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# Electron Spin Resonance of $Cu^{2+}$ in $Zn(HCOO)_2 \cdot 2H_2O$: Isolated Ions and Exchange-Coupled Pairs*

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The ESR spectrum of $Cu^{2+}$ introduced substitutionally into single crystals of zinc formate dihydrate, $Zn(HCO_2)_2 \cdot 2H_2O$, has been investigated at $X$ band in the temperature range 4.2 to 77°K. At low concentrations ($Cu:Zn<0.005$) the spectra from isolated $Cu^{2+}$ ions occupying each of the four metal-ion sites per unit cell have been observed and fitted to a spin Hamiltonian of axial symmetry. For the type-1 sites, which are coordinated by a slightly distorted octahedron of oxygen atoms belonging to six different carboxyl groups, the spin Hamiltonian parameters are: $g_{\parallel}=2.416\pm0.005$, $g_{\perp}=2.077\pm0.007$, $A^{63}=0.0124\pm0.0002$ cm$^{-1}$, $B^{63}=0.0023\pm0.0002$ cm$^{-1}$, $Q'^{63}=0.00095\pm0.00002$ cm$^{-1}$. For the type-2 sites, which are coordinated by a slightly distorted octahedron of four oxygen atoms from water molecules and two oxygens from two different carboxyl groups, the parameters are: $g_{\parallel}=2.420\pm0.005$, $g_{\perp}=2.066\pm0.007$, $A^{63}=0.0134\pm0.0005$ cm$^{-1}$, $B^{63}=0.0026\pm0.0012$ cm$^{-1}$, $Q'^{63}\approx0.0015$ cm$^{-1}$. At both kinds of sites the symmetry axis is directed toward the oxygen belonging to the formate group which links nearest-neighbor type-1 and type-2 sites. In a sample of higher concentration ($Cu:Zn=0.034$) we have observed a spectrum which we attribute to pairs of exchange-coupled $Cu^{2+}$ ions occupying nearest-neighbor type-1 sites. From the temperature dependence of the intensity of the spectrum we have determined the isotropic exchange interaction to be antiferromagnetic and given by $|J|=33\pm1$ cm$^{-1}$.

## INTRODUCTION

The dihydrated formates of Cu, Fe, Mn, and Ni have been found to exhibit anomalous magnetic properties at low temperatures. Magnetic susceptibility,[1–6] heat-capacity,[7] and resonance[4,8] studies of the manganous salt suggest that one-half of its paramagnetic ions undergo long-range spin ordering above 1°K, possibly in two abrupt cooperative transitions at 3.7 and 1.7°K. The other ionic moments appear to remain nearly independent to a much lower temperature. Magnetic[9] and thermal[7] data on the nickelous salt reveal a cooperative transition at 15°K and behavior below that temperature which also suggests the independence of one-half of the ionic moments. In this case, however, the evidence is less clear cut and an interesting alternative[10] exists which implies the cooperative ordering of all moments.

The ferrous salt undergoes a cooperative transition[9] at 3.7°K below which there is no suggestion of the independence of any of the $Fe^{2+}$ moments. Low-temperature susceptibility data on cupric formate dihydrate are not yet complete. Preliminary results[11] suggest, however, an anomalous peak near 25°K with $\chi_M$ continuing to rise rapidly as the temperature is further reduced. This perhaps indicates that the cupric and manganous salts are similar in some ways.

Recent x-ray studies[9,12–14] have shown that the dihydrated formates of Cd, Cu, Fe, Mg, Mn, Ni, and Zn are isostructural. Their over-all symmetry is monoclinic[15] with the unit cell corresponding to the space group $P2_1/c$ and containing four metal ions situated on two kinds of inequivalent sites. See Fig. 1. The $M1$ sites are arrayed in sheets parallel to (001).[16] Each $M1$ site is coordinated by a distorted octahedron of oxygen atoms from formate groups. Four of these oxygens belong to formates which link the $M1$ site to four other $M1$'s in the sheet, and two belong to formates which link the $M1$ to two $M2$'s in adjoining sheets. The $M2$'s are also arrayed in sheets parallel to (001). They are coordinated by distorted octahedra which consist of four water molecules and two oxygen atoms from formates. Each $M2$ is linked by a formate group to two $M1$'s in adjoining sheets but there are no formate linkages between $M2$ ions.

It has been pointed out that the formate group in these salts, as in the case of $Cu(HCO_2)_2 \cdot 4H_2O$, may act as an effective superexchange path between magnetic

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[15] P. Groth, *Chemische Krystallographie* (Leipzig, 1910), Vol. 3, p. 21.

[16] We use the notation of Groth, Ref. 15. Notice that Refs. 12, 13, and 14 interchange the *a* and *c* axes.

ions.[1,17–19] This suggests that in those dihydrated formates in which long-range spin order is established first among one-half of the paramagnetic ions, these are most likely to be the $M1$ ions linked in sheets by formate groups. Correspondingly one might expect $M2$ ions to be the ones remaining independent since they have no mutual formate links. Uryû[20] has shown that the susceptibility of the ferrous salt above its transition temperature can be calculated with a four-sublattice molecular-field model which attributes similar properties to $M1$ and $M2$ $Fe^{2+}$ ions and identical antiferromagnetic exchange integrals $J$ to all formate links. This model is less successful in accounting for the behavior of the other magnetic formates. It appears likely that allowance must be made for inequality of some of the exchange interactions in these substances. Our ESR results suggest how this inequality may come about, as we shall see later.

The fact that there are several diamagnetic salts included in this isostructural family presents the possibility of diluting the magnetic formates and directly measuring the exchange interactions between the magnetic ions. This paper reports such a measurement for $Cu^{2+}$ ions in $Zn(HCO_2)_2\cdot 2H_2O$. We have observed the ESR spectrum of one kind of isolated pair of $Cu^{2+}$ ions in a single crystal of $Cu:Zn(HCO_2)_2\cdot 2D_2O$ with $Cu:Zn = 3.4$ mole percent. We believe these pairs to consist of nearest-neighbor $M1$ ions. By measuring the temperature dependence of the intensity of the spectrum we have obtained the isotropic exchange interaction $J$.

In the course of our investigation we have necessarily determined the spin Hamiltonians for single isolated $Cu^{2+}$ ions on each of the four sites in the unit cell. For each site we have been able to fit the resonance data with a conventional spin Hamiltonian of axial symmetry and have located the symmetry axes for each site relative to the crystallographic axes.

