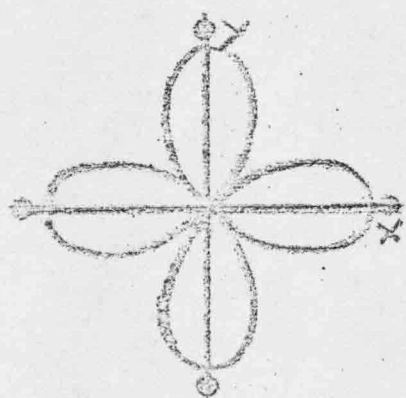
$$YZ r^{-2}$$

$$\Psi_{12}^1 - \Psi_{12}^{-1}$$



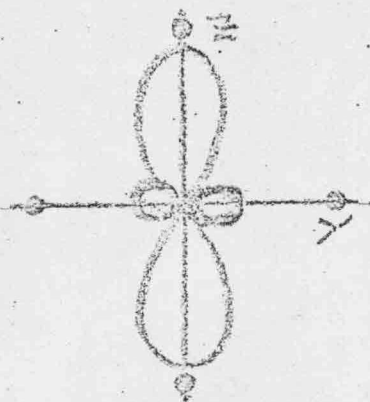
$$ZX r^{-2}$$

$$\Psi_{12}^1 + \Psi_{12}^{-1}$$



$$(X^2 - Y^2) r^{-2}$$

$$\Psi_{12}^a + \Psi_{12}^{-a}$$



$$(3Z^2 - r^2) r^{-2}$$

$$\Psi_{12}^0$$

Consider $\Psi_2^{\pm 1} = \frac{1}{81\pi} \frac{(z)^{3/2}}{a_0} \frac{z^2 r^2}{a_0^2} e^{-2r/3a_0} \sin\theta \cos\theta e^{\pm i\phi}$

or more simply

$$\Psi_2^{\pm 1} = A f(r) \sin\theta \cos\theta (\cos\theta \pm i \sin\theta) r^{-2}$$

so $\Psi_2^2 - \Psi_2^{-2} = A f(r) y z r^{-2} = \Psi_2^{-1}$

Now, consider negative point charges symmetrically placed along the axis (Fig. 1). The energy levels for $\Psi_2^{\pm 1}$ and Ψ_2^{-2}

will be raised the same amount and they will be triply degenerate. It is not obvious that Ψ_2^2 and Ψ_2^0 will be lowered by the same amount but this is indeed the case.⁴ This will cause a double degeneracy.

Now consider the non-symmetric situation caused by moving the charges on the Z axis out by a small amount. We can see that

Ψ_2^2 and Ψ_2^{-1} will be raised the same but Ψ_2^{-2} will be lowered. The degeneracy in Ψ_2^2 and Ψ_2^0 will also be lifted (Fig. 2). This leads to one doubly degenerate and three singlet

