$$(B_2^0)_{\text{equ}(4p)} = -\tfrac{6}{35} B_3^0 (B_1^0)_{ij} \mathfrak{F}(3, 1, 2) - \tfrac{72}{245} B_3^0 (B_3^0)_{ij} \mathfrak{F}(3, 3, 2) - \tfrac{36}{49} B_3^3 (B_3^3)_{ij} \mathfrak{F}(3, 3, 2) - \tfrac{2}{15}\sqrt{7}\, B_1^0 (B_1^0)_{ij} \mathfrak{F}(1, 1, 2) - \tfrac{6}{35} B_1^0 (B_3^0)_{ij} \mathfrak{F}(3, 1, 2) ,$$

where $\mathfrak{F}(k, \rho, 2)$ are similar to the $\mathfrak{F}(k, \rho, 4)$ but replacing $\langle 3d | r^4 | 3d \rangle$ by $\langle 3d | r^2 | 3d \rangle$.

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Measurement of Temperature-Dependent Correlations by Electron-Spin Resonance: Application to $Cu(NH_3)_4SO_4 \cdot H_2O$†

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It is shown that fruitful information can be obtained about dynamic correlations of exchange-coupled spin operators by considering both the linewidth ΔH and area A of a spin-resonance absorption curve. The product $A\,\Delta H$ is more directly related to the zero-frequency component of a dynamic correlation than is ΔH itself. The technique is applied to the linear-chain salt $Cu(NH_3)_4SO_4 \cdot H_2O$ (CTS). Measurements of A and ΔH are reported and the temperature variation of $A\,\Delta H \coth(\hbar\omega_0/2k_BT)$ is compared with the calculations of Carboni and Richards for finite chains. Below $T = 77$ K, $A\,\Delta H \coth(\hbar\omega_0/2k_BT)$ decreases as temperature is lowered. Good agreement is obtained for the applied field along the a and b axes, but results are less satisfactory along the chain c axis. The effective exchange frequency ω_e is also deduced as a function of T from A, ΔH, and Carboni and Richards's calculations of static correlation functions.

I. INTRODUCTION

The width ΔH of an exchange-narrowed electron-spin-resonance (ESR) line is related both to the static and dynamic (time-dependent) correlations of spin operators. Although many experimental studies of ΔH in strongly exchange-coupled systems have appeared in the literature, in most instances[1,2] no attempt has been made to sort out the static from the dynamic part. Since the dynamics of spin fluctuations often are of primary concern in ESR investigations, it is desirable to extract as much information about them as possible from the data. In this paper we present a general method of analyzing the temperature dependence of exchange-narrowed linewidths, which we feel is most useful for comparison with theory. The technique is applied to the linear-chain salt $\mathrm{Cu(NH_3)_4SO_4\cdot H_2O}$ (referred to as CTS) by comparing measurements reported here with the calculations of Carboni and Richards[3] on time correlations in finite spin-$\frac{1}{2}$ Heisenberg linear chains.

The method simply is to measure both ΔH and the area A under the resonance curve and to study the function $\Delta HA\coth(\hbar\omega_0/2k_BT)$ as a function of temperature T (k_B is Boltzmann's constant and ω_0 is the angular resonance frequency). As we show in Sec. II, it is this quantity which is most directly related to the zero-frequency component of a dynamic correlation function. We are also able to estimate the temperature dependence of the effective frequency ω_e which characterizes the rate of exchange-induced spin fluctuations.

II. THEORY

The exchange-narrowed linewidth at a finite temperature can be expressed as[4]

$$\gamma\Delta H=\frac{\int_{-\infty}^{\infty}F(\tau)\,d\tau}{8\hbar^2\langle M_x^2\rangle}\quad, \tag{1}$$

where $F(\tau)$ is defined as

$$F(\tau)=\langle g^\dagger(\tau)g(0)\rangle+\langle g(\tau)g^\dagger(0)\rangle\ ; \tag{2}$$

$g^\dagger(\tau)$ is given by

$$g^\dagger(\tau)=[\tilde{\mathcal{H}}_P(\tau),M_+]\ , \tag{3}$$

where $\tilde{\mathcal{H}}_P(\tau)$ is in the interaction representation

$$\tilde{\mathcal{H}}_P(\tau)=e^{+i\mathcal{H}_0\tau/\hbar}\mathcal{H}_P e^{-i\mathcal{H}_0\tau/\hbar}\ . \tag{4}$$

Here $\mathcal{H}_P$ is the perturbation responsible for broadening and $\mathcal{H}_0$ is the unperturbed part, which includes the Zeeman and exchange Hamiltonians. In the above expression γ is the gyromagnetic ratio, M_x is the total x component of magnetization, and M_+ is the usual raising operator.

