$$\sum_m \delta n^\sigma_{B\,dm}(\vec{r}) \xrightarrow[r\to\infty]{} -\frac{5\alpha}{4\pi^2} A r^2 e^{-\lambda r} \frac{2\epsilon_F}{k_F r^2} \frac{2m}{\hbar^2} (I_{dk_F} - J_{dk_F}) \times \frac{\sin\delta^\sigma_d(\epsilon_F)}{\Gamma_d(\epsilon_F)} \cos[k_F r + \delta^\sigma_d(\epsilon_F)] . \quad \text{(B2)}$$

The contribution of $\delta n^\sigma_{dm\,B}(\vec{r})$ is exactly the same as Eq. (B2). Using Eq. (22b) for A and Eq. (26b) for $\Gamma_d(\epsilon_F)$, the sum of Eqs. (8b) and (8c) is

$$\delta n^\sigma_{Bd}(r) = \sum_m [\delta n^\sigma_{B\,dm}(\vec{r}) + \delta n^\sigma_{dmB}(\vec{r})] \xrightarrow[r\to\infty]{} -\frac{5\alpha}{2\pi^2} k_F^3 \left[\frac{32}{45}\left(\frac{\lambda}{k_F}\right)^7 \frac{\epsilon_F}{\Gamma_d(\epsilon_F)}\right]^{1/2} \times \sin\delta^\sigma_d(\epsilon_F)\, e^{-\lambda r} \cos[k_F r + \delta^\sigma_d(\epsilon_F)] . \quad \text{(B3)}$$

The contribution of Eq. (8a) is given for any r by

$$\delta n^\sigma_{dd}(r) = \frac{5}{4\pi} A^2 r^4 e^{-2\lambda r} . \quad \text{(B4)}$$

Of course, the well-known asymptotic form of Eq. (8d) is

$$\delta n^\sigma_{BB}(r) \xrightarrow[r\to\infty]{} -\frac{5\alpha^2}{4\pi^2 r^3} \sin\delta^\sigma_d(\epsilon_F) \cos[2k_F r + \delta^\sigma_d(\epsilon_F)] . \quad \text{(B5)}$$

Typical parameters for systems of the CuMn type are $k_F \sim 1$ Å^{-1}, $a_{nn} \sim 3$ Å, and $\lambda \sim 5$ Å^{-1}. Using these values in Eqs. (B3)–(B5) yields the estimates

$$k_F^{-3}\delta n^\sigma_{dd}(a_{nn}) \sim 8.4\times 10^{-9} ,$$

$$k_F^{-3}|\delta n^\sigma_{Bd}(a_{nn})| \lesssim 0.5\alpha \sin\delta^\sigma_d(\epsilon_F)\times 10^{-4} ,$$

and

$$k_F^{-3}|\delta n^\sigma_{BB}(a_{nn})| \lesssim 0.5\alpha^2 \sin\delta^\sigma_d(\epsilon_F)\times 10^{-2} . \quad \text{(B6)}$$

It is seen that δn^σ_{dd} and δn^σ_{Bd} are orders of magnitude smaller than δn^σ_{BB}. These estimates are based on using asymptotic forms even as close as the first-nearest-neighbor distance, but these are quite adequate for obtaining relative orders of magnitude.

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Magnetic Susceptibility Measurements of the Spin-$\frac{1}{2}$ Linear-Chain *α-bis*-(N-Methylsalicylaldiminato)-Copper (α-CuNSal)†

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The susceptibility of the spin-$\frac{1}{2}$ linear chain α-CuNSal has been measured by the Faraday-balance technique from 2–300 K. The measurements over the entire range can be understood in terms of several approximations applicable to the high- or low-temperature regimes of the Heisenberg linear chain. From these models the nearest-neighbor-exchange strength has been obtained by two different techniques and its value determined to be $J/k = -3.2 \pm 0.2$ K. The excellent fit of the magnitude and temperature dependence of the data to these approximations over this wide temperature range confirms the one dimensionality of the system and yields an accurate measurement of the exchange constant.

