both lasers.

Spectra were taken of the output beams and showed a linewidth of about 3 cm^{-1} and 100 cm^{-1} for the ruby and Nd:glass lasers respectively; these linewidths are compatible with the 10-psec and 1-psec pulses seen in the ruby and Nd:glass lasers, respectively.

We believe that the conclusion to be drawn from these observations and the theory[6-9] is that lasers with broad linewidths will quite generally tend to produce short pulses. Also, it is clear that many experiments, especially nonlinear experiments, done in the past with "ordinary" Q-switched lasers, have to be re-evaluated in terms of picosecond pulses of very high peak powers.

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EXCHANGE AND THE "10/3 EFFECT" IN $Cu(NH_3)_4SO_4 \cdot H_2O$ †

Robert N. Rogers*
Sandia Laboratory, Albuquerque, New Mexico, and Wesleyan University, Middletown, Connecticut

and

Fernando Carboni‡ and Peter M. Richards
Department of Physics, University of Kansas, Lawrence, Kansas

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Observations and calculation of the "10/3 effect" in $Cu(NH_3)_4SO_4 \cdot H_2O$ confirm a non-Gaussian form for one-dimensional spin time correlation functions.

"The esoteric phenomenon of the 10/3 effect"[1] has been a part of the literature of electron paramagnetic resonance (epr) since the original discussion by Anderson and Weiss in 1954.[2] Only recently, however, has a quantitative experimental verification of the effect been published (for measurements in $K_2CuCl_4 \cdot 2H_2O$).[3] In this Letter, observation and calculation of the effect in the magnetic linear chain material $Cu(NH_3)_4SO_4 \cdot H_2O$[4] are reported. The resulting agreement gives strong evidence that there exists a marked distinction between the one-dimensional spin time correlation functions and the commonly assumed Gaussian form.

The "10/3 effect" (more accurately described as "nonsecular line broadening"), in brief, refers to the increase in magnetic-resonance linewidth that occurs in an exchange-narrowed material due to the inclusion of nonsecular spin-spin terms when the Larmor frequency becomes of the order of or less than the effective "exchange frequency." Using the theory of Kubo and Tomita,[5,6] the frequency dependence of the dipolar linewidths of an exchange-narrowed paramagnetic salt may be written approximately as

$$\Delta H = \Delta H(\infty)[1 + \beta_1 j(\omega) + \beta_2 j(2\omega)], \quad (1)$$

where $\Delta H(\infty)$ is the infinite-frequency (secular) value of the linewidth, β_1 and β_2 give the relative nonsecular contributions (i.e., $\Delta M = \pm 1$ and $\Delta M = \pm 2$) to the linewidth (for CTS, $\beta_1 = 0.69$ and $\beta_2 = 0.65$),[5,7] and $j(\omega)$ is obtained from the time correlation function of the exchange-mod-

ulated dipolar interaction. At infinite temperature we have

$$j(\omega) = \sum_{ijkl} F_{ij} F_{kl} \int_{-\infty}^{\infty} e^{i\omega t} \times \langle S_{i+}(t) S_{j+}(t) S_{k-}(0) S_{l-}(0) \rangle dt, \quad (2)$$

where F_{ij} is proportional to the dipolar coupling between spins at lattice sites i and j (it is assumed here that the dipolar interaction is the dominant source of line broadening). The time dependence of the correlation function appearing in (2) is governed by the exchange interaction according to

$$\langle A(t)B(0) \rangle \times \langle \exp(i\mathcal{H}_{ex} t/\hbar) A(0) \exp(-i\mathcal{H}_{ex} t/\hbar) B(0) \rangle \quad (3)$$

for any operators A and B, where $\mathcal{H}_{ex}$ is the exchange Hamiltonian.

Since the quantity $j(\omega)$ is not readily calculable from (2) and (3), it has been the custom[2,5] to assume a Gaussian form, $j(\omega) = j(0) \exp(-\omega^2/2\omega_e^2)$, and thereby compute ω_e (which is proportional to the exchange coupling J) from the theoretically computed second and fourth moments[8] of the resonance line. In Ref. 3 it was found that using a Gaussian form for the correlation function gave an excellent fit to the data, and resulted in the prediction of a value for J which was in good agreement with various critical-point determinations. By contrast, Fig. 1 shows the comparison of our epr linewidth data for CTS ($\vec{H}_0 \| a$ axis) with the predicted linewidth variation using the Kubo and Tomita form of Eq. (1), where $J_k = 3.15°K$ as determined by Griffiths from his calculation of the thermal properties of a magnetic linear-chain system.[9] The Kubo-Tomita curve is seen to be in extremely poor agreement; a best fit of such a Kubo-Tomita curve to the data yields $J_k = 0.5°K$. Thus, unlike in Ref. 3, nonsecular line-broadening effects seemed poorly predicted by theory.