One can also express $\langle M_x^2\rangle$ in terms of the imaginary part of the dynamic susceptibility[4] $\chi''(\omega)$:

$$\langle M_x^2\rangle=\frac{\hbar}{\pi}\int_0^\infty\chi''(\omega)\coth\frac{\hbar\omega}{2k_BT}\,d\omega\ . \tag{5a}$$

Since we are concerned with narrow lines ($\gamma\Delta H\ll\omega_0$) centered about the resonance frequency ω_0, we can approximate

$$\langle M_x^2\rangle\sim\frac{\hbar}{\pi}\coth\frac{\hbar\omega_0}{2k_BT}\int_0^\infty\chi''(\omega)\,d\omega\ . \tag{5b}$$

The integral of $\chi''(\omega)$ can be obtained by experiment as the area under the absorption curve.[5] Thus the numerator in Eq. (1) is a measurable quantity expressed as

$$\int_{-\infty}^{\infty}F(\tau)\,d\tau=F_{\omega=0}\propto\Delta HA\coth\frac{\hbar\omega_0}{2k_BT}\ , \tag{6}$$

where $F_{\omega=0}$ is the Fourier component of $F(\tau)$ at the frequency $\omega=0$. It is this zero-frequency term which is most directly related to the theoretical treatments of time-correlation functions, rather than ΔH itself. The denominator $\langle M_x^2\rangle$ also may be inferred by measurements of the zero-field static susceptibility χ_0 since, for $\hbar\omega_0\ll k_BT$,

$$\langle M_x^2\rangle=\chi_0k_BT\ . \tag{7}$$

However, it can be advantageous to measure $\langle M_x^2\rangle$ by (5b), since then both A and ΔH can be studied in the same sample and under the same conditions of applied field.

The exact form of $F(\tau)$ depends upon the perturbing Hamiltonian through Eqs. (2) and (3). In the case of dipolar broadening, $F(\tau)$ involves commutators of the dipolar Hamiltonian with M_+ which reduce to sums of four-spin correlation functions such as

$$\langle S_i^+(\tau)S_j^+(\tau)S_k^-(0)S_l^-(0)\rangle\ ,$$

where $S_i^\pm$ are the usual raising and lowering operators for the spin at lattice site i. On the other hand, for the hyperfine interaction, $F(\tau)$ will reduce to sums of two-spin correlation functions such as

$$\langle S_i^+(\tau)S_k^-(0)\rangle\ .$$

The zero-frequency part of these correlation functions determines the temperature dependence of $\Delta HA\coth(\hbar\omega_0/2k_BT)$.

A common approach in describing the dynamics is to assume that $F(\tau)$ decays in a characteristic time of the order of $1/\omega_e$ such that

$$F_{\omega=0}=F(0)/\omega_e\ . \tag{8}$$

(We assume that $\omega_e\gg\omega_0$, so that the nonsecular terms which contain $e^{i\omega_0t}$ and $e^{2i\omega_0t}$ modulation factors have essentially the same zero-frequency component as the unmodulated secular terms.) The temperature dependence of ω_e can be determined from the experimentally measured zero-frequency component by use of Eqs. (6) and (8) provided the static correlation function $F(0)$ is known as a function of temperature.

Carboni[3] has computed the frequency components of the two- and four-spin correlation functions for spin-$\frac{1}{2}$ Heisenberg linear chains containing as many as ten spins. We can thus compare our experimental data in the form $\Delta HA\coth(\hbar\omega_0/2k_BT)$ with his zero-frequency calculations.[6] Moreover, we will examine the temperature dependence of ω_e by using static correlation functions which

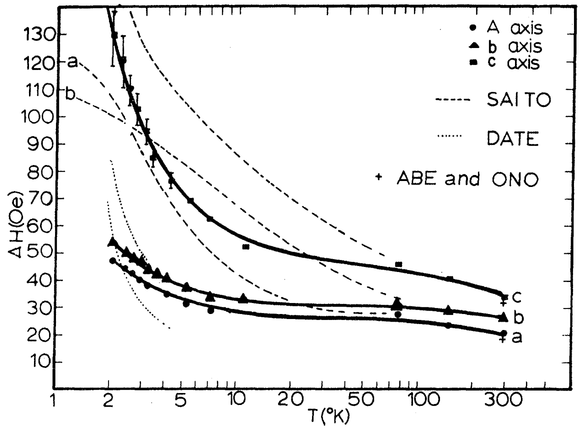

FIG. 1. Full linewidth of $Cu(NH_3)_4SO_4 \cdot H_2O$ vs temperature. The error bars represent the variation of the linewidth along the c axis from sample to sample. The light curves show data taken by Saito (Ref. 9) (dashed curve) and Date (Ref. 8) (dotted curve). We also show the room-temperature results of Abe and Ono (Ref. 7).

are obtained by summing all the calculated frequency components of the time-dependent correlation functions.