## EXPERIMENTAL

### Apparatus

All the ESR measurements reported here have been made with an $X$-band, superheterodyne spectrometer which has been fully described elsewhere.[21] A rectangular $\lambda_g/2$ cavity was used which operated in the $TE_{10}$ mode. The cavity was matched by a variable coupler described by Gordon.[22] The samples were glued with Duco cement to the narrow wall of the cavity at the $\lambda_g/4$ position. The temperature of the sample was measured below 20°K by a carbon resistance thermometer attached to the outside of the cavity just opposite the sample. Glyptal was used for good thermal contact to the cavity wall. The cavity and coupler were surrounded by a brass can which prevented the cryogenic liquid from getting into the cavity and causing noise by bubbling. During the low-temperature runs, a small amount of helium exchange gas was kept in the can to provide thermal contact between the cavity and the cryogenic liquid.

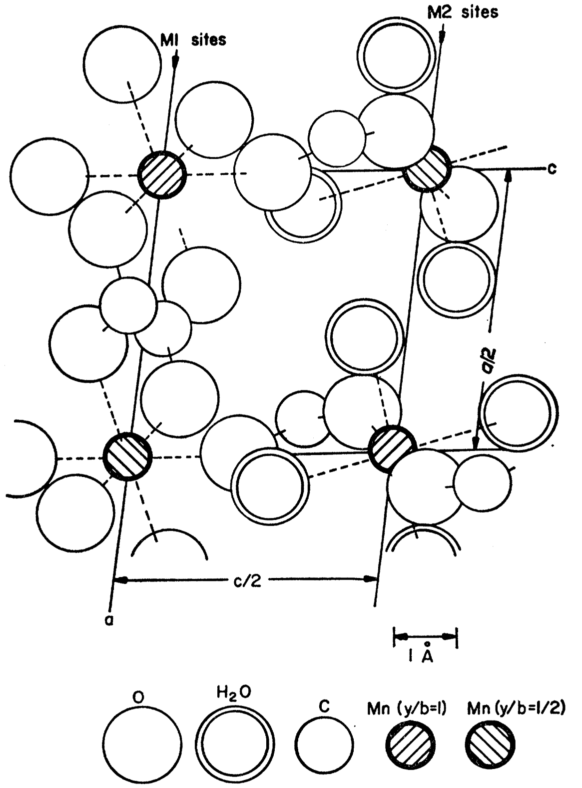

FIG. 1. The projection of the unit cell of $Mn(HCO_2)_2\cdot 2H_2O$ on an (010) plane. This projection was taken from the paper of Abe and Matsuura (Ref. 8) and the $a$ and $c$ axes were interchanged to be consistent with the notation of Groth (Ref. 15).

### Samples

All the samples used in this experiment were "home grown" from aqueous solutions by the evaporation technique. It was found that single crystals of $Cu:Zn(HCO_2)_2\cdot 2H_2O$ grown from mixed solutions of zinc and copper formate contained almost the same concentration of $Cu^{2+}$ as the parent mixed solution.

The saturated zinc formate solution was obtained by reacting Baker analyzed, reagent-grade zinc carbonate with formic acid and water. The reaction was carried out at 90°C with a few percent excess acid in the solution. After cooling, the solution was filtered several times.

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[17] R. B. Flippen and S. A. Friedberg, Bull. Am. Phys. Soc. **5**, 296 (1960).

[18] S. A. Friedberg and R. B. Flippen, *Proceedings of the Seventh International Conference on Low-Temperature Physics, 1960* (University of Toronto Press, Toronto, Canada, 1960), p. 122.

[19] T. Haseda, A. R. Miedema, H. Kobayashi, and E. Kanda, in *Proceedings of the International Conference on Magnetism and Crystals* (The Physical Society of Japan, Bunkyo-Ku-Tokyo, 1962); H. Kobayashi and T. Haseda, J. Phys. Soc. Japan **18**, 541 (1963).

[20] Norikiyo Uryû, J. Chem. Phys. **42**, 234 (1965).

[21] J. L. Hall and R. T. Schumacher, Phys. Rev. **127**, 1892 (1962); also J. L. Hall, thesis, Carnegie Institute of Technology, 1961 (unpublished).

[22] J. P. Gordon, Rev. Sci. Instr. **32**, 658 (1961).

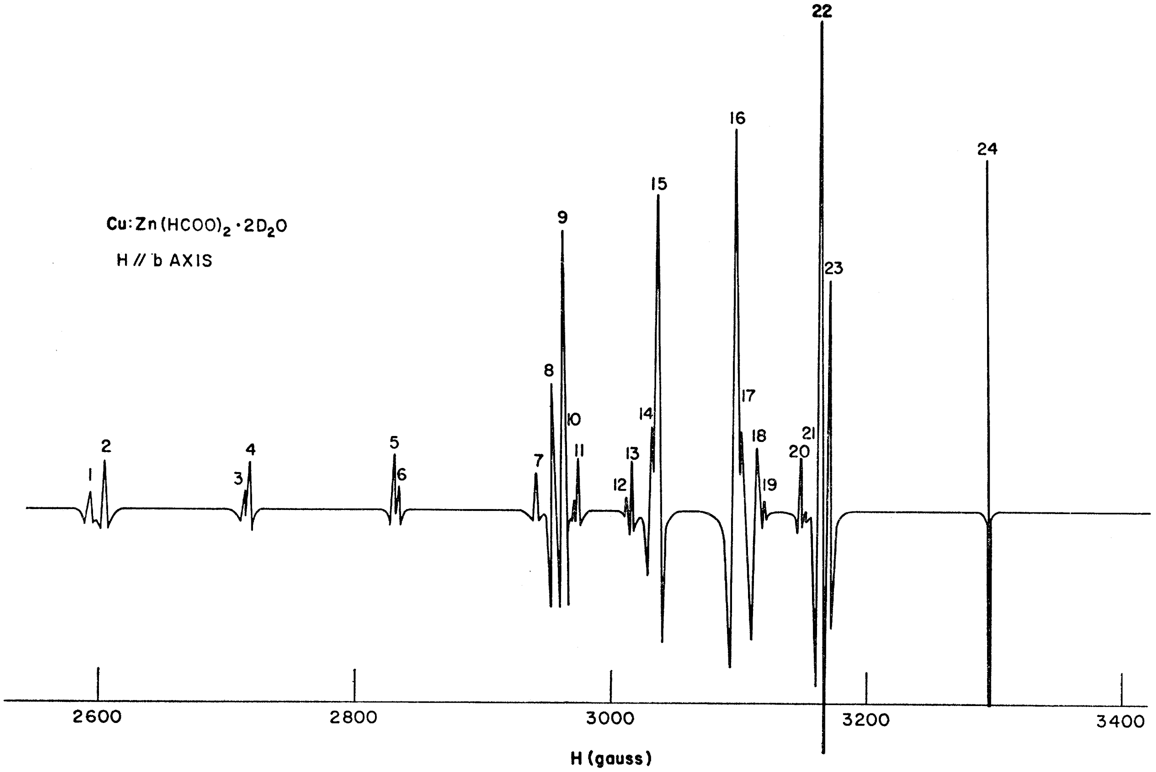

FIG. 2. Second derivative of ESR absorption with the external magnetic field along the *b* axis of a crystal of Cu:Zn$(HCO_2)_2 \cdot 2D_2O$ for which Cu:Zn = 0.2 mole percent. The spectrum was taken at $T = 77$°K with a microwave frequency $\nu = 9215$ Gc/sec. The numbered peaks are identified in the text.

