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Linear-Chain Behavior of the Spin-$\frac{1}{2}$ Copper Salt *α-bis*(*N*-Methylsalicylaldiminato)-Copper(II)

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The spin-$\frac{1}{2}$ linear-chain system *α-bis*(*N*-methylsalicylaldiminato)-copper(II) has been investigated by two techniques to elucidate its one-dimensional behavior. First, room- and low-temperature structural information as determined by x-ray diffraction points out that the Cu(II) spin-$\frac{1}{2}$ ions are ordered in a linear arrangement 3.33 Å apart along the chain with a large 9.19-Å separation between chains. Then electron-spin-resonance (ESR) data are presented to show that the magnetic system is also one dimensional. The relevant ESR data are the linewidth anisotropy and the line shape at several orientations. Both of these quantities measured by ESR show marked differences from normal three-dimensional behavior and are explained in terms of a one-dimensional model.

INTRODUCTION

Because of the interesting structural properties of *α-bis*(*N*-methylsalicylaldiminato)-copper (*α*-CuNSal), an investigation to refine the structural data and elucidate its magnetic properties was undertaken. Structural determinations show that this material consists of a series of linear chains of Cu(II) ions. Along a given chain, the Cu-Cu separation is 3.33 Å, while the minimum distance between chains is 9.19 Å. Since the Cu(II) ion has one unpaired *d* electron with quenched orbital magnetism, it is usually described as a nearly free spin with $S=\frac{1}{2}$.[1] If the spins are coupled through an exchange interaction, the system should exhibit properties characteristic of an isolated linear magnetic chain. The thermodynamics and the spin dynamics of a linear chain are both of current theoretical interest and it is the purpose of this paper to present experimental results on one well-characterized system. The present work presents more detailed information than appears in a preliminary account[2] of this and another copper linear chain. In the present paper two types of measurements are presented. First, the structural data are presented and used as evidence to point out the one-dimensional character of this material. Then, electron-spin-resonance (ESR) data which show the one dimensionality of the spin dynamics will be treated. The exchange strength along the chain has been determined by susceptibility measurements[3] which also reflect the one-dimensional behavior of this system.

STRUCTURAL PROPERTIES

Crystals of *α*-CuNSal were grown by first preparing *bis*-salicylaldehyato-copper(II) (from the reaction of stoichiometric quantities of reagent-grade copper acetate and spectroscopic-grade salicylaldehyde in a slightly ammoniated solution), which was then dissolved in ethyl alcohol and reacted with methylamine. The material was recrystallized twice from chloroform. Green orthorhombic needles ~ 1 cm long were grown by the slow evaporation of the chloroform solution.

At room temperature, *α*-CuNSal crystallizes in space group *Ibam* with cell constants $a_0=9.191(1)$ Å, $b_0=24.592(2)$ Å, and $c_0=6.660(1)$ Å, as determined by a least-squares refinement of high (2θ) angles obtained with a 115-mm-diam Weissenberg cassette employing Straumanis film loading. The crystal structure consists of stacks of planar copper-chelate molecules [Fig. 1(a)] situated parallel to the *c* axis.[4] The Cu-Cu separation along such stacks is 3.33 Å, while the two next-nearest separations to adjacent stacks are 9.19 and 13.1 Å. In this structural arrangement, the copper ions are located in 000, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and $\frac{1}{2}\frac{1}{2}0$ on sites of $2/m$ symmetry while the remainder of the chelate molecule lies on the symmetry mirror in a *trans*-configuration. The present refinement of 560 three-dimensional observed Mo $K\alpha$ intensity data is in good agreement with the previous study.[4] With these data, the molecules are shown to undergo anisotropic thermal vibrations, with a component along the *c* direction generally about three times as large as that for the in-plane (*ab*) component.

Upon cooling to ~ 190 K, the crystal structure reversibly transforms from orthorhombic to monoclinic symmetry. Lattice constants for this low-temperature phase are $a_0=9.16(1)$ Å, $b_0=24.54(3)$ Å, $c_0=6.55(1)$ Å, $\beta=94.2°$. Although crystals were invariably twinned in the low-temperature phase, systematic absences suggest the probable space group to be $I2/a$. The striking similarity of the room-temperature and low-temperature photographs (when the usual temperature dependence of the intensity data is taken into account) suggests very small, if any, changes in the