INTRODUCTION

X-ray crystallography studies[1,2] have shown that *α-bis*-(N-methylsalicylaldiminato)-copper (α-CuNSal) is highly one dimensional in structure with a Cu-Cu separation of 3.33 Å along the chain or *c* axis and a minimum distance between chains of 9.19 Å. Electron-spin-resonance- (ESR) line-shape experiments[2,3] indicate that the exchange interaction between non-nearest-neighbor Cu atoms is small compared to nearest-neighbor exchange coupling. Previously, the classic spin-$\frac{1}{2}$ linear-chain system $Cu(NH_3)_4SO_4 \cdot H_2O$ has been shown,[4] on the basis of magnetic-susceptibility and specific-heat data, to agree with the calculations of Bonner and Fisher[5] (BF) for a spin-$\frac{1}{2}$ one-dimen-

sional antiferromagnet. In this paper we report bulk magnetic-susceptibility measurements on powdered samples of α-CuNSal at temperatures between 2 and 300 K. Above 10 K the results are analyzed in terms of the constant-coupling approximation (CCA).[6] J/k, the exchange constant divided by Boltzmann's constant, is found to be -3.2 K, the minus sign implying antiferromagnetic interaction between Cu atoms. Below 10 K the data are compared to calculations of Bonner and Fisher.[5] The value of J obtained from this analysis agrees with the high-temperature result.

MEASUREMENTS

Samples of α-CuNSal, used in the x-ray and ESR studies,[1-3] were analyzed for impurities by atomic-absorption spectroscopy. It was found that the concentration of magnetic impurities was below 5 ppm. Essentially identical susceptibility results were obtained after the samples were recrystallized several times.

Measurements were taken using a Faraday balance[7] designed to operate in the temperature region 2–300 K. The absolute accuracy has been determined from several calibration runs to be $\pm 1\%$ for susceptibility values and ± 0.2 K for temperatures. Typically, four different field gradients were used at each temperature to provide a check on random errors. In addition, the bulk magnetic moment at 300 K was recorded for several values of the magnetic field ranging from 1 to 5.5 kOe. Plotting moment vs field gives a straight line passing through the origin if there are no ferromagnetic particles present.

ANALYSIS

In Fig. 1, $(\chi-\chi_0)^{-1}$ is displayed as a function of temperature above 10 K. The constant χ_0, which arises principally from orbital diamagnetism, was determined from a least-squares analysis of the data to

$$\chi = \chi(T) + \chi_0 \ . \tag{1}$$

χ_0 was found to be -1.0×10^{-4} emu/mole, which is in reasonable agreement with the computed orbital diamagnetism.[8]

The Hamiltonian for a system in which only nearest neighbors interact through a Heisenberg exchange mechanism can be written

$$\mathcal{H} = -2J\sum_{i=1}^{N}\vec{S}_i\cdot\vec{S}_{i+1} - g\mu_B\sum_{i=1}^{N}\vec{H}\cdot\vec{S}_i \ , \tag{2}$$

when the system is acted upon by an applied field $\vec{H}$. In this expression μ_B is the Bohr magneton and g is the gyromagnetic ratio appropriate to the system. At finite temperatures the statistical mechanics arising from this Hamiltonian for an infinite chain cannot be solved exactly. BF have solved Eq. (2) exactly for $S=\frac{1}{2}$ and finite chains with $N\leq 11$.[5] Over a wide temperature range around $|J|/kT=1$, they were able to extrapolate their results to the infinite chain case. Other approximate schemes have been employed for the solution to Eq. (2). Molecular-field theory simply treats one spin in the presence of an effective field which averages over the interactions with its neighbors. The CCA treats a pair of spins exactly and again employs an effective field. The advantage of the latter schemes is that they yield analytic expressions for the susceptibility vs temperature while the BF results are tabular.

The temperature-dependent part of the susceptibility $\chi(T)$ in Eq. (1) can in general be represented by a power series[9] in $j=J/kT$,

$$\chi(T) = (C/T)\,(1 + A_1 j + A_2 j^2 + \cdots) \ . \tag{3}$$

The molecular-field-approximation (MFA) expression for a system with a spin density of N and z neighbors coupled by an exchange interaction J is

$$\chi_{\mathrm{MFA}}(T) = \frac{C}{T+\theta} = \frac{C}{T}\left(1 - \frac{\theta}{T} + \frac{\theta^2}{T^2} - \cdots\right) \ , \tag{4}$$

where C is the Curie constant $\equiv Ng^2\mu_B^2 S(S+1)/3k$ and θ is the Curie temperature $\equiv -2zJS(S+1)/3k$. Equation (4) is correct to the $A_1 j$ term in Eq. (3) and is therefore a reasonable estimate of $\chi(T)$ for sufficiently large temperatures that $\theta^2/T^2 < \epsilon$, where ϵ reflects the fractional accuracy of the data ($\sim 1\%$ in our case). Since $\theta = -J/k$ for a spin-$\frac{1}{2}$ linear chain, the lowest acceptable temperature is $10\theta \cong 30$ K. Fitting susceptibility data to Eq. (4) above 10θ however, gives poor results for the determination of $J/k = -\theta$. Since θ is the temperature at which $\chi^{-1}=0$, it is obtained by extrapolating

