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

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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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

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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 ethylendiammonium 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:

$$E = -\vec{\mu} \cdot \vec{H_o}$$

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

where h is Planck's constant, r 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-sphereical 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_o.

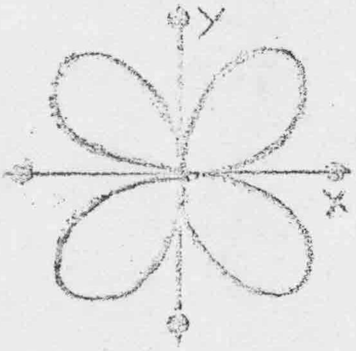
The free ion orbital can be represented by $\psi_\ell^{m_\ell}$. This is an eigenfunction of L_z. For a free ion, the hamiltonian will be invariant under rotation about the Z axis, and so it will commute with L_z. But for an ion in the crystal lattice, there isn't spherical symmetry so that this commutation 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:

$$\Psi_\ell^{\pm m_\ell} = \psi_\ell^{m_\ell} \pm \psi_\ell^{-m_\ell}.$$

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

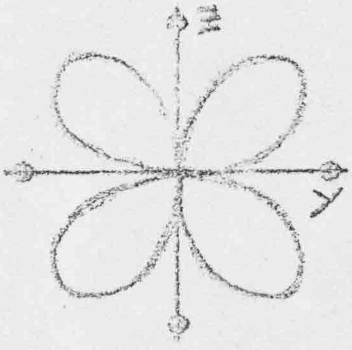
FIGURE I

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



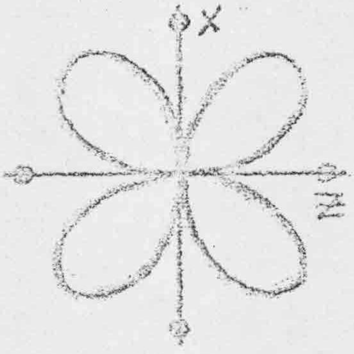
XYr^{-2}

$\psi_2^{2} - \psi_2^{-2}$



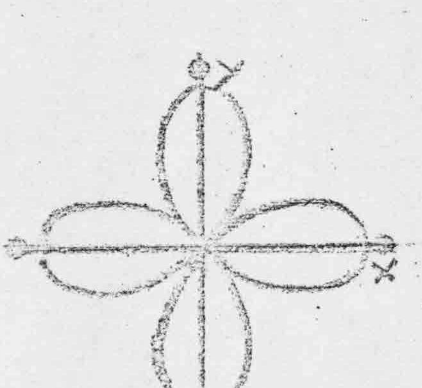
YZr^{-2}

$\psi_2^{1} - \psi_2^{-1}$



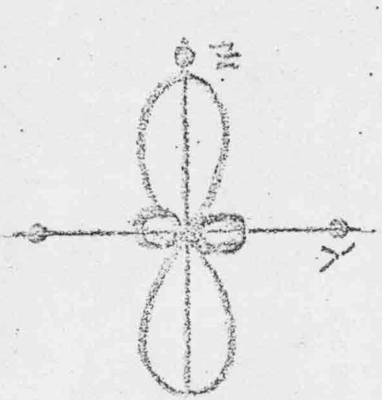
ZXr^{-2}

$\psi_2^{1} + \psi_2^{-1}$



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

$\psi_2^{2} + \psi_2^{-2}$



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

ψ_2^{0}

Consider $\psi_2^{\pm 1} = \frac{1}{81\pi}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2 r^2}{a_0^2}e^{-Zr/3a_0}\sin\theta\cos\theta\, e^{\pm i\phi}$