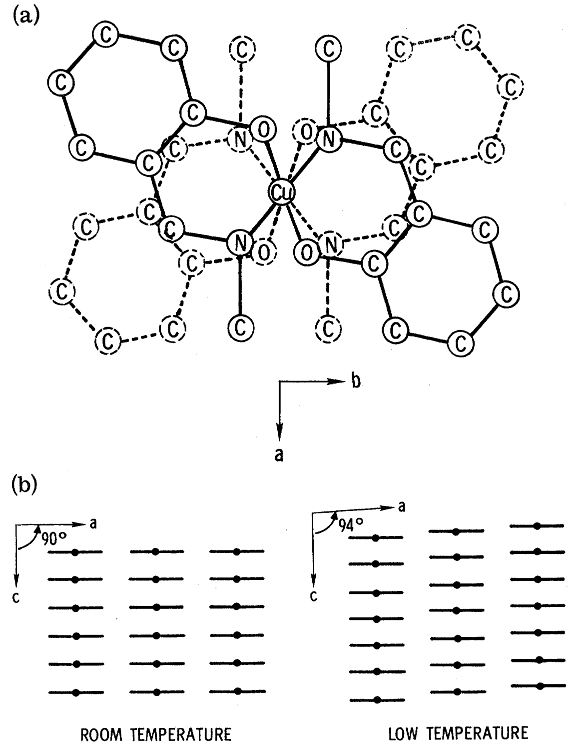

FIG. 1. (a) This view illustrates two molecules of CuNSal. One is shown in dashed lines, the other in solid. The planar molecules stack upon each other as illustrated along the crystallographic c axis. (b) The spatial arrangement of the CuNSal molecules is shown for both the high-temperature and the most probable low-temperature phases. The linear chain stacking of Cu(II) ions is clearly evidenced in this structure.

relative orientation of the molecules in the c-axis linear chains. This is evidenced by the fact that no transition effects were noted in the ESR spectrum or the susceptibility.[3] The relative positions of the copper ions to one another shift slightly, as indicated in Fig. 1(b). It is probable that this small repositioning of the chains results from the short near-neighbor molecular contact separations. It should be noted that this low-temperature polymorph is different from the other two forms (besides the room-temperature *Ibam* α form) which have been reported.[5]

ELECTRON-SPIN-RESONANCE DATA

The ESR of the Cu(II) ions was performed in a 100-kHz field-modulated spectrometer operating at 23.37 GHz. The spectrometer is capable of operating from 2 to 300 K, but the measurements discussed here were taken at 76 K. The data at room temperature are identical but the lower temperature was chosen because of increased signal strength. Susceptibility measurements[3] show that the exchange strength J/k is 3.2 K and is antiferromagnetic. The 76-K temperature is thus well in the high-temperature region. The site symmetry at the Cu site is $2/m$ so it is expected that the spin-$\frac{1}{2}$ system would have three orthogonal principal axes with three corresponding g values. The crystalline c axis, by symmetry, is clearly one of these axes. First, the crystal was mounted so that the magnetic field could be rotated in the plane perpendicular to the c axis. In this plane the field for resonance, i.e., g value, and the linewidth were independent of orientation; this indicates that the symmetry of the g tensor is at least axial and characterized by at most two g values, i.e., $g_\parallel$ along the c axis and $g_\perp$ in the perpendicular plane. For all subsequent work, the crystal was oriented so that the applied magnetic field could be varied from the c axis to the perpendicular plane. In this plane the field for resonance was dependent on the orientation and followed the behavior expected for an axial system. The g values measured were

$$g_\parallel = 2.214 \pm 0.001\ , \quad g_\perp = 2.047 \pm 0.001\ .$$

These values are typical of those found for the Cu(II) ion.[1]

LINE-BROADENING MECHANISM

Magnetic-dipole line-broadening mechanisms resulting from coupled spin systems yield information about the dimensional behavior of such spin systems and have previously been considered. Although no exact or definitive treatment has been presented, several models have proven very useful to explain the relaxation and line-broadening mechanisms in a wide variety of physical systems. Van Vleck[6] calculated the second and fourth moments of the absorption line shape. He showed that the second moment is independent of the exchange strength, but the exchange increased the value of the fourth moment. From this information he argued that the exchange interaction narrows the linewidth measured experimentally. Anderson and Weiss,[7] using statistical arguments and certain assumptions about the line-broadening mechanisms, used the moments of Van Vleck to predict the actual line shapes and widths found in ESR measurements. They found that the Fourier transform of the line shape $\varphi(\omega)$ could be expressed as

$$\varphi(\tau) = \exp\left[-\omega_p^2 \int_0^\tau dt\,(\tau - t)\,\Psi_{\Delta\omega}(t)\right]\ , \tag{1}$$

where ω_p^2 is the Van Vleck second-frequency moment of the line and $\Psi_{\Delta\omega}(t)$ is the normalized $[\Psi(0) = 1]$ correlation function of the random modulation of the spins by the perturbing interaction. To derive expression (1), an assumption of Gaussian random modulation was employed. In three-dimensional systems where many neighbors are involved