Similarly, a saturated solution of copper formate was prepared by reacting reagent-grade cupric oxide, obtained from the Mallinckrodt Chemical Company, with formic acid and water. The reaction was carried out at 100°C and again the solution was filtered several times after cooling.

Mixed crystals with Cu:Zn ranging from 0.2 to 3.4% were obtained by mixing the appropriate amounts of the prepared solutions, placing the resulting solutions in a desiccator containing $H_2SO_4$ and maintaining them at room temperature. Crystals of a few mm in cross section were obtained in about 5 weeks. The copper content of the crystals used in the experiment was determined by the Schwarzkopf Microanalytical Labs., Woodside, New York.

In order to reduce the width of the observed resonances, crystals of Cu:Zn$(HCO_2)_2 \cdot 2D_2O$ were also used. These were grown by first crystallizing a large amount of $Zn(HCO_2)_2 \cdot 2H_2O$ from the solution as prepared above, dehydrating it at 80°C, and then redissolving it in $D_2O$.

Orientation of the crystals was achieved by measuring the angles between external faces and comparing them with those of Groth.[15] Most of the crystals grown exhibited the less prominent (100) plane which intersects the most prominent (001) plane to form the *b*-axis. This locates the crystallographic axes unambiguously.

## SINGLE IONS

### Theoretical Background

In this section we present a brief review of the theory necessary to the understanding of the ESR spectrum of isolated $Cu^{2+}$ ions occupying $Zn^{2+}$ sites in $Zn(HCO_2)_2 \cdot 2H_2O$. In anticipation of the result given in the next section that the symmetry of the crystalline field at the $Cu^{2+}$ sites is tetragonal, we will use a spin Hamiltonian having this symmetry.

The electronic configuration of $Cu^{2+}$ is $3d^9$, with one electron missing from the complete $3d$ shell. The ground state of the free ion is $^2D$. The fivefold orbital degeneracy is completely removed by a tetragonal crystal field and spin-orbit coupling, leaving a Kramers doublet lowest. In the presence of an external magnetic field **H**, the energy levels of the ground state, including nuclear-spin effects, are determined by the following spin Hamiltonian:

$$\begin{aligned}\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) \\ + A S_z I_z + B(S_x I_x + S_y I_y) \\ + Q'[I_z^2 - \tfrac{1}{3}I(I+1)] - \gamma\beta_N \mathbf{H}\cdot\mathbf{I}, \quad (1)\end{aligned}$$

where $S = \frac{1}{2}$, $I = \frac{3}{2}$, and $Q'$ is related to the nuclear quadrupole moment $Q$ by $Q' = 3eQq/4I(I-1)$. The axes $(x,y,z)$ are the principal axes of the crystalline field at a copper ion site and must be located with respect to the crystallographic axes. The $z$ axis has been taken as the symmetry axis.

The energy levels of Eq. (1) have been evaluated to second order in $A$, $B$, and $Q'$. The result is that hyperfine transitions in which $\Delta m=0$ ($m=$nuclear-spin quantum number) occur at fields given by[23]

$$H_m=\frac{h\nu}{g\beta}-\frac{1}{g\beta}\left\{Km+\frac{B^2}{4h\nu}\left(\frac{A^2+K^2}{K^2}\right)\left(\frac{15}{4}-m^2\right)\right.$$
$$+\frac{1}{8h\nu}\left(\frac{A^2-B^2}{K}\right)^2\left(\frac{g_{\parallel}g_{\perp}}{g^2}\right)^2 m^2\sin^2 2\theta$$
$$-\frac{Q'^2\sin^2 2\theta}{2K}\left(\frac{ABg_{\parallel}g_{\perp}}{K^2g^2}\right)^2 m(14-8m^2)$$
$$\left.+\frac{Q'^2\sin^4\theta}{2K}\left(\frac{Bg_{\perp}}{Kg}\right)^4 m\left(\frac{13}{2}-2m^2\right)\right\}, \quad (2)$$

where

$$g^2=g_{\parallel}^2\cos^2\theta+g_{\perp}^2\sin^2\theta,$$
$$K^2g^2=A^2g_{\parallel}^2\cos^2\theta+B^2g_{\perp}^2\sin^2\theta,$$

and $\theta$ is the angle between **H** and the symmetry axis. Here, $\nu$ is the microwave frequency.

In the present case, crystal symmetry dictates that the $z$ axes of the two $M1$ sites in the unit cell make equal angles with the $ac$ plane. Also, they must lie in a plane which contains the $b$ axis. The same is true for the two $M2$ sites. By observing the spectrum with **H** rotated in two or more crystallographic planes, the values of $g_{\parallel}$, $g_{\perp}$, $A$, $B$, $Q'$, and the directions of the $z$-axes for the different sites are obtained.

The transitions given by Eq. (2) are the so-called allowed transitions for which $\Delta m=0$. When the nuclear quadrupole term $Q'$ is of the same order of magnitude as $B$, normally forbidden transitions, for which $\Delta m=\pm 1$, $\pm 2$, may be quite strong. Bleaney[23] has derived the position and intensity of these lines. Their intensity is proportional to the square of $Q'$, and both their intensity and position are complicated functions of $\theta$. The reader is referred to Bleaney's paper for the exact formulas. These transitions provide a convenient way to measure $Q'$.

## Results and Discussion

Equation (2) predicts that in first order there will be four hyperfine lines which are equally spaced in field by $K/g\beta$. Because there are two isotopes of copper which have different magnetic moments, there are eight lines rather than four. Thus, with the applied field in an arbitrary direction, the four sites in the unit cell will yield thirty-two allowed transitions. This is indeed what we observe. A spectrum which is somewhat less complicated, but still exhibits all the noteworthy features is shown in Fig. 2. This spectrum was taken with the static magnetic field along the $b$ axis. For this orientation all $M1$ sites are equivalent, as are all $M2$'s. Our identification of the lines is the following. Lines 1 through 7 are seven of the eight hfs lines from both isotopes occupying $M2$ sites. Lines 8, 9, 14, 15, 16, 17, 22, and 23 are the corresponding hfs lines from ions on $M1$ sites. Lines 10, 11, 13, 18, 20, and 21 are $\Delta m=\pm 1$ "forbidden" transitions from $M1$ sites, with 10 and 11 and 20 and 21 again being due to the different isotopes. Lines 12 and 19 are $\Delta m=\pm 2$ transitions from $M1$ sites. Line 24 is a $g$ marker having the free-electron $g$ value. It occurs at 3289 G.