or more simply

$$\psi_2^{\pm 1} = A f(r)\sin\theta\cos\theta(\cos\phi \pm i\sin\phi)r^{-2}$$

so $$\psi_2^{1} - \psi_2^{-1} = A f(r)\, yz\, r^{-2} = \Psi_2^{-1}$$

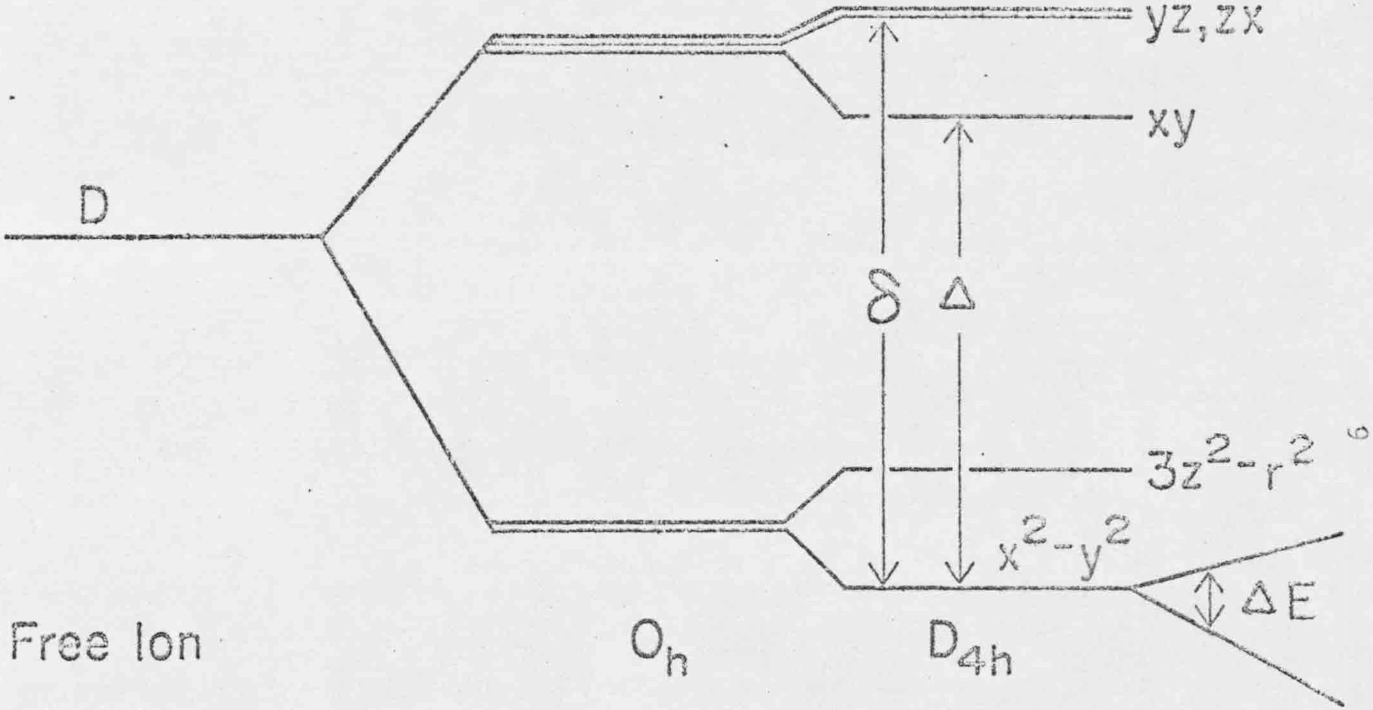
Now, consider negative point charges symmetrically placed along the axis (Fig. 1). The energy levels for $\Psi_2^{\pm 1}$ and Ψ_2^{-2} will be raised the same amount and they will be triply degenerate. It is not obvious that Ψ_2^{2} and Ψ_2^{0} will be lowered by the same amount but this is indeed the 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^{1} 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.


yz, zx
xy
D
δ
Δ
3z^2-r^2
x^2-y^2
ΔE
Free Ion
O_h
D_4h

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:

$$\Psi^{\pm 2}_{\alpha 2} = \alpha \frac{1}{\sqrt{2}}\left(\psi_2^{2} \pm \psi_2^{-2}\right)$$

$$\Psi^{\pm 2}_{B 2} = B \frac{1}{\sqrt{2}}\left(\psi_2^{2} \pm \psi_2^{-2}\right)$$

$$\Psi^{\pm 1}_{\alpha 2} = \alpha \frac{1}{\sqrt{2}}\left(\psi_2^{1} \pm \psi_2^{-1}\right)$$

$$\Psi^{\pm 1}_{B 2} = B \frac{1}{\sqrt{2}}\left(\psi_2^{1} \pm \psi_2^{-1}\right)$$

$$\Psi^{0}_{\alpha 2} = \alpha \psi_2^{0}$$

$$\Psi^{0}_{B 2} = B \psi_2^{0}$$

$$\Psi'_m = \Psi_m - \sum_K \Psi_K \frac{\langle k|\lambda \vec{L}\cdot\vec{S}|m\rangle}{E_K - E_m}$$

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

$$\langle \Psi'^{2}_{\alpha 2} | L_z | \Psi'^{2}_{\alpha 2} \rangle = 4\varepsilon$$

$$\langle \Psi'^{2}_{\beta 2} | L_z | \Psi'^{2}_{\beta 2} \rangle = -4\varepsilon$$

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

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:

$$\langle \Psi'^{2}_{\alpha 2} | \mathcal{H}_z | \Psi'^{2}_{\alpha 2} \rangle = (-\tfrac{1}{2} g_e + 4\varepsilon)\beta H_z$$

$$\langle \Psi'^{2}_{\beta 2} | \mathcal{H}_z | \Psi'^{2}_{\beta 2} \rangle = (\tfrac{1}{2} g_e - 4\varepsilon)\beta H_z .$$

At resonance the magnetic splitting will then be

$$\Delta E = (g_e - 8\varepsilon)\beta H_z$$

which modifies the free g value: $g_z = (g_e - 8\varepsilon)$.