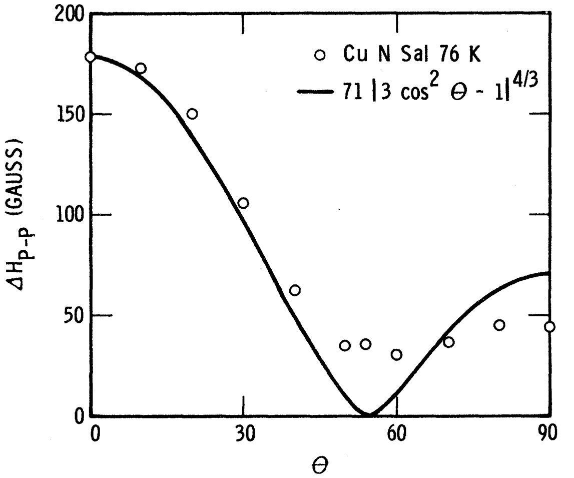

FIG. 2. Angular dependence of the peak-to-peak derivative linewidth for the spin-$\frac{1}{2}$ system CuNSal as measured at 76 K. This is compared with the functional form of the dominant linewidth mechanism expected for a one-dimensional system. Here θ is the angle of the applied field from the chain axis.

in the modulation of a given site, this seems to be justified; however, in the one-dimensional case, this is open to question. Kubo[8] has shown that (1) is the first term in a cumulant expansion and that correction terms to (1) disappear for a Gaussian random process. Since information on the correlations involved in $\Psi_{\Delta\omega}(t)$ was lacking at the time, Anderson and Weiss[7] were forced into a second Gaussian assumption. They chose a Gaussian form for $\Psi_{\Delta\omega}(t)$ in order to use their limited information to calculate actual line-shape functions from the calculated moments of the line. Since that time, more information has become available on the correlations involved in $\Psi_{\Delta\omega}(t)$. Carboni and Richards[9] have calculated $\Psi_{\Delta\omega}(t')$ for finite chains using exact numerical correlation functions of the form $\langle S_i^+(t) S_j^z(t)\, S_l^z(0)\, S_m^-(0)\rangle$. Gulley *et al.*[10] have worked with non-Gaussian forms of $\Psi_{\Delta\omega}(t)$ which they justify in terms of a spin-diffusion model and have achieved success in fitting three-dimensional linewidths. Their theory has also been applied with some success to the one-dimensional case.[11] Hennesy, McElwee, and Richards[12] have treated the four-spin functions explicitly for the one-dimensional case. They conclude that the individual four-spin functions, as the one above, do not show the one-dimensional diffuse behavior. The functions individually have a time dependence which for long times goes as t^{-1}. The sum of these functions, which appears in the expression for the EPR line shape, however, shows a long-time dependence which goes as $t^{-1/2}$. This $t^{-1/2}$ behavior is the same as the long-time dependence of the two-spin functions which represent spin diffusion. The latter point is discussed in Ref. 11.

The term $\Psi_{\Delta\omega}(t)$, which appears in the expression for the EPR line shape (1), arises from the dipole-dipole interaction Hamiltonian. As is customary in a treatment of exchange narrowing, it is convenient to separate the dipolar Hamiltonian into two parts. The first is the secular part, i.e., the part that is diagonal in the unperturbed or Zeeman Hamiltonian, of the form $[F(r_{ij})(3\cos^2\theta - 1)(\vec{S}_i \cdot \vec{S}_j - 3S_i^z S_j^z)]$. The second part, containing the nonsecular terms, has an angular dependence of $\sin\theta\cos\theta$ and $\sin^2\theta$ and a time dependence of $e^{-i\Delta M\omega_0 t}$, where $\Delta M = 1, 2$ is the change in Zeeman quantum number associated with the transition. As a result of the modulation of the time dependence of the nonsecular terms, the very-long-time diffusive behavior is washed out. These terms then have a finite integral in (1) and this contributes a simple exponential to $\varphi(t)$. The final expression for $\varphi(t)$ is that given in Ref. 11,

$$\varphi(t) \sim \exp[-A_1(3\cos^2\theta - 1)^2 t^{3/2} - A_2 f(\theta) t] \; . \qquad (2)$$

