COMMENTS AND ADDENDA

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Interchain exchange in nearly one-dimensional $Cu(NH_3)_4PtCl_4$ †

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(Received 7 November 1973)

An interchain exchange $J' = 500 \pm 100$ G is found in $Cu(NH_3)_4PtCl_4$, a nearly one-dimensional crystal with intrachain exchange $J = 5200$ G along the ...CuPtCuPt... stack of square-planar complexes, by combining EPR measurements of $\omega = 0$ Fourier components of high-temperature spin correlation functions with numerical results for purely one-dimensional systems. J' is obtained from approximate theories of three-dimensional cutoffs to the slow $t^{-1/2}$ decay of one-dimensional spin correlations. The method is generally applicable to nearly one-dimensional crystals in which the angular and frequency dependence of the EPR linewidth yields high-temperature Fourier components of spin correlation functions.

We have recently shown[1] that the angular and frequency dependence of the exchange-narrowed EPR linewidth in single-crystal $Cu(NH_3)_4PtCl_4$ (hereafter CTP) provides a direct measurement of Fourier components of high-temperature spin correlation functions. CTP is a nearly one-dimensional crystal, with strong exchange along the ... CuPtCuPt... chains[2] formed by alternately stacking square-planar paramagnetic $Cu(NH_3)_4^{++}$ and diamagnetic $PtCl_4^{--}$ complexes. We show here that the $\omega = 0$ Fourier components provide a convenient method for evaluating the small exchange J' between second-neighbor $Cu(NH_3)_4^{++}$ complexes in different chains. The present method requires only that various spin correlation functions for a purely one-dimensional system, such as those shown[3] in Fig. 1, be known at high temperature. Thus CTP also provides detailed comparison between measured and calculated Fourier components of *specific* spin correlation functions.

When $J' \ll J$, the short-time behavior of any spin correlation function is largely determined by the nearest-neighbor intrachain exchange J. Weak interchain or lifetime contributions are important at long time, where they effectively cut off the slow diffusive decay $t^{-1/2}$ of one-dimensional systems.[4,5] The short-time behavior of the correlation function $C_j(t) = 4\langle S_i^z(t) S_{i+j}^z(0)\rangle$ was shown by Blume and Hubbard[6] (BH) to depend on the rms exchange $\hat{J}$, which for the body-centered tetragonal lattice of Cu^{++} in CTP is

$$\hat{J}^2 = \sum_j J_{ij}^2 = 2J^2 + 8(J')^2 \quad . \tag{1}$$

The BH model does not explicitly invoke dimensionality. The purely one-dimensional case, with J the exchange between successive $S = \frac{1}{2}$ $Cu(NH_3)_4^{++}$ sites in the ... CuPtCuPt... chain, is

$$\mathcal{H}_e^{(0)} = \sum_j J S_j S_{j+1} \tag{2}$$

and has been recently solved numerically[7] for classical ($S_i = \infty$) spins. At infinite temperature, there cannot be significant differences between a chain of $S = \frac{1}{2}$ and $S = \infty$ spins, and CTP was shown[1] to be in the infinite temperature limit even at 77 °K. Curves I and VI in Fig. 1 show the similar short-time behavior of $C_0(t)$ for nearest-neighbor exchange in a linear chain $\mathcal{H}_e^{(0)}$ and in a simple cubic lattice with the same $\hat{J}$. All high-frequency Fourier components in CTP (at $\omega = \omega_X$, $2\omega_X$, ω_Q, $2\omega_Q$; with $\omega_X \sim 9.5$ GHz and $\omega_Q \sim 35$ GHz, the X- and Q-band Larmor frequencies) were quantitatively given[1] by $\hat{J} = 7400 \pm 500$ G. The rms exchange [Eq. (1)] in a nearly one-dimensional system ($J' \ll J$) thus gives the intrachain exchange $J = \hat{J}/\sqrt{2} \sim 5200$ G. The high-frequency ($\omega \gtrsim J/\hbar$) Fourier components based on the BH expression for $C_0(t)$ are negligibly