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)

$$\mathcal{H}_x = (L_x + g_e S_x)\beta H_x.$$

Since the diagonal matrix elements vanish we have

$$\langle \Psi'^{2}_{\alpha 2} | \mathcal{H}_x | \Psi'^{2}_{\beta 2} \rangle = (\tfrac{1}{2} g_e - \eta)\beta H_x$$

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

where δ is equal to the crystal field splitting (Fig. 2). Solving the secular determinant

$$\begin{vmatrix} -E & (\tfrac{1}{2} g_e - \eta)\beta H_x \\ (\tfrac{1}{2} g_e - \eta)\beta H_x & -E \end{vmatrix}$$

we get

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

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

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

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

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

where

$$g_x = g_y = g_\perp$$

$$g_z = g_\parallel .$$

Finally we see that this is a tensor 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 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

$$\mathcal{H}_{eff} = \beta H \left(g_\perp S_\perp \sin\theta + g_\parallel S_z \cos\theta \right)$$

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

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

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:

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

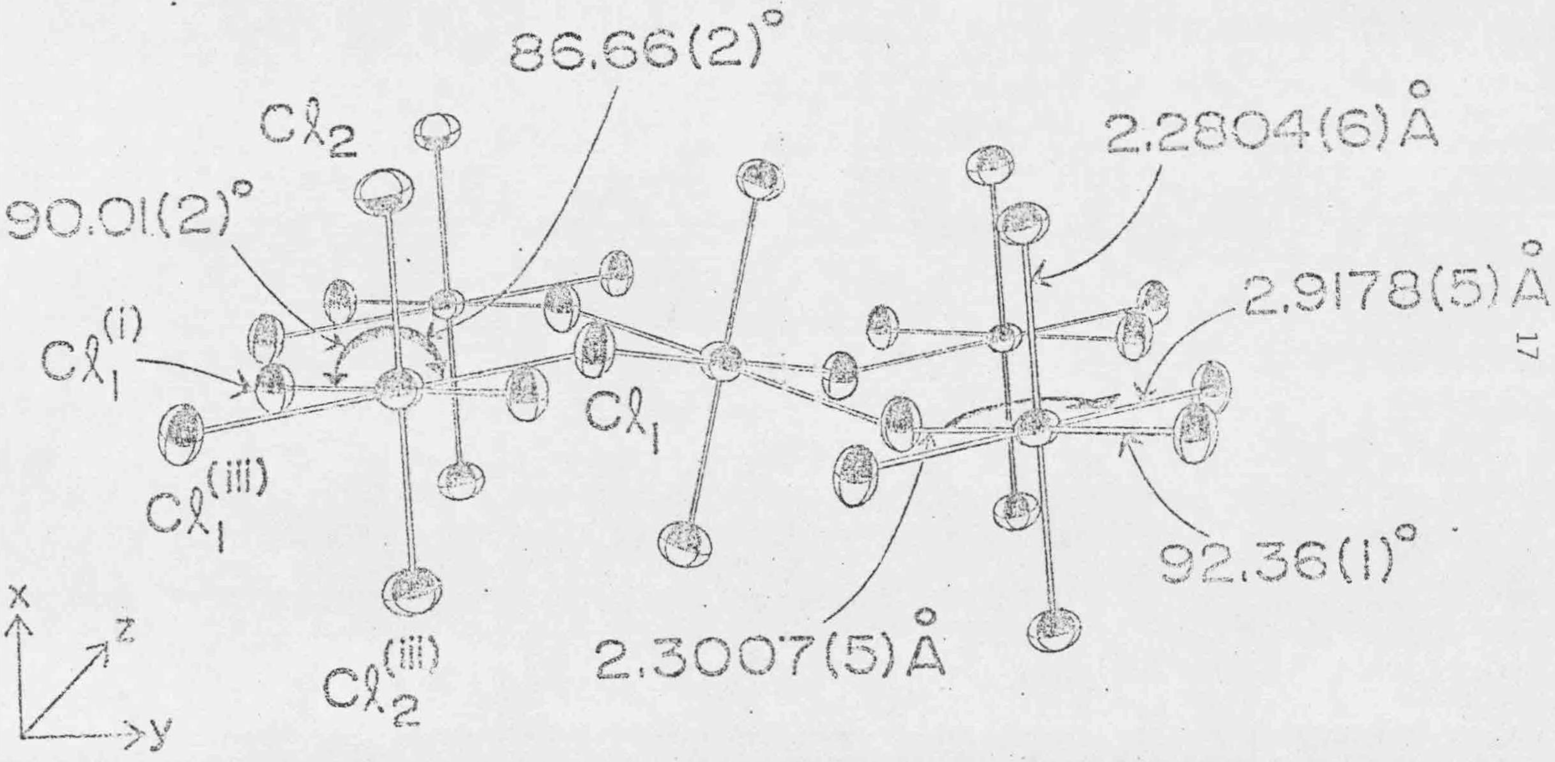
Now within the copper-chlorine plane in ALTC, the Z axis of the neighboring Cu^{++} ions are perpendicular (Fig. 3). Because of the superexchange interaction between the neighboring copper sites the g_z and g_y values will be intermixed so that