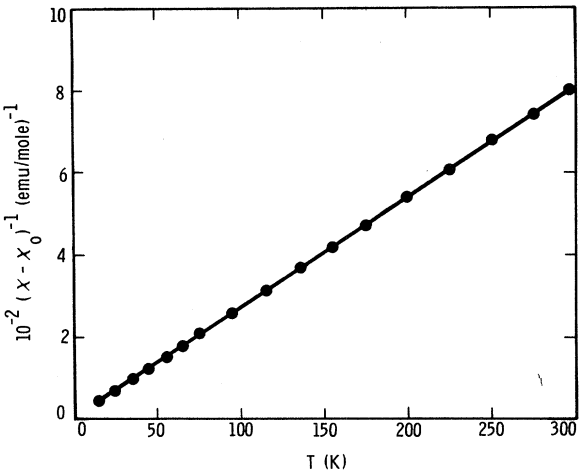

FIG. 1. Reciprocal susceptibility above 10 K after correction for temperature-independent contributions. The solid curve represents a least-squares fit of the data to the constant-coupling approximation.

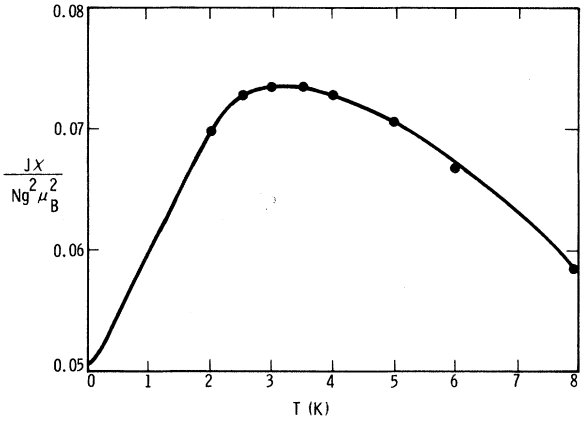

FIG. 2. Comparison of low-temperature susceptibility to the calculation of Bonner and Fisher (solid curve) for a spin-$\frac{1}{2}$ linear-chain antiferromagnet.

χ^{-1} vs T to $T=-\theta$, and this cannot be very precise if the minimum temperature is 10θ. In fact, it was our experience that systematic truncation of the data set just above 30 K resulted in significant variations in the value of J and its standard deviation.

In order to improve the fitting procedure, it is necessary to include additional terms in Eq. (3). This is conveniently accomplished in analytical form by using the expression for $\chi(T)$ from CCA theory[6]

$$\chi_{\mathrm{CCA}}(T)=\frac{C}{T}\left(\frac{4}{ze^{-2j}-(z-4)}\right), \tag{5}$$

where z is the number of magnetic nearest neighbors. For $z=2$ and spin-$\frac{1}{2}$ particles,

$$\chi_{\mathrm{CCA}}(T)=\frac{2C}{T}\left(\frac{1}{e^{-2j}+1}\right) \tag{6}$$

with $C=Ng^2\mu_B^2/4k$. This expression is correct to the j^2 term in Eq. (3), since the CCA takes pairwise interactions into account explicitly. For a one-dimensional system there can be no closed diagrams[10] involving three particles; thus, Eq. (6) is correct to j^3 for a linear chain. This lowers the estimated cutoff temperature to about 10 K, a significant improvement over the molecular-field approximation. In fact, comparison of Eq. (5) with the BF results[5] shows less than 1% difference at $2|J|/k$ or 6 K in this case. Using Eqs. (1) and (6) to fit the data above 10 K resulted in $J/k=-3.2$ K, which was insensitive to the truncation procedure. The solid curve in Fig. 1 represents the best fit to Eq. (6).