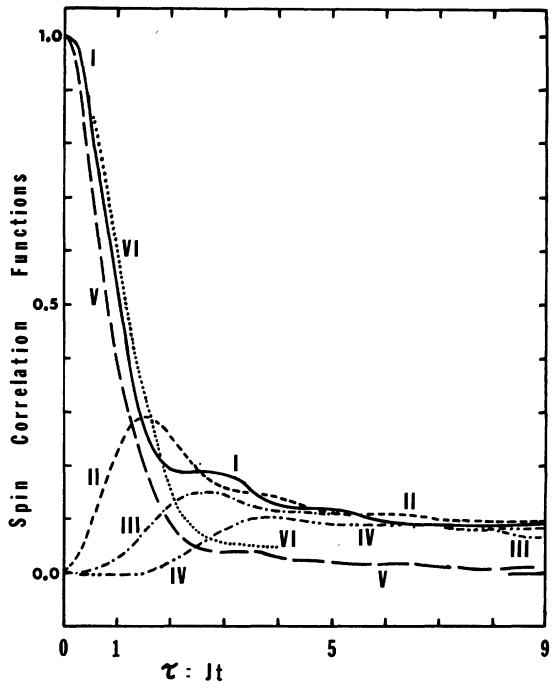

FIG. 1. Numerical results (Ref. 3) for infinite-temperature spin-correlation functions in a linear chain $\mathcal{H}_e^{(0)}$ in Eq. (2). Curve I is the autocorrelation function $C_0^{(0)}(t) = 4\langle S_i^x(t)S_i^x(0)\rangle$; curve II is the first-neighbor correlation $C_1^{(0)}(t) = 4\langle S_i^x(t)S_{i+1}^x(0)\rangle$; curve III is $C_2^{(0)}(t) = 4\langle S_i^x(t)S_{i+2}^x(0)\rangle$; curve IV is $C_3^{(0)} = 4\langle S_i^x(t)S_{i+3}^x(0)\rangle$; and curve V is the intrachain four-spin correlation $F(t) = 4\langle S_i^+(t)S_{i+1}^+(t)S_i^-(0) \times S_{i+1}^-(0)\rangle$. Curve VI is the two-spin autocorrelation function (Ref. 6) for nearest-neighbor exchange in a simple cubic lattice normalized to the same rms J.

changed[8] on using a purely one-dimensional $C_0^{(0)}(t)$.

The $\omega = 0$ Fourier components reflect the long-time behavior of the spin correlation and depend sensitively on J', since $g_0(0)$, the zero-frequency Fourier component of $C_0(t)$, diverges[5,9] for $J' = 0$ and is finite for $J' \neq 0$. The Lorentzian EPR lines observed[1] in CTP also indicate three-dimensional interactions which spoil the characteristic one-dimensional line shape. We introduce below a three-dimensional cutoff[4,5] t_0 to limit the $\omega = 0$ divergence of the purely one-dimensional two-spin correlations. The CTP data gave three $\omega = 0$ Fourier components[1]: $g_0(0)$ from the Cu hyperfine broadening and both an intrachain and an interchain four-spin correlation arising from dipolar broadening. As shown in Table I, all three are consistent with the cutoff $t_0 = 21J^{-1}$.

The exact shape of the three-dimensional cutoff of the $t^{-1/2}$ decay of one-dimensional two-spin correlations cannot be important[4,5,10] when $J' \ll J$ and the short-time effects in Fig. 1 occur before J' contributes. An exponential cutoff[4,10]

$$C_j(t) = C_j^{(0)}(t)e^{-\omega_c t} \tag{3}$$

with $\hbar\omega_c \sim J'$ is often convenient. All two-spin correlations $C_j^{(0)}(t)$ governed by $\mathcal{H}_e^{(0)}$ are truncated around $t \sim \omega_c^{-1}$, while four-spin correlations involving a product of two $C_j^{(0)}(t)$ are truncated around $t \sim (2\omega_c)^{-1}$. For simplicity we instead choose here a sharp cutoff t_0 defined by

$$C_j(t) = C_j^{(0)}(t), \quad t \leq t_0 \tag{4}$$

$$= 0, \qquad t > t_0$$

for all spin correlations. As shown below, the cutoff $\frac{1}{2}t_0$ for four-spin correlations suggested by Eq. (3) does not change the results significantly.

The cutoff t_0 is only important near $\omega = 0$, since the largest correction to the autocorrelation is, for $J' = 0$,

$$\Delta g(\omega) = \int_{t_0}^{\infty} dt \cos\omega t \; C_o^{(0)}(t) \; . \tag{5}$$

Assuming t_0 to occur in the asymptotic region $b(Jt)^{-1/2}$, with $b = 0.27$ obtained from $C_0(\tau)$ in Fig. 1 for $\tau > 5$, we obtain

$$\Delta g(\omega) = b\left(\frac{2\pi}{\omega}\right)^{1/2}\left(\frac{1}{2} - \int_0^{X_0} dx \cos\tfrac{1}{2}\pi x^2\right) \tag{6}$$

with $X_0 = (2\omega t_0/\pi)^{1/2}$. The $\omega^{-1/2}$ singularity, and the rapid oscillation of the Fresnel integral[11] in Eq. (6) about $\frac{1}{2}$ as X_0 increases, ensure that, for $J' \ll J$ or large t_0, $\Delta g(\omega)$ is small except near $\omega = 0$. As already indicated, the high-frequency (short-time) Fourier components reflect the rms exchange $\hat{J}$.