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

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]

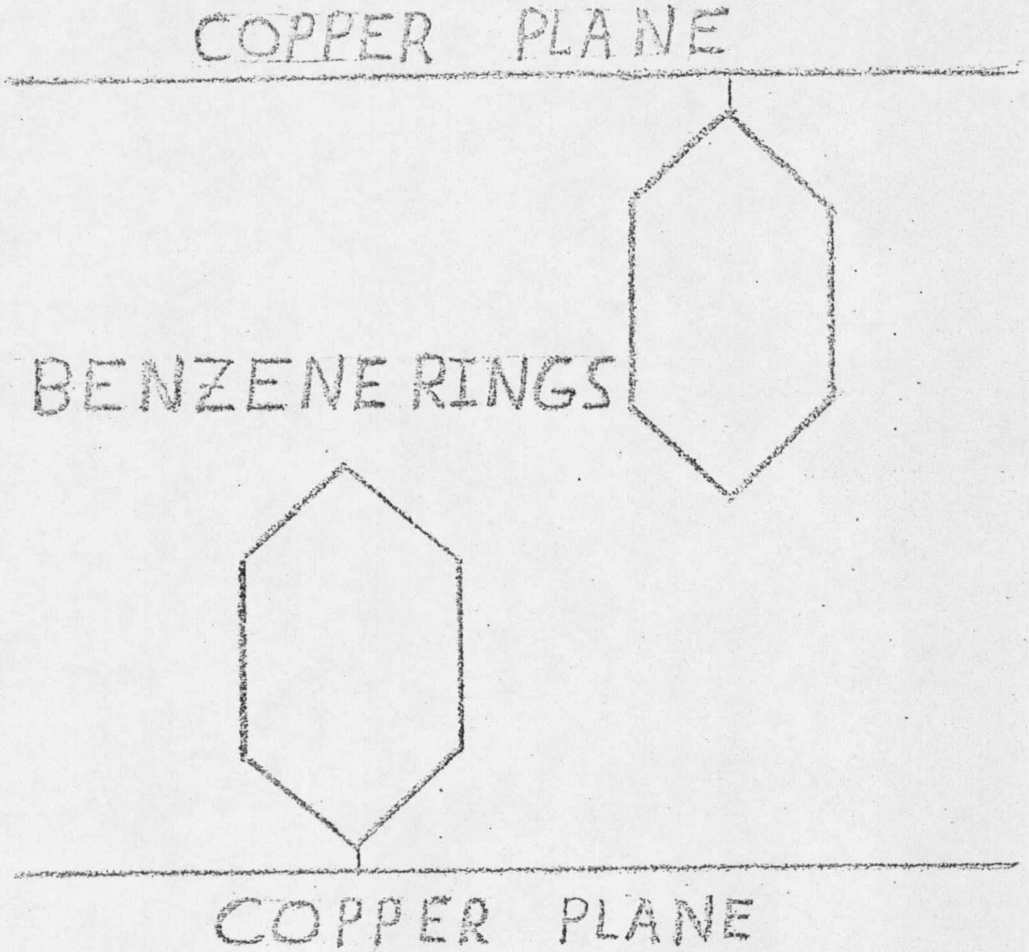

86.66(2)°
Cl₂
2.2804(6) Å
90.01(2)°
2.9178(5) Å
Cl₁⁽ⁱ⁾
Cl₁
Cl₁⁽ⁱⁱⁱ⁾
92.36(1)°
x
z
y
Cl₂⁽ⁱⁱⁱ⁾
2.3007(5) Å

III. DATA

Anilinium tetrachlorocuprate (ALTC), $(C_6H_5NH_3)_2$ $CuCl_4$, is monoclinic with a space group $P2_1/c$ and with a = 15.050A^{o}, b = 7.443A^{o}, c = 7.180A^{o}; = 100.7^{o} and Z = 2 as shown in Figure 3.[5] The copper ions lie in a plane and are surrounded by six chlorine ligands. Four of these chlorine ligands bind the copper ions to other copper ions in the same plane, and the two out of plane chlorine ligands bind the copper ions to benzene rings which bridge the copper planes (see Fig. 4).[6] Additional information provided by Larsen gives the "correct" orientation of the copper-chlorine bonds. The lengths of the copper-chlorine bonds along the X, Y, and Z axis are 2.2804A^{o}, 2.3007A^{o}, and 2.9178A^{o} respectively. The Z axis at one copper site is connected by a chlorine ligand to the X axis of the next copper site, and the angles between the copper and chlorine are not all exactly 90^{o} (Fig. 3). Also the copper-chlorine bonds between the Y and Z axis lie out of the copper plane, so the X axis does not lie along a line perpendicular to the copper-copper planes. Since the EPR data for ethylenediammonium tetrachlorocuprate (EDTC), $(C_2H_4(NH_3)_2)$ $CuCl_4$, is similar to that of ALTC, their structures were assumed to be similar.