The angular dependence of $f(\theta)$ is that connected with the nonsecular terms discussed previously. The dominant line-broadening term is the first one except when the angular factor causes it to be small. In this term the time is scaled by $[3\cos^2\theta - 1]^{4/3}$. This angular factor, then, is expected to dominate the angular dependence of the linewidth if the long-time diffusive behavior is found in a

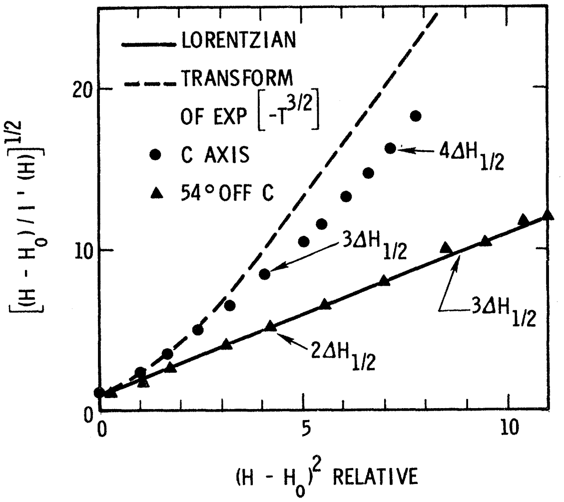

FIG. 3. ESR derivative spectrum. The coordinates are chosen so as to yield a straight line for a Lorentzian shape. The scale is such that data and theory are normalized to a slope of 1 and a value of 1 at the origin. Multiples of the respective half-widths at half-power absorption are indicated.

one-dimensional system. The angular dependence of the peak-to-peak derivative linewidth is shown in Fig. 2 along with the predicted functional form. The angular dependence as seen here is in very good agreement with the one-dimensional form. The expression for $\varphi(t)$ above also predicts several other facets of the EPR line shape. At $\theta = 0^\circ$, i.e., with the magnetic field along the chain axis, $\varphi(t)$ is given by $\exp(-4A_1 t^{3/2})$ since the angular factors in the second term vanish at this orientation. At θ near 54°, where $3\cos^2\theta - 1 = 0$, the line shape should be Lorentzian. Figure 3 shows a comparison of the line shape with the predicted form for these two angles. In the present experiment the data derived from the field-modulated EPR spectrometer are the derivative line shapes. For this reason the function plotted in Fig. 3 is in terms of the line-shape derivative. The function chosen for the ordinate of the plot is one that gives a straight line for a Lorentzian when plotted versus the square of the position from line center. The line-shape function derived from the Fourier transform of $e^{-t^{3/2}}$ is also presented on this figure for comparison with experiment. The predictions of the one-dimensional exchange-narrowing theory are seen to be followed in both figures. The deviations from predicted behavior at $\theta = 0^\circ$ in Fig. 3 are due possibly to residual interchain-coupling effects.[12]

CONCLUSION

The theory of the effects of diffusion on EPR line shape has been treated previously and confirmed in the spin-$\frac{5}{2}$ linear chain $(\mathrm{CH_3})_4\mathrm{NMnCl_3}$ (TMMC).[11] The case of spin $\frac{1}{2}$, however, is unique in many ways and uncertainty had grown about whether the same theory applied in this case. The classic spin-$\frac{1}{2}$ linear chain $\mathrm{Cu(NH_3)_4SO_4 \cdot H_2O}$ (CTS)[13,14] has a Lorentzian line shape[15,12] out to at least 13 half-widths for fields directed along the crystalline c axis. From this evidence it could be speculated that the case of spin $\frac{1}{2}$ is anomalous because of the large quantum fluctuations which occur. An example of this is the x-y model[16] where moments predict transport in a linear chain which is only expected to be diffusive for $S \neq \frac{1}{2}$. In these systems certain coefficients which appear have factors of $(2S-1)$ which change the character of the problem for spin $\frac{1}{2}$. This points out the fact that spin-$\frac{1}{2}$ anomalies are possible and different behavior could occur for a $S = \frac{1}{2}$ system. The present experiment points out the evidence that the correlation functions involved in the EPR linewidth are diffusive and that the spin-$\frac{1}{2}$ system is not anomalous in this case.

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