t_0 is obtained from the $\omega = 0$ Fourier component of $C_0(t)$,

$$Jg_0(0) = \int_0^{Jt_0} C_0^{(0)}(\tau)\, d\tau \; , \tag{7}$$

where we have introduced $\tau = Jt = (1/\sqrt{2})\hat{J}t$. The sharp cutoff t_0 thus permits a simple integration of purely one-dimensional correlations, in this case curve I of Fig. 1, and does not require difficult longer-time results.[12] The approximation $C_0^{(0)}(\tau) = b\tau^{-1/2}$, with $b = 0.27$, was used for $\tau > 9$. The CTP results of $J = 7400 \pm 500$ G and $g(0) = (0.55$

TABLE I. Comparison of $\omega = 0$ Fourier components of spin correlation functions in CTP with calculation based on cutoff $t_0 = 21\,J^{-1}$.

Spin correlation function	CTP data[a]	Calculated
$Jg_0(0)$[b]	2.86 ± 0.20	2.86[c]
$Jf_1(0)$[d]	1.15 ± 0.10	1.18
$Jf(0)$[e]	2.18 ± 0.15	2.16

[a]Reference 1, with quoted error limits.
[b]Two-spin autocorrelation function, $4\langle S_i^x(t)S_i^x(0)\rangle$.
[c]Defines t_0; fit is automatic.
[d]Intrachain four-spin correlation function, Eq. (9).
[e]Interchain four-spin correlation function, Eq. (11).

$\pm 0.02)\times 10^{-3}$ G^{-1} lead to the cutoff $Jt_0 = 21 \pm 2$, which is well outside the short-time region.

The only important[1,13] intrachain four-spin correlation function arising from electron dipolar interactions in a linear chain is

$$F(t) = [3/2S(S+1)]^2 \langle S_i^+(t) S_{i+1}^+(t) S_i^-(0) S_{i+1}^-(0) \rangle , \quad (8)$$

where $S_i^{\pm} = S_i^x \pm S_i^y$, $S = \frac{1}{2}$ and i, $i+1$ are successive $Cu(NH_3)_4^{++}$ sites in the ... CuPtCuPt... chain. The correlation function $\langle S_i^+(t) S_{i+1}^+(t) S_{i+1}^-(0) S_{i+2}^-(0) \rangle$ is an order of magnitude smaller,[13] while other intrachain correlations can be neglected in the linewidth on account of the rapid r_{ij}^{-3} decrease of the dipolar factors. $F(\tau)$, with $\tau = Jt$, is shown[3] in curve V of Fig. 1, and is related to the measured intrachain Fourier component $f_1(0)$ by

$$Jf_1(0) = \int_0^{Jt_0} F(\tau)\, d\tau \quad . \quad (9)$$

The region from $\tau = 9$ to $\tau = 21$ was approximated by the decoupling[1,13] $[C^{(0)}(\tau)]^2$ and is less than 10% of the contribution $0 \le \tau \le 9$, where no decoupling was used. Thus, neither the assumed decoupling for $\tau > 9$ nor the possibly different cutoff for two- and four-spin correlations is important. The measured[1] and calculated values of $f_1(0)$ in Table I agree to within experimental error.

The interchain dipolar contributions decouple exactly for $J' = 0$, with

$$\langle S_i^+(t) S_j^+(t) S_{i+k}^-(0) S_{j+m}^-(0) \rangle = 4 C_k(t) C_m(t) \quad (10)$$

for spins ik on one chain, and jm on a different chain. We retain Eq. (10) even for $0 < J' \ll J$. The $\omega = 0$ Fourier component of interchain dipolar contributions to the EPR linewidth[1,8,13] is

$$Jf(0) = \int_0^{Jt_0} d\tau \left([C_0^{(0)}(\tau)]^2 + 2 \sum_{j \ge 1} [C_j^{(0)}(\tau)]^2 \right) \quad , \quad (11)$$

which involves squares of the curves I–IV shown in Fig. 1 for $j = 0$, 1, 2, and 3. The usual Van Vleck approximation[1] is to retain *only* the $C_0^{(0)}(\tau)$ term in (11), since the other C_j vanish at $\tau = o$; this approximation is very well satisfied[8] for the ω_X, $2\omega_X$, ω_Q and $2\omega_Q$ Fourier components of CTP, and only the Fourier components of $[C_0^{(0)}]^2$ were required at high frequencies.[1] The integral (11) to $\tau = 21$ yields 0.97 for $j = 0$; 0.54 for $j = 1$; 0.31 for $j = 2$; and 0.22 for $j = 3$; or a total of 2.04.