FIGURE IV

Drawing of copper planes separated by benzene rings.


COPPER PLANE
BENZENE RINGS
COPPER PLANE

Data for both ALTC and EDTC were taken on a standard Varian E-3 EPR spectrometer. A scan time of 8 minutes was used, the modulation was 100 kilohertz, and the microwave frequency was 9.523 megahertz for ALTC and 9.155 megahertz for EDTC at room temperature, and 9.155 megahertz for ALTC and 9.153 megahertz for EDTC at 77^0 K. The scan range was 250 Gauss with a time constant of 1 second.

The resonant magnetic field H_0 vs. angle θ is given in Figure 5. These are the typical cosine curves one would expect from the angular dependence of the g equation. Solving the energy equation for g gives:

$$g = \frac{h\nu}{\beta H}.$$

Calculated values of g_{max} and g_{min} for both ALTC and EDTC are given in Table 1. The data was taken at both room temperature (300^0 K) and liquid nitrogen temperature (77^0 K).

Willett has shown in his investigations of monomeric copper (II) chlorides that $\Delta \approx 10{,}000 \mathrm{cm}^{-1}$ and $\zeta \approx 12{,}000 \mathrm{cm}^{-1}$, for Cu (II).[8] If the assumption is made that $g_x = g_y$ and that $g_{max} = \frac{1}{2}(g_y + g_z)$ no consistent value for the spin-orbit coupling constant is possible. This of course is because the structure, given earlier, of ALTC is more complicated than the above assumptions.

FIGURE V

Magnetic field (H) versus angle (Θ) for ALTC and EDTC.

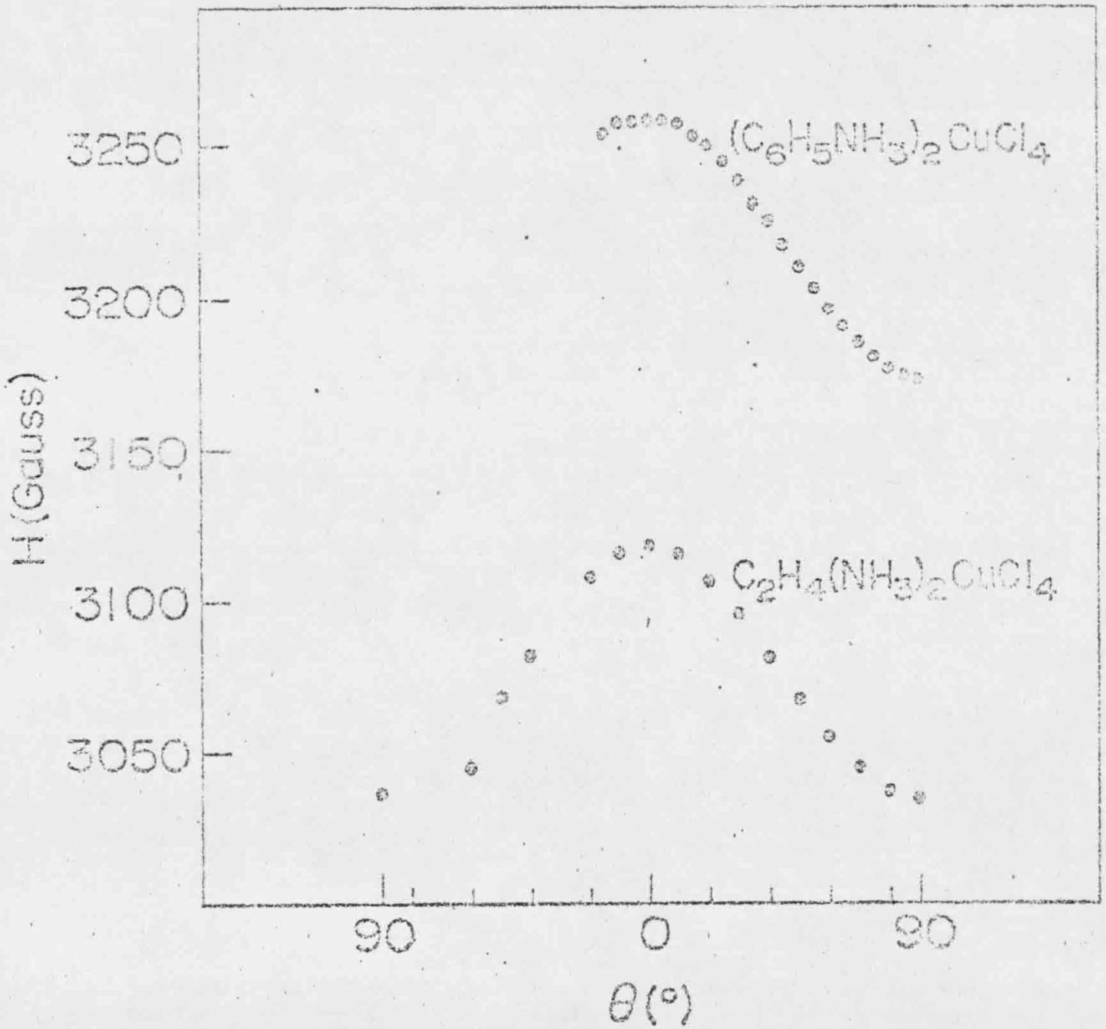

3250
3200
3150
3100
3050
H (Gauss)
$(C_6H_5NH_3)_2CuCl_4$
$C_2H_4(NH_3)_2CuCl_4$
90
0
90
θ(°)