Motivated in part by this anomaly, we have performed exact calculations[7] of two-spin and four-spin time correlation functions in closed (periodic boundary conditions) chains of up to $N = 10$ spins coupled by a nearest-neighbor Heisenberg exchange interaction. Bonner and Fisher[10] and others have computed thermodynamic properties of finite chains and made very plausible extrapolation to $N = \infty$. Thermodynamic properties are dependent only on eigenvalues, whereas our calculations required eigenfunctions as well. In terms of the exact eigenfunctions Ψ_α and eigenvalues E_α, Eq. (3) becomes

$$\langle A(t)B(0) \rangle = \sum_{\alpha,\beta} A_{\alpha\beta} B_{\beta\alpha} \exp[-i(E_\alpha - E_\beta)t/\hbar] P_\alpha, \quad (4)$$

where $A_{\alpha\beta}$ is the matrix element between states Ψ_α and Ψ_β, and P_α is the thermal-equilibrium probability that the state Ψ_α is occupied. Our procedure has been to obtain the Ψ_α and E_α (by numerical techniques) and then perform the manipulations indicated by Eq. (4) (the manipulations actually require more computer time than the diagonalization of $\mathcal{H}_{ex}$).

Results are obtained in the form of histograms. By widening the interval to $\Delta\omega = 0.8J/\hbar$, we get a regular variation for the sequence $N = 6, 7, 8, 9, 10$ from which extrapolation to $N = \infty$ appears quite feasible. The functions have a very non-Gaussian character, rising sharply near zero frequency and having broad tails. Using the computed correlation functions in Eq. (3) we obtain the histogram, extrapolated to $N = \infty$, of ΔH vs ω for $J_k = 3.15°K$, shown in Fig. 2.

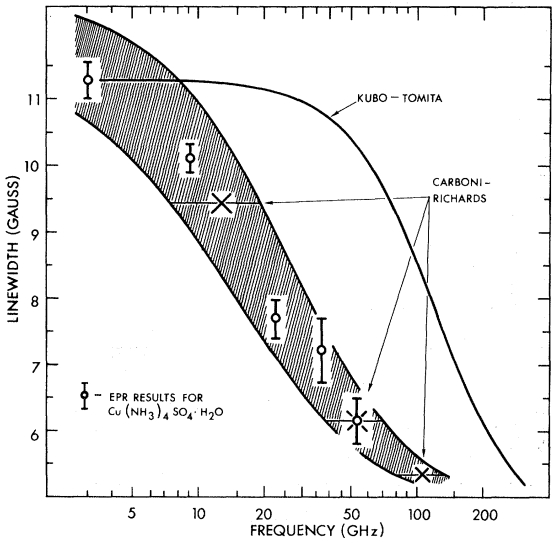

FIG. 1. Experimental epr linewidths ($H_0 \| a$ axis, $\Gamma \simeq 300°K$) as a function of frequency compared with the predictions of Kubo and Tomita for a Gaussian correlation function, and with Carboni and Richards, both for $J = 3.15°K$. The shaded area representing the Carboni-Richards results is derived from a smooth-curve fit to the calculated results shown in Fig. 2. The width of the curve is arbitrarily determined to be one-half the intervals shown on the histogram plot in Fig. 2. In the case of both curves, the ordinates have been scaled to fit a convenient data point.

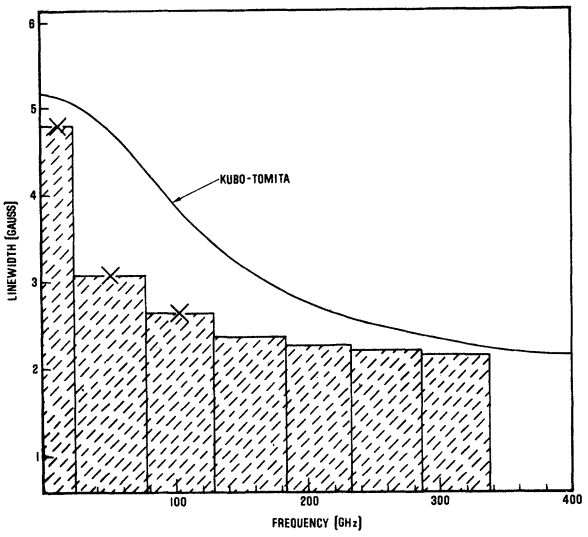

FIG. 2. Predicted nonsecular line broadening of CTS as determined from the one-dimensional dipolar time correlation function results of Carboni and Richards. The three lowest frequency points indicated appear in Fig. 1. For comparison, the Kubo-Tomita curve assuming a Gaussian correlation function is again shown. Here the ordinate is not scaled, and gives the actual calculated value of the linewidth.

The agreement with experiment, as shown in Fig. 1, is most satisfactory.

Besides the relative frequency dependence of ΔH, we can also calculate its magnitude (due to dipolar broadening). This number comes out to be too small by about a factor of 2 in comparison with experiment, which is similar to the discrepancy found in Ref. 3. Hyperfine coupling and anisotropic exchange are other possible sources of broadening.[11] However, since these involve the same or similar spin time correlation functions in their contributions to $\Delta H(\omega)$, their inclusion will not alter the predicted frequency dependence.

In summary, we have observed nonsecular line broadening in the epr spectrum of copper tetrammine sulfate monohydrate. The agreement of the results with our calculations gives support to the conclusions of Griffiths concerning the magnetic properties of this material, as well as indicating the special nature of the dipolar time correlation functions in the one-dimensional case.

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*Present address: Department of Physics and Astrophysics, University of Colorado, Boulder, Colorado.

‡Present address: University of Costa Rica, San José, Costa Rica.

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