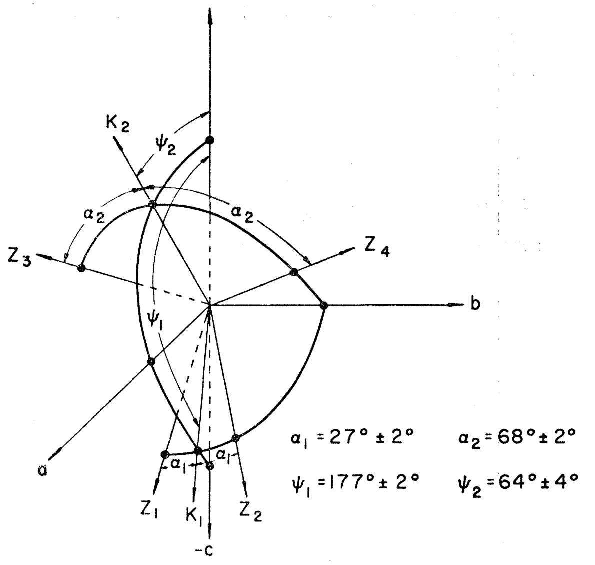

FIG. 3. The directions of the symmetry axes at the four metal ion sites in the unit cell of $Cu{:}Zn(HCO_2)_2 \cdot 2H_2O$ are shown. The axes $\mathbf{Z}_1$ and $\mathbf{Z}_2$ belong to the two $M1$ sites and $\mathbf{Z}_3$ and $\mathbf{Z}_4$ belong to the two $M2$ sites. The vectors $\mathbf{K}_1$ and $\mathbf{K}_2$ lie in the $ac$ plane and bisect the angles between $\mathbf{Z}_1$ and $\mathbf{Z}_2$ and between $\mathbf{Z}_3$ and $\mathbf{Z}_4$, respectively.

Lines 9, 15, 16, and 22 should be of equal height, but a slight misalignment of the crystal has probably caused **H** not to be exactly along the $b$ axis and has produced the height differences. The resonances from ions on $M1$ sites are about eight times as intense as those from $M2$ sites. We have found this to be the case in all crystals that we have investigated. So far, our only explanation for this is that $Cu^{2+}$ ions must prefer $M1$ sites when substituted in small amounts into $Zn(HCO_2)_2 \cdot 2H_2O$. This reasoning may also help to explain why Ingram reported resonances from just two sites per unit cell when he investigated manganese-doped zinc formate.[24] The crystal structure was unknown at that time, and he concluded that it was similar to that of the Tutton salts. His failure to see resonances from two kinds of sites may be due to the fact that the $Mn^{2+}$ ions also preferentially occupy one type of site when put into zinc formate dihydrate.

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[24] D. J. E. Ingram, Phys. Rev. **90**, 711 (1953).

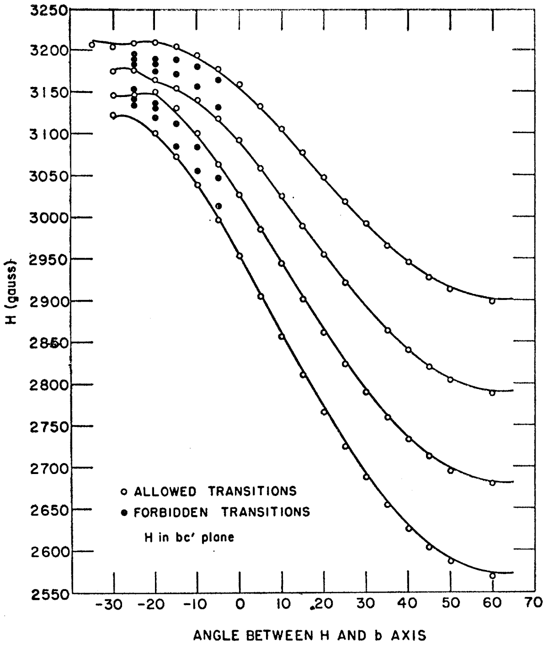

FIG. 4. The angular variation of the position of the resonances from half of the $Cu^{63}(2+)$ ions occupying $M1$ sites is plotted for **H** in the $bc'$ plane ($c'$ is perpendicular to the $ab$ plane). The resonances from the other half of the $Cu^{63}(2+)$ ions on $M1$ sites are symmetrically located about the $b$ axis. The open circles represent the $\Delta m=0$ transitions while the closed ones are $\Delta m=\pm 1$, $\pm 2$ transitions. The solid curves are a computer fit of Eq. (2) to the observed data. The spin-Hamiltonian parameters used for the best fit appear in Table I.

Our assignment of the weaker transitions to ions occupying $M2$ sites is based on the following observation. When the applied field is at an arbitrary direction in the crystal, we observe four distinct spectra, two strong ones and two weak ones. By observing the angular dependence of the $g$ values for each group while **H** was rotated in the $ac$, $a'b$, and $bc'$ planes,[25] we have determined the direction of the symmetry axes relative to the crystal axes for each of the four spectra. These symmetry axes, labeled $\mathbf{Z}_1$, $\mathbf{Z}_2$, $\mathbf{Z}_3$, and $\mathbf{Z}_4$, are shown in Fig. 3. The $\mathbf{Z}_1$ and $\mathbf{Z}_2$ axes are from the strong resonances, while $\mathbf{Z}_3$ and $\mathbf{Z}_4$ are from the weak ones. Now by comparing the directions of these axes to the detailed structure analysis of the nickel salt,[13] we find that $\mathbf{Z}_3$ and $\mathbf{Z}_4$ lie along the O-Cu-O axes at the $M2$ sites. This direction is nearly perpendicular to the plane of four water molecules surrounding the $M2$ site and is expected to be the direction of highest local symmetry. Similarly, the $\mathbf{Z}_1$ and $\mathbf{Z}_2$ axes lie along the O-Cu-O axes at the $M1$ sites, where the oxygens belong to formate groups linking the $M1$ site to the $M2$ sites on either side of it. The identification of this direction as being the symmetry axis at the $M1$ site is consistent with the results of Mössbauer measurements[9,26] on $Fe(HCO_2)_2\cdot 2H_2O$. There it was found that a tetragonal elongation of the oxygen ions surrounding the $M1$ site would produce the ordering of the orbital levels necessary to explain the ratio of the quadrupole splittings observed at the $M1$ and $M2$ sites. Structure analysis indeed shows such an elongation in the direction of this axis.