III. EXPERIMENT

The paramagnetic resonance of CTS has been well studied.[7–9] However, our measurements are different from previous ones in that we measure both the integral of the absorption and the linewidth of the same sample. The desirability of this procedure is evident from Sec. II.

The measurements were made in an X-band cavity at 8.68 GHz using dc detection with the frequency locked to the cavity frequency. The absolute-intensity measurements were corrected for changes in coupling and cavity Q. The coupling coefficient was measured using a directional coupler. The loaded Q was deduced from the time constant of the transient response.

Three samples were tried. They were prepared by allowing a mixture of copper sulfate pentahydrate and concentrated ammonia to evaporate. All three samples had linewidths and areas which were within 15% of one another above 4.2 K.

IV. RESULTS

The temperature dependence of the full linewidth is shown in Fig. 1. Our measurements differ somewhat from data previously published by other authors. The dashed curve represents data reported by Saito.[9] We do not observe the anomalous crossing of the a- and b-axis[10] linewidths that Saito reports; nor do we see as much increase in the c-axis linewidth. The dotted line shows data reported by Date.[8] Our a- and b-axis linewidths are generally lower than Date's, but our c-axis data are identical. A possible explanation for the large discrepancy in the data previously published may be sample age and deterioration. In order to avoid this we prepared fresh samples before each experiment and kept the samples in a dry atmosphere during the experiment.

In Fig. 2 we plot the results of the area-under-the-absorption measurements as AT versus temperature. All three axes showed the same variation within experimental error. Our data agree quite well with $\chi_0 T$ obtained from static susceptibility measurements made by Fritz and Pinch[11] and Watanabe and Haseda.[12] The solid curve is the theoretical fit of the susceptibility by Griffiths[13] using the results of Bonner and Fisher[14] for a linear chain (spin $\frac{1}{2}$) of 11 spins with an exchange interaction of -3.15 K.

Using our linewidth and static susceptibility measurements, we display the temperature dependence of $\Delta HA \coth(\hbar\omega_0/2k_B T)$ in Fig. 3 with all axes normalized at room temperature. The slow increase in $\Delta HA \coth(\hbar\omega_0/2k_B T)$ from 300 to 77 K does not agree with Carboni's calculations, which show a very slight decrease as the temperature is lowered to 77 K. This gradual increase in linewidth as the temperature is lowered may be due to lattice contraction. Below 77 K this effect should not be important, because thermal expansion is then negligible. At lower temperatures $\Delta HA \coth(\hbar\omega_0/2k_B T)$ decreases sharply, which is expected on the basis of Carboni's calculations.

An enlarged view of the data at lower temperature is presented in Fig. 4, where all the axes have been renormalized to the same value at 77 K.

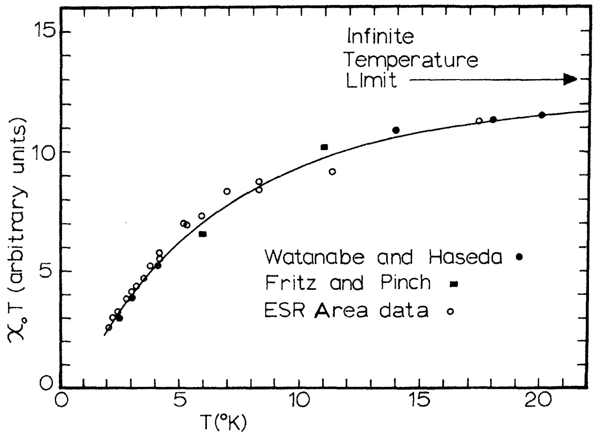

FIG. 2. AT vs temperature. Open circles: AT obtained here from integrated absorption spectra, which, after normalization to room temperature, were independent of crystal axis. The other data are static susceptibility measurements in the form $\chi_0 T$ made by Watanabe and Haseda (Ref. 12) and Fritz and Pinch (Ref. 11). The curve is a linear-chain fit of the static susceptibility by Griffiths (Ref. 13).