levels. Now each of these states is doubly degenerate because

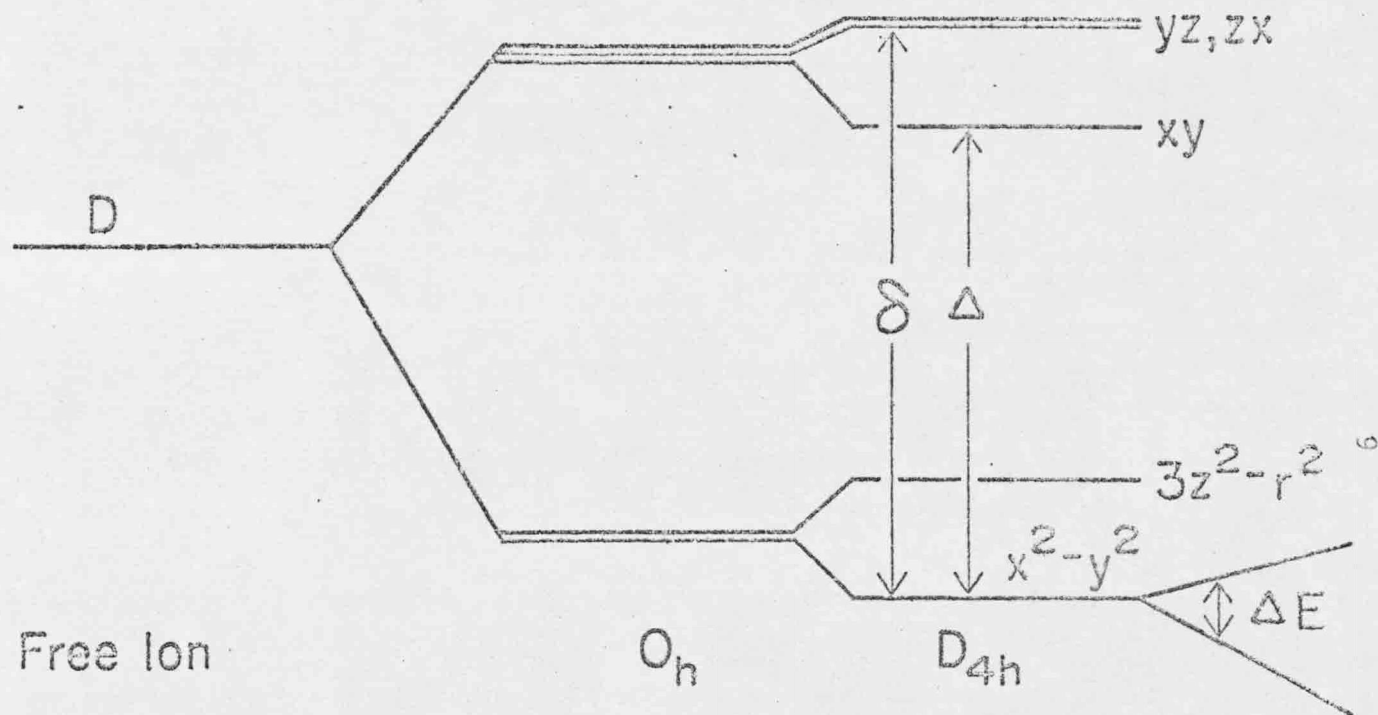
of spin, with $\Psi_{\alpha 2}^2$ and $\Psi_{\beta 2}^2$ as the lowest or ground state (Fig. 2), where α is spin up and β is spin down.

Consider the expectation value of L_z for the state

$\Psi_{\alpha 2}^2$ (see appendix). The vanishing of the expectation value

FIGURE II

Splitting of the D term by a tetragonally distorted cubic field.



of L_z is called "quenching" of the orbital angular momentum.

To see any effect of the spin-orbit interaction the perturbed

wave function Ψ'_m must be used.

Then:

$$\underline{\Psi}_{A2}^{\pm 2} = A \frac{1}{\sqrt{2}} (\Psi_2^{\pm 2} \pm \Psi_2^{\mp 2})$$

$$\underline{\Psi}_{B2}^{\pm 2} = B \frac{1}{\sqrt{2}} (\Psi_2^{\pm 2} \mp \Psi_2^{\mp 2})$$

$$\underline{\Psi}_{A2}^{\pm 1} = A \frac{1}{\sqrt{2}} (\Psi_2^{\pm 1} \pm \Psi_2^{\mp 1})$$

$$\underline{\Psi}_{B2}^{\pm 1} = B \frac{1}{\sqrt{2}} (\Psi_2^{\pm 1} \mp \Psi_2^{\mp 1})$$

$$\underline{\Psi}_{A2}^0 = A \Psi_2^0$$

$$\underline{\Psi}_{B2}^0 = B \Psi_2^0$$

$$\Psi'_m = \Psi_m - \sum_K \underline{\Psi}_K \frac{\langle K | \vec{L} \cdot \vec{S} | m \rangle}{E_K - E_m}$$

where the summation runs over all states including spin, except

$m=K$.

The expectation value of L_z on the perturbed wave function does not vanish (see appendix). Then to first order for the ground state

$$\langle \Psi_{A_2}^{\prime 2} | L_z | \Psi_{A_2}^{\prime 2} \rangle = 4\varepsilon$$

$$\langle \Psi_{B_2}^{\prime 2} | L_z | \Psi_{B_2}^{\prime 2} \rangle = -4\varepsilon$$

$$\varepsilon = \frac{\lambda}{\Delta}$$

where Δ equals the crystal field splitting (Fig. 2). We see that the spin-orbit interaction adds a small amount of angular momentum and because of this, spin only properties cannot be expected.