TABLE I. Measured values of the parameters appearing in the axial-spin Hamiltonian, $\mathcal{H}=g_{\parallel}\beta H_zS_z+g_{\perp}\beta(H_xS_x+H_ys_y)+AS_zI_z+B(S_xI_x+S_yI_y)+Q'[I_z^2-\frac{1}{3}I(I+1)]$.

| | Site 1 | Site 2 |
|---|---|---|
| $g_{\parallel}$ | 2.416 ±0.005 | 2.420 ±0.005 |
| $g_{\perp}$ | 2.077 ±0.007 | 2.066 ±0.007 |
| $A^{63}$ | 0.0124 ±0.0002 $cm^{-1}$ | 0.0134±0.0005 $cm^{-1}$ |
| $B^{63}$ | 0.0023 ±0.0002 $cm^{-1}$ | 0.0026±0.0012 $cm^{-1}$ |
| $Q'^{63}$ | 0.00095±0.00002 $cm^{-1}$ | ≈0.0015 $cm^{-1}$ |

It should be noted that our symmetry axes do not corresponds to those found by Shimada *et al.*[27] for a concentrated specimen. However, the lattice parameters of the crystal they used do not correspond with those of $Cu(HCO_2)_2\cdot 2H_2O$ measured by several other authors.[12,15] Thus, they may not have investigated copper formate dihydrate, but one of several related salts which grow from the same or similar solution.

The spin Hamiltonian parameters for the various sites are listed in Table I. As an example of how they were obtained we show in Fig. 4 the angular variation of the resonances from one $M1$ site as **H** is rotated in the $bc'$ plane. The solid lines are a computer fit of Eq. (2) to the data with the values in Table I yielding the best fit. The unusual angular variation near $-20°$ to the $b$ axis is caused by the second-order terms in Eq. (2) and is reproduced quite well by the solid lines. The value of $Q'$ listed for the $M1$ sites was the best value from the fit to the allowed lines, and also was derived from the position of the "forbidden" lines using the equations of Bleaney.[23] Because the $M2$ spectra are weaker and in general somewhat obscured by the $M1$ lines, we could not get the $M2$ parameters as accurately as the $M1$'s. For instance, the value of $Q'$ listed for the $M2$ sites is based on the observation that the ratio of the intensities of the forbidden lines to allowed lines is approximately four times the corresponding ratio in the $M1$ spectra. As noted previously, this ratio is proportional to $Q'^2$.

It is somewhat surprising that the spin-Hamiltonian parameters are so similar for the two kinds of sites. It is true that both sites are surrounded by six oxygen atoms, but these are quite different oxygens, belonging entirely to formate groups on one site and to both water molecules and formate groups on the other. Our $g$ values are very similar to those obtained for $Cu^{2+}$ in the Tutton salts,[28,29] but significantly different than those for $Cu^{2+}$

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[25] The $a'$ direction is defined as perpendicular to the $b$ and $c$ axes; $c'$ is similarly defined.

[26] G. R. Hoy and F. de S. Barros, Phys. Rev. **139**, A929 (1965).

[27] J. Shimada, H. Abe, and K. Ono, J. Phys. Soc. Japan **11**, 137 (1956).

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[29] B. Bleaney, R. P. Penrose, and B. I. Plumpton, Proc. Roy. Soc. (London) **A198**, 406 (1949).

in $TiO_2$, where the copper ion is surrounded by six oxygen atoms.[30]

## PAIRS

### Background

The technique of electron spin resonance has been used on several occasions to measure the exchange interactions between paramagnetic ions in magnetically dilute solids. This is usually accomplished by replacing a large fraction of the magnetic ions in a crystal with diamagnetic ones, so that the resulting semidilute crystal has a measurable number of isolated pairs of nearest-neighbor (n.n.) magnetic ions. The ESR spectrum from such isolated pairs then yields information about the exchange interaction between the ions. When the isotropic exchange is large enough, it may be measured by observing the temperature dependence of the intensity of the spectrum. The anisotropy in the exchange is obtained from the dependence of the position of the spectrum on the direction of the external magnetic field. In the present case we have measured the isotropic part of the exchange interaction, but because the pair spectrum is obscured by the single-ion spectra for most directions of the external field, we have not been able to determine the anisotropic part.

As noted previously, it is thought that the mechanism for interaction between the metal ions in the magnetic formates is superexchange via the formate linkages. Thus, in a crystal of $Cu:Zn(HCO_2)_2 \cdot 2H_2O$ there are two possible kinds of isolated pairs of n.n. $Cu^{2+}$ ions. The kind which we shall call a $P1$ pair consists of two $Cu^{2+}$ ions occupying n.n. $M1$ sites and the kind we shall call a $P2$ pair consists of one $Cu^{2+}$ ion on an $M1$ site and one on a n.n. $M2$ site. If the ESR spectra from both these kinds of pairs could be observed, the exchange interaction between the ions making up each kind could be measured. The ratio of these exchange constants is important to the understanding of the bulk magnetic properties of $Cu(HCO_2)_2 \cdot 2H_2O$. However, we have observed only one kind of pair spectrum and thus have measured only one exchange energy, the isotropic part of which is 33 $cm^{-1}$. We believe this spectrum to be from $P1$ pairs. The evidence for this and some remarks about the absence of a spectrum from $P2$ pairs will be given after a brief discussion of the spin Hamiltonian for a pair of exchange-coupled ions.

The spin Hamiltonian for a pair of interacting $Cu^{2+}$ ions occupying n.n. $M1$ sites in $Cu:Zn(HCO_2)_2 \cdot 2H_2O$ may be written approximately as the sum of the single-ion Hamiltonians and the exchange terms.

$$\mathcal{H}=\beta(\mathbf{S}_1\cdot\mathbf{g}_1\cdot\mathbf{H}+\mathbf{S}_2\cdot\mathbf{g}_2\cdot\mathbf{H})+\mathbf{S}_1\cdot\mathbf{A}_1\cdot\mathbf{I}_1+\mathbf{S}_2\cdot\mathbf{A}_2\cdot\mathbf{I}_2 \\ +J\mathbf{S}_1\cdot\mathbf{S}_2+\mathbf{S}_1\cdot\mathbf{\Gamma}\cdot\mathbf{S}_2+\mathfrak{D}\cdot\mathbf{S}_1\times\mathbf{S}_2. \quad (3)$$