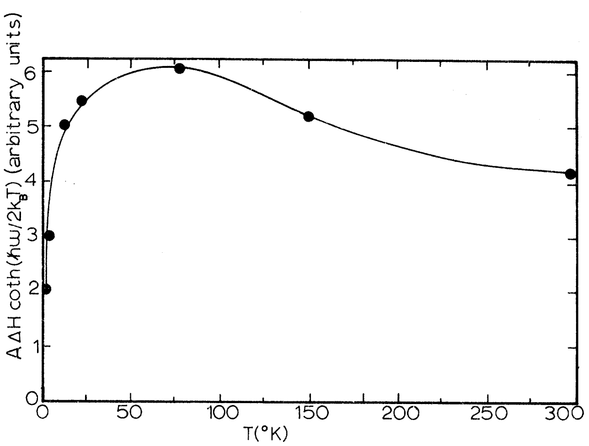

FIG. 3. $\Delta HA\ \coth(\hbar\omega_0/2k_BT)$ vs temperature for $Cu(NH_3)_4SO_4\cdot H_2O$. All axes have been normalized at 300 K. Differences between axes at lower temperatures are not shown.

The curves in the figure are theoretical values of the four-spin correlation functions computed by Carboni and Richards[3] for a spin-$\frac{1}{2}$ linear chain having a nearest-neighbor exchange interaction $J/k_B=-3.15$ K, the same value used by Griffiths.[13] The particular combination of four-spin functions plotted is the zero-frequency component of

$$\sum_{i=1}^{N}\langle S_i^+(\tau)S_{i+1}^+(\tau)S_1^-(0)S_2^-(0)\rangle$$

for a chain of N spins. It represents the correlation encountered for nearest-neighbor intrachain dipolar coupling, and therefore is the dominant one. The four-spin values follow the data along the a and b axes quite well, but there is noticeable departure from the theory along the c axis.

In Fig. 5, we display ω_e as a function of temperature. Values of ω_e are obtained from the $\Delta HA\coth(\hbar\omega_0/2k_BT)$ data and from Carboni's calculation of $F(0)$ for a linear chain of spin $\frac{1}{2}$ and exchange interaction $J/k_B=-3.15$ K. The relationship used to evaluate ω_e follows from Eqs. (6) and (8), so that

$$\omega_e\propto\frac{F(0)}{\Delta HA\coth(\hbar\omega_0/2k_BT)}\ . \tag{9}$$

Note that since $F_{\omega=0}=F(0)/\omega_e$ and since $F(0)$ is not measured directly, Fig. 5 gives essentially the same comparison as Fig. 4. The two curves in the figure are theoretical values of ω_e using Eq. (9) based upon Carboni's calculations of $F(0)$ and $F_{\omega=0}$ for spin-$\frac{1}{2}$ linear chains consisting of eight and nine spins. The theoretical solutions for ω_e generally increase faster than the data as the temperature is lowered. The b axis and, to some extent, the a axis are reasonably close to the theory, though, as is consistent with Fig. 4, the c-axis data deviate severely. The c-axis data for ω_e do show a sizable increase as the temperature is lowered, but this appears at a much lower temperature than Carboni's calculations suggest.

That the a- and b-axis data agree quite well with Carboni's linear-chain results but the fact that the c-axis data do not might be explainable in terms of the anomalous line shape expected for an ideal linear chain. It has been well established[15,16] that the secular components give rise to a non-Lorentzian line shape which is the Fourier transform of $e^{-t^{3/2}}$. This is a result of the divergence of the one-dimensional correlation functions at zero frequency. The Zeeman-modulated nonsecular terms, however, produce a well-behaved Lorentzian line since the $\omega=0$ divergence is removed by