Now let's consider the effect of an external magnetic field H_0 applied to the crystal. First we will consider the component of the hamiltonian in the Z direction:

$$\mathcal{H}_z = (L_z + g_e S_z) \beta H_z.$$

Then to first order for the ground state we find:

$$\langle \Psi_{A_2}^{\prime 2} | \mathcal{H}_z | \Psi_{A_2}^{\prime 2} \rangle = (-\frac{1}{2}g_e + 4\varepsilon) \beta H_z$$

$$\langle \Psi_{B_2}^{\prime 2} | \mathcal{H}_z | \Psi_{B_2}^{\prime 2} \rangle = (\frac{1}{2}g_e - 4\varepsilon) \beta H_z.$$

At resonance the magnetic splitting will then be

$$\Delta E = (g_e - \beta\epsilon) \beta H_z$$

which modifies the free g value: $g_z = (g_e - \beta\epsilon)$.

If we now apply the external field in the X direction, which for now we will consider equivalent to the Y direction, we find (see appendix)

$$H_x = (L_x + g_e S_x) \beta H_x.$$

Since the diagonal matrix elements vanish we have

$$\langle \Psi_{d2}^{\prime 2} | H_x | \Psi_{B2}^{\prime 2} \rangle = (Y_2 g_e - \eta) \beta H_x$$

$$\eta = \frac{\lambda}{S}$$

where S is equal to the crystal field splitting (Fig. 2).

Solving the secular determinant

$$\begin{vmatrix} -E & (Y_2 g_e - \eta) \beta H_x \\ (Y_2 g_e - \eta) \beta H_x & -E \end{vmatrix}$$

we get

$$E = \pm \left(\frac{1}{2} g_e - \gamma \right) \beta H_x$$

$$h\nu = (g_e - 2\gamma) \beta H_x$$

$$g_x = g_y = g_e - 2\gamma.$$

We have an effective "spin" hamiltonian which can be written

$$\mathcal{H}_{\text{eff}} = \beta \left(g_{\perp} (S_x H_x + S_y H_y) + g_{\parallel} S_z H_z \right)$$

where

$$g_x = g_y = g_{\perp}$$

$$g_z = g_{\parallel}.$$

Finally we see that this is a tensor \underline{g} which can be represented by a 3 x 3 matrix which will relate $\vec{\mu}$ to \vec{S} :

$$\vec{\mu} = \beta \underline{g} \cdot \vec{S}.$$

The result of all this is that the perturbation due to angular momentum can be collapsed into this \underline{g} tensor and only the spin needs to be considered.

So far we have considered only the g values along the various site axis X, Y, and Z. However, the external magnetic field H_0

can be in any arbitrary direction relative to the site axis so we must consider the hamiltonian for any angle θ . The hamiltonian then becomes

$$X_{\text{eff}} = \beta H (g_{\perp} S_{\perp} \sin \theta + g_{\parallel} S_z \cos \theta)$$

where θ is the angle between H_0 and the Z axis, and

$$S_{\perp} = \frac{1}{2} (S_+ e^{-i\phi} + S_- e^{i\phi})$$

where ϕ is an angle in the X, Y plane:

$$g_{\parallel} = g_z$$

$$g_{\perp} = g_y = g_x.$$

Solving the secular determinant

$$\frac{1}{2} \begin{vmatrix} g_{\parallel} \cos \theta - \frac{2E}{\beta H} & g_{\perp} \sin \theta \\ g_{\perp} \sin \theta & -g_{\parallel} \cos \theta - \frac{2E}{\beta H} \end{vmatrix}$$

we have:

$$g(\theta) = \pm \frac{1}{2} (g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{1/2}.$$

Now within the copper-chlorine plane in ALTC, the Z axis of the neighboring Cu^{++} ions are perpendicular (Fig. 3). Because of the superexchange interaction between the neighboring copper sites the g_z and g_y values will be intermixed so that

$$g_{\text{mix}} = \frac{1}{2}(g_y + g_z)$$

We will still assume that g_x equals g_y and that g_x is equal to g_{\perp} , but g_{\perp} will now be called g_{min} .

FIGURE III

Orientation of the copper-chlorine bonds in ALTC.⁷