TABLE I

MEASURED g VALUES AND LINEWIDTHS

Compound	g_{min}	g_{max}	linewidth g_{max}	linewidth g_{min}	
$(C_6H_5NH_3)_2$ $CuCl_4$	2.088±.01	2.144±.01	42.5 gauss	41.25 gauss	300^{o}K
	2.090±.01	2.146±.01	9.4	15.6	77^{o}K
$C_2H_4(NH_3)_2$ $CuCl_4$	2.097±.01	2.155±.01	45.9	38.7	300^{o}K
	2.097±.01	2.154±.01	11.25	9.7	77^{o}K

The values that are consistant with the above assumptions will range between -200cm^{-1} and -600cm^{-1}.

The linewidths at an angle of $\Theta = 0^0$ are shown at 77^0 K and 300^0 K in Figure 6. These were the only temperatures available to use and are preliminary temperatures to be used to further test the model proposed by Zaspel in his Ph.D. thesis.[9] By considering optical phonon modulation of the symmetric exchange integral, the model predicts a linear temperature dependence of the linewidths ΔH. Although the model supposes no preferred geometry, layered compounds such as ALTC and EDTC are expected to behave in this manner. A linear temperature dependence of the exchange constant has been shown for $K_2CuCl_4 \cdot H_2O$ and other layered compounds.[10]

Linewidths vs. angle at both 77^0 K and 300^0 K are also interesting and are given in Figure 7. ALTC displays the expected angular dependence while curiously EDTC shows just the opposite angular dependence. Richards has proposed a model which gives lineshape as a function of angle by a Fourier transform of a relaxation function which is expressed in terms of exchange modulation of the dipole-dipole perturbation for S state ions. In general, however, the perturbations may include spin-orbit, crystal field couplings, etc.[11] Drumheller has found other compounds which depart from the Richards model, such as the methyl and

FIGURE VI

Linewidths (ΔH) versus temperature at an angle of zero degrees for ALTC and EDTC.