Having established the value of J, we turn to an analysis for $T<10$ K. In Fig. 2 the solid curve represents the BF result[5] for $\chi(T)$, with $\gamma=1$ (Heisenberg case) and $J<0$; the dots are our data. The maximum susceptibility $\chi_{\max}$ is related to J through

$$\chi_{\max}=0.07346\, Ng^2\mu_B^2/|J| \ . \tag{7}$$

Using the powder average for $g^2=\frac{1}{3}g_{\parallel}^2+\frac{2}{3}g_{\perp}^2=4.427$ obtained from ESR data,[2] we find $|J|/k=3.2$ K in good agreement with the analysis above 10 K. BF also relate J to the temperature $T_{\max}$ at which $\chi_{\max}$ occurs: $kT_{\max}=1.282|J|$. This is expected to be far less sensitive than Eq. (7) and predicts $T_{\max}=4.1$ K. The spin density N in Eq. (7) is required to be known with reasonable accuracy in order to obtain an accurate measure of J. To check this point the absolute susceptibility measured at $T>10$ K was checked against that calculated from Eq. (6) using the known g values, molecular weight of the material, the diamagnetic correction, and the mass as given by the balance. The agreement in absolute susceptibility, particularly $C=0.410\pm0.003$ emuK/mole from Eq. (6), was within 1% of the calculated value. This confirms the accuracy of the constants used in the computation of J/k from Eq. (6).

CONCLUSIONS

By measuring the susceptibility of a powder sample of α-CuNSal over the temperature range 2–300 K, a value of the nearest-neighbor exchange constant $J/k=-3.2\pm0.2$ K has been determined. Utilizing the information from structural and ESR measurements that this system is highly one-dimensional, the susceptibility could be fit to an appropriate model. In the high-temperature region $T>3|J|/k$, the CCA gave an excellent fit to the data. In this regime the exchange constant is derived from the shape of the susceptibility curve while the absolute magnitude of χ is used as a spin counting measurement to confirm the purity of the sample. At low temperatures $T\sim|J|/k$ the maximum value of the susceptibility is directly related to J/k. The consistency of the two measurements and the fit of the susceptibility to the BF model for a one-dimensional spin-$\frac{1}{2}$ chain confirms the previous interpretation of this system and establishes the magnitude of the coupling strength along the chain.

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Temperature Dependence of the Ferromagnetic-Resonance Linewidth*

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A calculation of the temperature dependence of the magnetic-resonance linewidth in ferromagnetic crystals is presented. It is based on the Kubo–Tomita relaxation function and Van Vleck's method of moments, generalized to finite temperatures. Our work differs from previous general theories in that detailed calculations are performed including the applied field so that meaningful comparison between theory and experiment is possible over a wide range of temperatures including the Curie region. The temperature dependence of the moments is calculated in two steps. First, the four- and six-spin correlation functions which occur in the second and fourth moments, respectively, are decoupled into sums of products of two-spin correlation functions. These two-spin thermal averages are then computed in the constant-coupling approximation, since we show that nearest-neighbor static correlations are by far the most important. In this manner linewidth calculations are made for two ferromagnets, $K_2CuCl_4 \cdot 2H_2O$ and Ni, for temperatures ranging from $T = 0$ K to $T = 10T_C$. It is found that the method gives reasonable agreement with the experiments of Ford and Jeffries on $K_2CuCl_4 \cdot 2H_2O$ and of Bhagat and Chicklis and of Salamon on Ni.

I. INTRODUCTION

In this paper we investigate the behavior of the exchange-narrowed ferromagnetic-resonance linewidth as a function of temperature. In spite of much previous effort on the general theory of magnetic-resonance linewidth,[1,2] there appear to be no detailed calculations of the temperature dependence of the linewidth which can be directly applied to the full range of experimental parameters for a ferromagnet. Treatments at finite temperature have tended to be either phenomenological or limited to nonrealistic situations such as zero applied field.[3,4] It is particularly important that the external field be included, because it removes the divergence of the uniform susceptibility at the Curie point, and this can drastically alter the linewidth in the critical region. Since experiments have been performed over a wide range of temperatures above and below the transition point in finite fields, there is considerable interest in having general formulas for finite-temperature linewidths and performing the computations necessary for meaningful comparison between theory and experiment.

The linewidth is calculated in terms of the second and fourth moments as originally proposed by Van Vleck.[5] The stochastic theory of Anderson and Weiss[6] and the relaxation-function approach of Kubo and Tomita also utilize the moments and reproduce Van Vleck's results in the infinite-temperature limit. Richards[7] has shown that these methods may also be applied at finite temperature; so one essentially has only to compute the second and fourth moments at the temperature of interest in order to compute the linewidth within the framework of Kubo and Tomita's general theory.

Describing the linewidth by second and fourth moments can be risky for pathological line shapes; however, for a well-behaved line shape—Lorentzian near the center and more sharply cut off in the wings—this has been shown to produce reasonable results in the infinite-temperature limit. Also, as mentioned by Kawasaki,[3] use of moments may be more correct for large external fields, as encountered in this work.

Green's-function techniques have also been used[8] to calculate temperature dependence of the line-