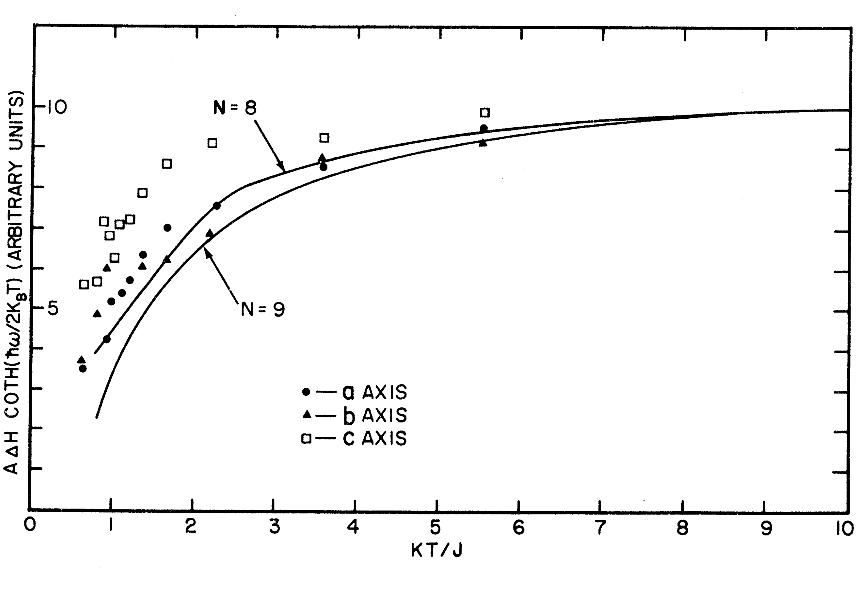

FIG. 4. $A\Delta H\ \coth(\hbar\omega_0/2k_BT)$ at low temperatures for $Cu(NH_3)_4SO_4\cdot H_2O$. All axes are normalized to the same value at 77 K ($k_BT/J=24$). The curves represent Carboni's calculations of four-spin correlation functions at $\omega=0$, as explained in the text, for eight spins and nine spins.

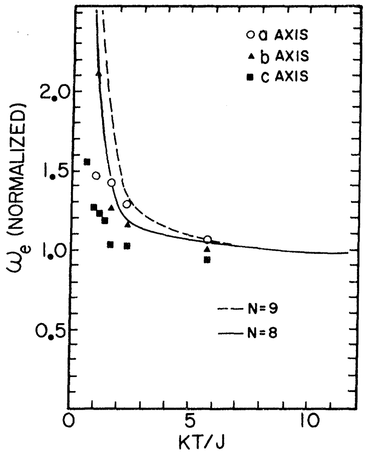

FIG. 5. Effective exchange frequency ω_e as a function of temperature for $Cu(NH_3)_4SO_4\cdot H_2O$. All axes are normalized at 77 K ($k_BT/J=24$). The curves are theoretical values of ω_e based upon $\sum_i\langle S_i^+(0)S_{i+1}^+(0)S_1^-(0)S_2^-(0)\rangle$ as computed by Carboni for a spin-$\frac{1}{2}$ linear chain. The solid curve is an eight-spin calculation; the dashed curve is the result for the nine-spin chain. Here and in Fig. 4, the theoretical value for an infinite number of spins probably lies between the two curves because calculations for even chains up to $N=8$ are close to the $N=8$ curve, whereas calculations for odd chains up to $N=9$ lie near the $N=9$ curve.

the modulation. Thus Carboni's histogram results, which show a finite value for the interval centered at $\omega=0$, may be quite reliable for the nonsecular contributions to the linewidth, but they could be in serious error for estimating the secular contribution. Evidence for their ability to predict the nonsecular terms comes from the good agreement obtained for the frequency dependence[3,17] of ΔH, which is governed by the nonsecular components. For the magnetic field H along the chain c axis, the secular terms dominate the linewidth, whereas the nonsecular terms are relatively more important[15] when the field is perpendicular to the c axis; on this basis it is reasonable to expect better agreement for the a and b axes. A further complication in CTS is that, in fact, a nearly Lorentzian line is observed for H along the c axis. This appears[18] to be due to interchain coupling, which, of course, is not accounted for in Carboni's calculations. Once again, the interchain coupling is probably not important for the nonsecular parts of ΔH, since the Zeeman frequency ω_0 produces a much more rapid modulation than does the weak interchain interaction.

In conclusion, we have shown that useful information about the dynamic correlation function $F(\tau)$ can be obtained by studying the product of the linewidth times the area under the absorption curve times $\coth(\hbar\omega_0/2k_BT)$. This can lead to a more fruitful comparison with theory than considering only the linewidth ΔH in exchange-narrowed ESR. The method has been applied to the temperature dependence of ΔH in the linear-chain salt CTS, and reasonable agreement has been obtained with the finite-chain calculations of Carboni and Richards for the case of H applied perpendicular to the chain axis.

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[5] In practice, χ'' is measured as a function of field H rather than frequency ω. However, for narrow lines we have $\int_0^\infty\chi''(\omega)\,d\omega = \gamma\int_0^\infty\chi''(H)\,dH$.

[6] The frequency-dependent correlation functions in Ref. 3 are given in histogram form, with the interval width 0.4 $J/\hbar$. Thus, by "zero-frequency" component we mean, in referring to the calculations, the height of the histogram covering the interval $-0.2J/\hbar\le\omega\le 0.2J/\hbar$. This avoids any question of divergence of the zero-frequency component in one dimension, as discussed in Ref. 3.

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