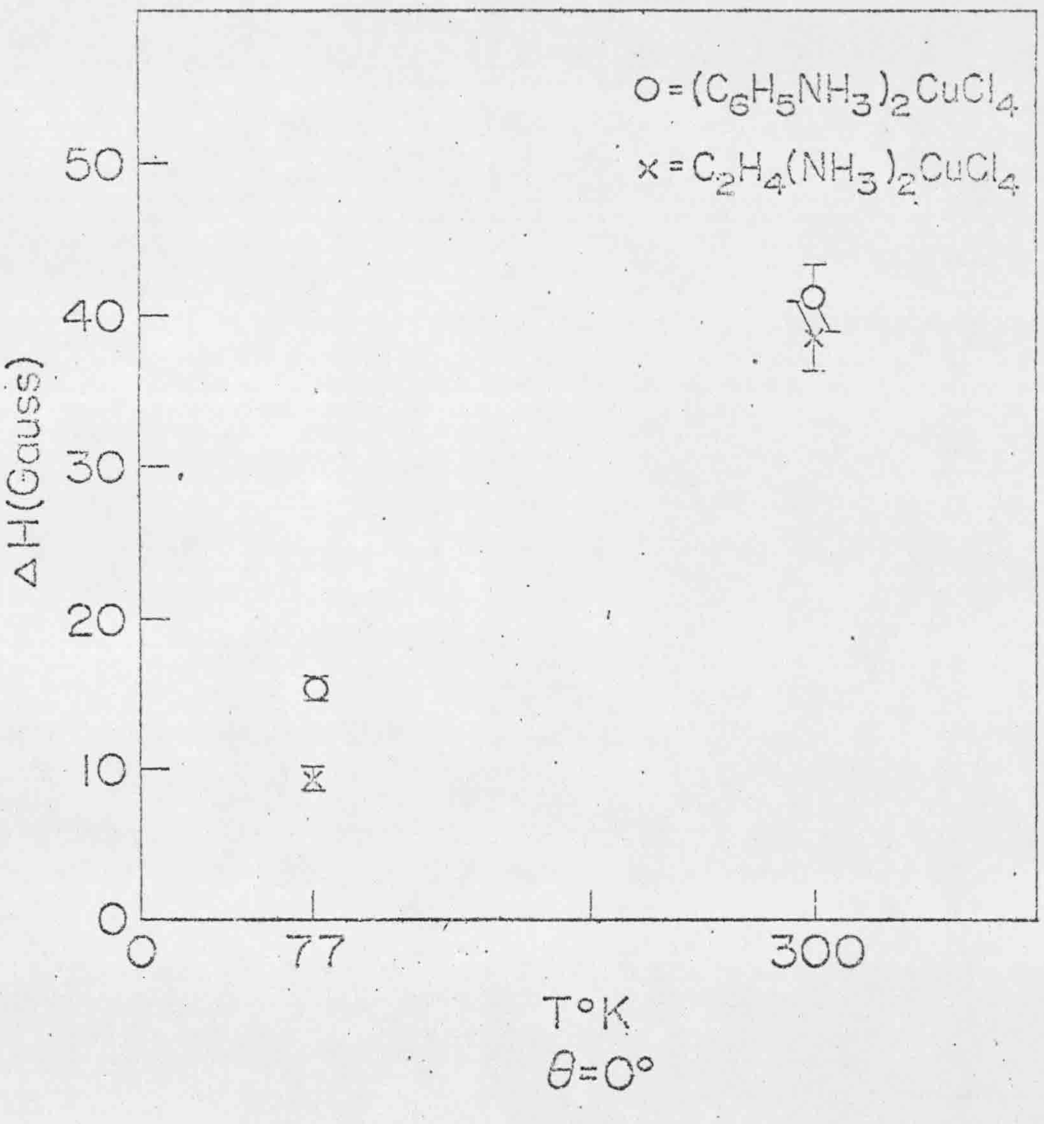
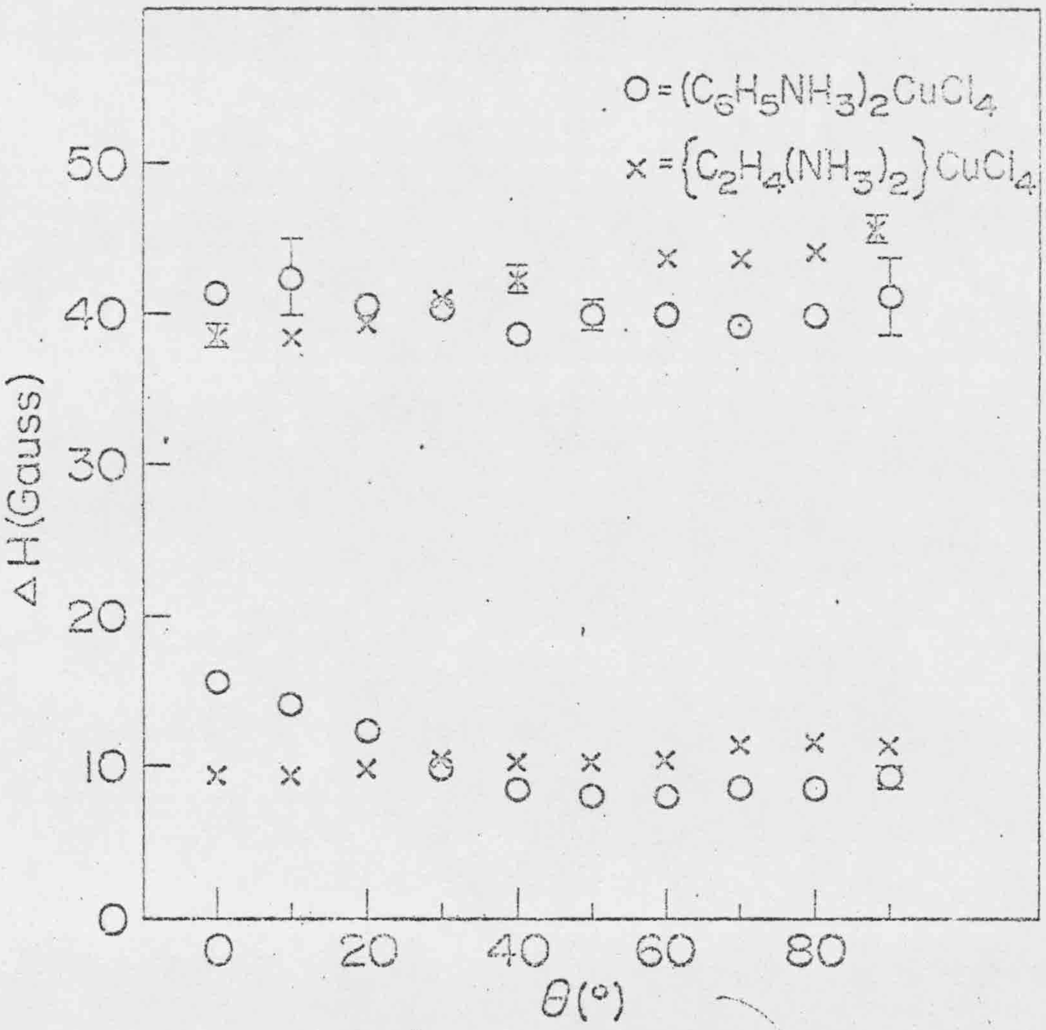

O = $(C_6H_5NH_3)_2CuCl_4$
x = $C_2H_4(NH_3)_2CuCl_4$
ΔH(Gauss)
0
10
20
30
40
50
0
77
300
T°K
θ=0°

FIGURE VII

Linewidths (ΔH) versus angle (θ) for ALTC and EDTC.