Here, $J$ is the usual isotropic exchange term, $\mathbf{\Gamma}$ is a traceless tensor representing the symmetric, anisotropic exchange, and the last term involving $\mathfrak{D}$ is the antisymmetric, anisotropic exchange discussed by Dzyaloshinsky[31] and Moriya.[32] We must include this last term because it is allowed by crystal symmetry. Uryû has pointed out that $\mathfrak{D}$ is probably perpendicular to the $b$ axis of the crystal in this case.[20] The $g$ tensors and hyperfine tensors in Eq. (3) are axially symmetric with their axes of symmetry being $\mathbf{Z}_1$ and $\mathbf{Z}_2$ in Fig. 3. It can be shown[33] that when expressed in a system of axes where $\mathbf{K}_1$ of Fig. 3 is the $z$ axis and the $xz$ plane is the $ac$ plane, $\mathcal{H}$ is given approximately by

$$\mathcal{H}\cong g_z\beta S_zH_z+g_x\beta H_xS_x+g_y\beta H_yS_y+A_xS_xI_x+A_yS_yI_y \\ +A_zS_zI_z+J\mathbf{S}_1\cdot\mathbf{S}_2+D[S_z^2-\tfrac{1}{3}S(S+1)] \\ +E(S_x^2-S_y^2)+\mathfrak{D}\cdot\mathbf{S}_1\times\mathbf{S}_2, \quad (4)$$

where

$$S=S_1+S_2, \quad I=I_1+I_2$$

and

$$\begin{aligned} g_x&=g_\perp, \\ g_y&=g_\perp\cos^2\alpha_1+g_{\shortparallel}\sin^2\alpha_1, \\ g_z&=g_\perp\sin^2\alpha_1+g_{\shortparallel}\cos^2\alpha_1, \end{aligned}$$

and

$$\begin{aligned} A_x&=B, \\ A_y&=B\cos^2\alpha_1+A\sin^2\alpha_1, \\ A_z&=B\sin^2\alpha_1+A\cos^2\alpha_1. \end{aligned} \quad (5)$$

The values of $A$, $B$, $g_{\shortparallel}$, $g_\perp$, and $\alpha_1$ are those given in Table I for the $M1$ sites. The term in $D$ is from the axial part of $\mathbf{\Gamma}$, while $E$ is the rhombic component. Equation (4) has been derived assuming $J\gg D$, $E$, $g\beta H\gg A$, $B$, and we have neglected nuclear quadrupole effects. Under these conditions, Eq. (4) leads to the usual singlet and triplet energy levels separated by $J$. The terms in $D$, $E$, and $\mathfrak{D}$ lead to zero-field splittings of the triplet state. If we now put the applied field in the $z$ direction (along $\mathbf{K}_1$ in Fig. 3), and use the usual singlet and triplet wave functions given by

$$\begin{aligned} |0,0\rangle&=(\alpha_1\beta_2-\beta_1\alpha_2)/\sqrt{2}, \\ |1,0\rangle&=(\alpha_1\beta_2+\beta_1\alpha_2)/\sqrt{2}, \\ |1,+1\rangle&=\alpha_1\alpha_2, \\ |1,-1\rangle&=\beta_1\beta_2, \end{aligned} \quad (6)$$

we find the energy levels by perturbation theory to be

$$\begin{aligned} E_{0,0}&=0, \\ E_{1,0}&=J-\tfrac{2}{3}D+(\mathfrak{D}^2/4J)(1+\cos^2\gamma), \\ E_{1,+1}&=J+\tfrac{1}{3}D+g_z\beta H+(\mathfrak{D}^2/8J)(2+\sin^2\gamma) \\ &\qquad +E^2/2g_z\beta H+A_zm/2, \quad (7) \\ E_{1,-1}&=J+\tfrac{1}{3}D-g_z\beta H+(\mathfrak{D}^2/8J)(2+\sin^2\gamma) \\ &\qquad -E^2/2g_z\beta H-A_zm/2, \end{aligned}$$

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[30] H. J. Gerritsen and E. S. Sabisky, Phys. Rev. **125**, 1853 (1962).

[31] I. Dzyaloshinsky, J. Phys. Chem. Solids **6**, 241 (1958).

[32] T. Moriya, Phys. Rev. Letters **4**, 228 (1960); Phys. Rev. **117**, 635 (1960); **120**, 91 (1960).

[33] G. R. Wagner, thesis, Carnegie Institute of Technology, 1965 (unpublished).

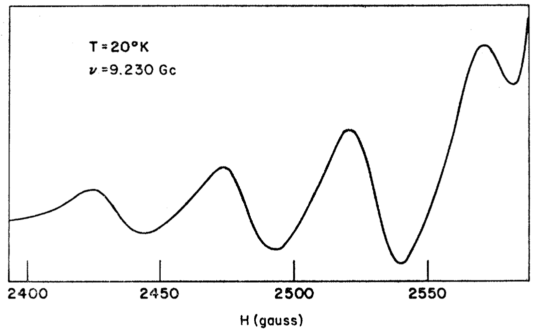

FIG. 5. First derivative of ESR absorption by exchange coupled pairs of $Cu^{2+}$ ions on nearest-neighbor $M1$ sites. Three and one-half of the expected seven hyperfine lines are shown with the high-field half of the spectrum obscured by single-ion resonances. The spectrum was taken with **H** along the $\mathbf{K}_1$ axis of a crystal of $Cu{:}Zn(HCO_2)_2 \cdot 2D_2O$ with $Cu{:}Zn = 0.034$.

where $m$ is the total nuclear-spin quantum number and takes values $m = 3, 2, 1, 0, -1, -2, -3$. The angle $\gamma$ is that between $\mathfrak{D}$ and $\mathbf{K}_1$.

Each of the two allowed transitions within the triplet state $(E_{1,0} \leftrightarrow E_{1,\pm 1})$ will consist of seven hyperfine lines separated in field by

$$A_z/2g_z\beta. \qquad (8)$$

These seven lines will have an intensity ratio of 1:2:3:4:3:2:1 corresponding to the number of ways each $m$ value may be made up.

The temperature dependence of the intensity of the transitions within the triplet state has been given by several authors.[34] If $J$ is the largest term in the Hamiltonian, as we have assumed, and $kT \gg g_z\beta H$, the intensity of the pair spectrum relative to that of a substance having $S = \frac{1}{2}$ and no excited state is given by

$$I \propto 1/(3 + e^{J/kT}). \qquad (9)$$

Thus by comparing the intensity of the pair spectrum to that of a Curie-law standard we may obtain $J$.

## Results

The spectrum which we attribute to pairs of $Cu^{2+}$ ions on n.n. $M1$ sites in $Cu{:}Zn(HCO_2)_2 \cdot 2H_2O$ is shown in Fig. 5. It was taken with **H** along $\mathbf{K}_1$ (defined in Fig. 3) in a crystal having $Cu{:}Zn = 3.4$ mole percent. Only three and a half of the expected seven hyperfine lines are seen because the upper half of the spectrum is obscured by the strong lines from single ions occupying $M1$ sites. The lines are seen to have the expected intensity ratios of 1:2:3:4 and an observed hyperfine separation of 49±2 Oe. The hyperfine separation of the isolated $M1$ ions with **H** in the $\mathbf{K}_1$ direction is 100±2 Oe. Equation (8) predicts that the hyperfine separation for a pair of n.n. $M1$ ions should be half the single ion spacing, and the observed value of 49±2 Oe is in good agreement with this.

We have measured the intensity of the spectrum relative to a paramagnetic standard[35] between 4.2°K and 77°K. The results are shown in Fig. 6. There the solid curve is the theoretical variation from Eq. (9) and the circles are the experimental data fitted to the curve at $T = 20°K$, using $J = 33 \pm 1$ cm$^{-1}$. The fit is excellent with no systematic deviations from the expected curve.