○ = $(C_6H_5NH_3)_2CuCl_4$
× = $\{C_2H_4(NH_3)_2\}CuCl_4$
ΔH (Gauss)
0
10
20
30
40
50
θ(°)
0
20
40
60
80

ethylammonium tetrachlorocuprate compounds.[12] So far there is no explanation for this anomalous behavior.

IV. CONCLUSION

By measuring the g values and observing the angular and temperature dependence of the linewidths for both ALTC and EDTC we have shown in this work several qualitative features which are of interest in the study of 2-dimensional magnetism. First we have shown that the structure of EDTC is layered and similar to ALTC. Also we have found two more examples that seem to substantiate the model proposed by Zaspel for temperature dependence of the linewidths and therefore the exchange energy. This information, however, does not give the nature of the exchange integral J, so the magnetic susceptibility for both ALTC and EDTC needs to be measured. From data, the inter-plane and intra-plane exchange can be found and the nature of J determined.

Eventually data on the magnetic specific heat C_m will be taken on these compounds, and it may be possible to determine from this data if the model proposed by Zaspel, which depends on the symmetric exchange interaction $S_i \cdot S_j$, is really responsible for the linear temperature dependence of the linewidths, or if it is due to the antisymmetric exchange interaction $S_i \times S_j$.[13] Both models predict a linear temperature dependence of the linewidths. Because we need non-central symmetry and non-S-state ions for the antisymmetric exchange to be present, the magnetic specific heat would behave differently for non-symmetric exchange than for symmetric exchange.[14] Also the angular dependence on the linewidths for EDTC needs to be further investigated and correlated to the apparently anomalous behavior in other compounds.

APPENDIX

APPENDIX

To show that the expectation value of L_z vanishes operate on the ground state wave function Ψ^{2}_{d2}.

$$L_z \Psi^{2}_{d2} = 2\Psi^{-2}_{d2}$$

so

$$\langle \Psi^{2}_{d2} | | L_z | \Psi^{2}_{d2} \rangle = 2 \langle \Psi^{2}_{d2} | | L_z | \Psi^{-2}_{d2} \rangle = 0.$$

Then we can see that because of the orthogonality of the wave functions the expectation value of L_z vanishes. The same, of course, will be true for L_x and L_y.

Because the perturbed wave function for the ground state

$$\Psi'^{2}_{d2} = \Psi^{2}_{d2} - \sum_{K} \Psi_K \frac{\langle \Psi_K | \lambda \vec{l} \cdot \vec{s} | \Psi^{2}_{d2} \rangle}{E_K - E^{2}_{d2}}$$

is a mixture of all other states except Ψ^{0}_{2}, whose matrix elements with respect to the ground state vanish, the expectation value of L_z no longer vanishes:

$$\Psi'^{2}_{d2} = \Psi^{2}_{d2} - \frac{\lambda}{\Delta} \Psi^{-2}_{d2} - \frac{\lambda}{\sqrt{2}\,\delta} \beta \Psi^{-1}_{2}$$

$$\langle \Psi'^{2}_{d2} | | L_z | \Psi'^{2}_{d2} \rangle = \frac{-4\lambda}{\Delta} - \frac{\lambda^2}{2\delta^2}.$$

So to first-order the expectation value of L_z on the perturbed ground state is equal to $\frac{-4\lambda}{\Delta}$, where λ is the spin-orbit coupling constant and Δ and δ are the crystal field splitting (Fig. 2). Since Δ is on the order of 10,000cm^{-1} at room temperature the population of the other states is insignificant.

Now we can show that the expectation value of the hamiltonian $\mathcal{H}_z$ on the perturbed ground state, where $\mathcal{H}_z = (L_z + g_e S_z)\beta H_z$ is equal to $\frac{1}{2} g_e - \frac{4\lambda}{\Delta}$.

Then the splitting

$$\Delta E = \left(g_e - \frac{8\lambda}{\Delta}\right)\beta H_z .$$

Now let's take the expectation value of $\mathcal{H}_x$ with respect to Ψ'^{2}_{d2} which because of symmetry is equivalent to the expectation value of $\mathcal{H}_y$.

$$\mathcal{H}_x = (L_x + g_e S_x)\beta H_x$$
$$L_x = \tfrac{1}{2}(L_+ + L_-)$$
$$S_x = \tfrac{1}{2}(S_+ + S_-)$$

The diagonal matrix elements vanish. With a little work it can be shown that to first order

$$\langle \Psi'^{2}_{B2} | \mathcal{H}_x | \Psi'^{2}_{d2} \rangle = \left(\tfrac{1}{2} g_e - \frac{\lambda}{\delta}\right).$$

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