There are several remarks to be made concerning the position of the pair spectrum. The experimental facts are the following: (1) With **H** in the $\mathbf{K}_1$ direction the pair spectrum occurs at a field 225 Oe below the center of the spectra belonging to isolated $M1$ ions. (2) This is the largest separation we have been able to observe, i.e., when **H** is rotated away from the $\mathbf{K}_1$ axis in any direction, the pair spectrum tends to move to higher field, merge with the single ion spectra, and become obscured. (3) We have not been able to find any other pair lines between 0 and 10 kOe. Our lack of any detailed knowledge of the angular dependence of the spectrum makes it impossible to say anything definite about the anisotropic exchange terms. We can, however, make a few qualitative remarks about the experimental evidence just presented. The separation between the pair spectrum and the single $M1$ ion spectrum is probably due to a zero-field splitting of the triplet state of the pairs, since we expect the $g$ values to be very nearly the same and equal to $g_z = 2.343$ in the $\mathbf{K}_1$ directions. [See Eq. (5)]. In fact, this is the maximum $g$ value expected for the pairs according to Eq. (5) and this is in agreement with experimental fact (2) above. If this separation is

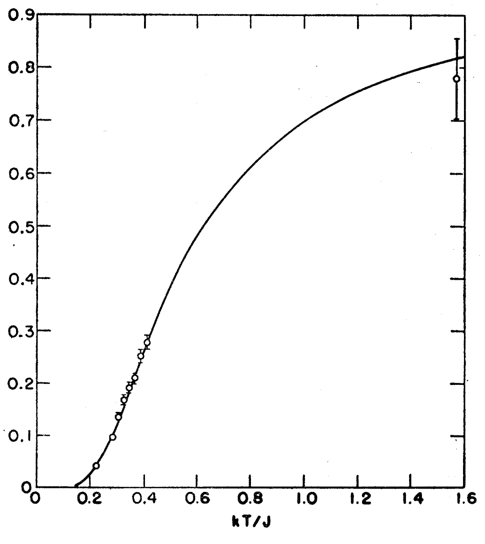

FIG. 6. Solid line is expected variation in intensity of resonance in triplet state which is above singlet ground state by an amount $J$. The curve has been normalized to unity in the high-temperature limit. The circles are our experimental data fitted to the curve at $T = 20°K$ using $J = 33$ cm$^{-1}$.

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[34] See, for example, B. Bleakney and K. D. Bowers, Proc. Roy. Soc. (London) A214, 451 (1952).

[35] As a Curie-law standard we used a bit of dextrose which was charred at 600°C, sealed in a small glass ampule and placed in the cavity with the sample. We are grateful to Professor N. S. Vander Ven for suggesting this as an intensity standard and for supplying us with the charred dextrose.

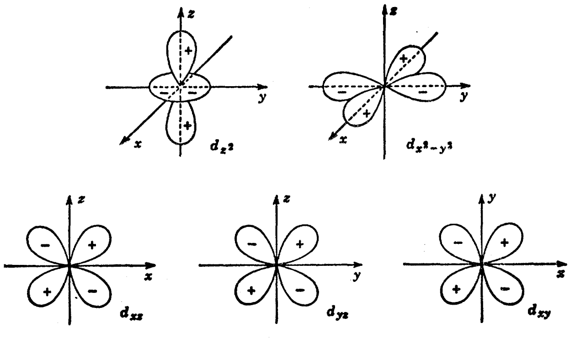

FIG. 7. The $d_\gamma$ and $d_\epsilon$ electronic densities.

due to a zero-field splitting, why have we observed only one of the two allowed transitions within the triplet state? From Eq. (7) we find (neglecting hyperfine terms) that the allowed transitions occur when

$$h\nu = |E_{1,\pm1} - E_{1,0}| = |D' \pm g_z\beta H \pm E'|\,,$$

where $D' = D + (1-3\cos^2\gamma)(\mathfrak{D}^2/8J)$ and $E' = E^2/2h\nu$. We could have $D' \gg h\nu \gg E'$ in which case the observed transition would be either $E_{1,\pm1} \leftrightarrow E_{1,0}$ depending on the sign of $L'$, but then we should observe the same transition at $H \cong 8000$ Oe and we have not. So it appears that $D' < h\nu$. It could be that $D' \approx 0.025$ cm$^{-1}$ and $E' \approx 0$, in which case we have observed one transition with the other falling about 225 Oe above the $M1$ spectrum. But this transition would be obscured by the $M2$ resonances which happen to fall there. It is possible that $D' = 0$, and then $E' = 0.025$ cm$^{-1}$ so that we have observed both transitions occurring at the same field. There is some evidence to indicate that such is the case. That is, the pair spectrum splits into two groups of lines as **H** is rotated away from $\mathbf{K}_1$ in the *ac* plane. All pairs should be equivalent with **H** in the *ac* plane, so this splitting may be due to the removal of the accidental degeneracy of the two transitions that occurs with **H** along $\mathbf{K}_1$. Of course the splitting may be due to a slight misalignment of the crystal, but it is not unreasonable for $D'$ to be zero. This happens if $(1-3\cos^2\gamma)(\mathfrak{D}^2/8J) = -D$. Moryia[32] has estimated $\mathfrak{D} = (g-2)J/g$ and Bleaney and Bowers[34] have derived an expression for $D$ in the case of large $J$; $D \approx [\frac{1}{4}(g_{\shortparallel}-2)^2 - (g_\perp - 2)^2 J]/8$. Using these estimates we find $\gamma \approx 0$ if $D' = 0$. The angle $\gamma$ can be calculated[32] in terms of crystal-field splittings, spin-orbit interactions, etc., but this calculation involves more estimates and some very complicated transfer integrals. A calculation of this type is not warranted here since we just want to show that $D'$ can be zero for some real value of $\gamma$. The direction of $\mathfrak{D}$ may be gotten more easily by magnetic susceptibility measurements on single crystals of these formates.

### Comparision of ESR and Susceptibility

The exchange constant ($|J| = 49$°K) deduced from our study of the $Cu^{2+}-Cu^{2+}$ pair spectrum in $Zn(HCO_2)_2 \cdot 2H_2O$ is larger than might be expected from what is known of the magnetic susceptibility of $Cu(HCO_2)_2 \cdot 2H_2O$. Powder data of Martin and Waterman[36] above 102°K and of Flippen and Friedberg[1] between 14 and 20°K could be well described by a Curie-Weiss law for $S = \frac{1}{2}$ with an average splitting factor $g = 2.13$ and a small ferromagnetic Weiss constant of $\approx 2$°K. Whether, in fact, the materials used in either of these investigations had the same lattice structure as the diluted crystals in which ESR has been studied is not known. Recently, low-temperature single-crystal susceptibility measurements have been undertaken in this laboratory on $Cu(HCO_2)_2 \cdot 2H_2O$ specimens shown by x-ray methods to possess this structure. Preliminary results[11] suggest a possible susceptibility anomaly near 25°K. While implying the presence of larger exchange constants than previously supposed, this result is still not simply reconciled with a $|J|$ value of 49°K. At present we can only suggest that $J$ is quite sensitive to lattice spacing and distortion of the formate group. On this basis, there would be no reason to expect the $J$ values for diluted and concentrated salts to be the same.

The unusual behavior of the dihydrated formates of $Mn^{2+}$ and perhaps also of $Ni^{2+}$ and $Cu^{2+}$ seems to indicate that half of their paramagnetic ions remain essentially free even at quite low temperatures. In contrast, the ferrous salt appears to undergo a single cooperative transition involving long-range ordering of all ionic moments. The following qualitative observations may be relevant to an explanation of this difference. Our ESR data indicate that the crystal field at the $M1$ and $M2$ sites is tetragonal. The symmetry axis (the $z$ axis) at the $M1$ site is along the line from the metal ion to the oxygen atoms from formate groups linking the $M1$ to the two n.n. $M2$'s. The $xy$ plane is that formed by the metal ion and the four oxygens from the four different formates linking the $M1$ site to the four other n.n. $M1$ sites. Similarly, the $z$ axis at the $M2$ sites is along the line from the $M2$ to the oxygens from formates linking the $M2$ to the two n.n. $M1$'s; and the $xy$ plane is that formed by the water molecules. At both sites the octahedral surroundings are distorted by a tetragonal elongation along the $z$ axis. In the case of $Cu^{2+}$, this means that the ground state is one in which the single hole in the $3d$ shell is in a $d_\gamma$ orbital designated as $d_{x^2-y^2}$ and conventionally represented as in Fig. 7. Thus the lobes of the hole wave function lie in the positive and negative $x$ and $y$ directions and the hole of the $M1$ ion interacts much more strongly with the formates linking it to other $M1$'s than to $M2$'s. Similarly, the wave function of the hole of the $M2$ ion points in the direction of the water molecules and not the formates which link it to n.n. $M1$'s. Thus, one expects the exchange between n.n. $M1$ ions to be much stronger than between $M1$'s and $M2$'s. (If this is the case, it explains why we have not been able to see a pair spectrum from $P2$ pairs.

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[36] R. L. Martin and H. Waterman, J. Chem. Soc. **1959**, 1359 (1959).

If the exchange interaction is quite small, the pair spectrum is not sufficiently different from the single-ion spectrum to be recognized.)

On the other hand, the ground state of the $Fe^{2+}$ ion at either the $M1$ or $M2$ site involves the $d_\epsilon$ orbitals indicated in Fig. 7. Consequently, there may be nearly equal interaction between the metal ions and each of their six ligands. Thus, the exchange interaction between n.n. $M1$ ions would be comparable to that between an $M1$ and an $M2$ yielding a cooperative transition involving all the ions at the same time.

In a similar manner, the behavior of the $Ni^{2+}$ salt might be explained by noting that the ground state in a cubic field consists of a "hole" in each of the $d_\gamma$ orbitals and that any tetragonal elongation along the $z$ axis will tend to concentrate the "hole" wave function in the $xy$ plane. This could lead, again, to a greater exchange interaction between two $M1$'s than between an $M1$ and an $M2$.

## ACKNOWLEDGMENTS

We are grateful to R. D. Pierce and Mrs. S. de S. Barros for permission to cite unpublished heat-capacity and magnetic-susceptibility data. We wish to thank Professor N. S. Vander Ven for several theoretical and experimental contributions to this work. We had several illuminating discussions with Professor N. Uryû. One of us (G.R.W.) gratefully acknowledges the financial support received from the Westinghouse Research Laboratories during the course of this work.

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# Magnetic Field Dependence of the Knight Shift*

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The apparent inconsistencies among the theories of de Haas–van Alphen oscillations in the Knight shift due to Das and Sondheimer, to Stephen, and to Dolgopolov and Bystrik are resolved. The calculation of the Knight shift is treated by a method which goes beyond the semiclassical approximation used by these authors. It is found that for polyvalent metals the dominant magnetic field dependence may be due to the behavior of the electronic wave function, rather than to the density of states.

## I. INTRODUCTION

A STRONG field dependence of the Knight shift has been observed in tin.[1] Since the magnitude of the effect is considerably larger than previous theoretical estimates would indicate, and since there are apparent disagreements among these theories a survey and appraisal of this work seems timely. In addition to serving these ends, some additional considerations are advanced leading to a field dependence whose nature lies outside the scope of the previous theories, and which may be important for the interpretation of experiments.

We begin with a rederivation of the magnetic shielding constant followed by an examination of validity of the usual expression for the zero-field limit. The earlier work on the oscillatory behavior of the Knight shift is then discussed and, beginning with Sec. II, a different theory for this phenomenon is presented.

The vector potential due to a nuclear magnetic moment may be written

$$\mathbf{A}(\mathbf{r})=\boldsymbol{\mu}_n\times r^{-3}\mathbf{r}.$$

When this is placed in the Hamiltonian for an electron in a magnetic field it gives rise to the terms

$$\begin{aligned}\mathcal{H}_n&=\mathcal{H}_d+\mathcal{H}_p,\\ \mathcal{H}_d&=(2\mu_0\mu_n/\hbar r^3)L_z+(e^2H\mu_n/2mc^2r^3)(x^2+y^2),\qquad(1.1)\\ \mathcal{H}_p&=(16\pi/3)\mu_0\mu_n\delta(\mathbf{r})S_z+2\mu_0\mu_n[(3z^2-r^2)/r^5]S_z,\end{aligned}$$

(the nuclear moment has been taken in the $z$ direction and $L_z$ is the component of angular momentum about the $z$ axis). The first term of the paramagnetic part is the Fermi contact interaction, the only term ordinarily considered in discussions of the Knight shift. The second term of $\mathcal{H}_p$ vanishes for cubic crystals and is responsible for the so-called anisotropic Knight shift. The diamagnetic terms are generally dismissed on the grounds that the orbital momentum of conduction electrons is quenched and that the diamagnetic shielding term is small compared to the singular Fermi term.

The Knight shift is given essentially by the magnetic shielding constant

$$\sigma=-H^{-1}(\partial F/\partial\mu_n)_{\mu_n=0},\qquad(1.2)$$

where $F$ is the free energy and $H$ is the applied magnetic field. We consider the independent-particle model for a metal and in addition neglect lattice vibrations.

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* This study was supported by the U. S. Air Force Office of Scientific Research Grant No. AF-AFOSR-260-66.

[1] J. M. Reynolds, R. Goodrich, and S. Kahn, Phys. Rev. Letters **16**, 609 (1966).