$Jf(0)$ potentially contains contributions from $j > 3$ terms in Eq. (11), as well as from cross terms discussed below. Large j contributions can be estimated from the long-time behavior[7] for $C_j(t)$,

$$C_j(t) \simeq [1/2(\pi D t)^{1/2}] e^{-j^2/4Dt} \quad . \quad (12)$$

For $S = \frac{1}{2}$, $D = 0.69J$ in one dimension.[3,7] The times of interest in CTP are $Jt \sim 10$ (for a cutoff at $Jt_0 = 21$), and the exponential in Eq. (12) is unity for $j \sim 5.2$. Thus $j \ge 6$ contributions are small for times up to the cutoff. The $j = 4$ contribution of ~ 0.12 is estimated from the extrapolation $b^2 t^{-1}$ between $9 < \tau < 21$; $j = 5$ is even smaller. The values $Jf(0) = 2.04$ (based on $j = 0$, 1, 2, 3) and $Jf(0) \sim 2.16$ (including $j = 4$) are in excellent agreement with experiment, as shown in Table I.

The $\omega = 0$ interchain Fourier components also contain contributions from cross terms of the type $C_0^{(0)}(\tau) C_j^{(0)}(\tau)$. The coefficient of the $j = 1$ term for the second neighbors is

$$Q = \left(\sum_{\vec{a}} F_{i,i+\vec{a}}^{(0)} F_{i,i+\vec{a}\pm 1}^{(0)} \right) \Big/ M_d' \quad , \quad (13)$$

where M_d' is the secular second moment[1] for spins in different chains, the secular dipolar coefficients are $F_{ij}^{(0)} = (3\cos^2\theta_{ij} - 1)\, r_{ij}^{-3}$ in terms of the angle[1] θ_{ij} between the applied field $\vec{H}_0$ and $\vec{r}_{ij}$, and both sites $i + \vec{a}$ and $i + \vec{a} \pm 1$ in the sum (13) are second neighbors of site i. The contribution to $f(0)$ is

$$Jf'(0) = Q \int_0^{Jt_0} C_0^{(0)}(\tau) C_1^{(0)}(\tau)\, d\tau \quad (14)$$

and similar contributions arise for other neighbors, with the four sites always on just two chains. These contributions depend on the orientation of $\vec{H}_0$, can be either positive or negative, since the numerator in Eq. (13) is no longer positive definite, and turn out to be small,[8] at most 1–2 G for any orientation of $\vec{H}_0$. Thus a *single* $f(0)$ was obtained experimentally for the full angular variation of the CTP linewidth (Table II of Ref. 1), and the experimental accuracy of about ± 1 G is insufficient to detect the $\omega = 0$ contributions (14) arising from cross terms of two-spin correlation functions.

The cutoff $t_0 = 21 J^{-1}$ is thus consistent with all three $\omega = 0$ Fourier components measured in CTP[1] and shown in Fig. 1. Hennessy *et al.*[5] and Reiter[14] have suggested the general relationship (with $\hbar = 1$)

$$J' t_0 = A (J'/J)^{-1/3} \quad (15)$$

for relating t_0 and J' in nearly one-dimensional systems. The numerical factor A is 1.19 (Ref. 5) and 0.70 (Ref. 14) for a simple tetragonal lattice. Since CTP forms a body-centered tetragonal Cu^{++} lattice, and the sharp cutoff is approximately $t_0 = (21 \pm 2) J^{-1}$, we use $A = 1$ in Eq. (15) to obtain $J' = 500 \pm 100$ G for $J = 5200$ G. The estimated uncertainty includes the factor $A^{3/4}$ from Eq. (15), the uncertainty in t_0, and the neglect of other small internal fields. A rougher estimate[4,10] can be obtained by assuming an exponential cutoff [Eq. (3)] to a purely $t^{-1/2}$ decay (which of course is a good approximation only for long t). The relative effectiveness of exchange narrowing in one- and three-dimensional systems is then $(2J'J)^{1/2}$ to J. The three-dimensional BH[6] result is $g_0(0) = 0.29$

$\times 10^{-3}$ G^{-1} for $\hat{J} = 7400$ G, which is 0.53 times the observed value. We find $(2J'/J)^{1/2} = 0.53$ and $J' = 0.14J = 730$ G.

In summary, the $\omega = 0$ Fourier components provide a sensitive evaluation of $J' = 500 \pm 100$ G in CTP, which consequently has a J'/J ratio of ~ 0.10. The generality of the present method depends on measuring specific Fourier components from an analysis of the angular and frequency dependence of the EPR linewidth. CTP presents several experimental advantages[1]: all $Cu(NH_3)_4^{++}$ sites are magnetically equivalent; the diamagnetic $PtCl_4^{--}$ sites provide sufficient dilution to make the hyperfine broadening important; the rms exchange $\hat{J} = 7400$ G, or $J = 5200$ G, permits a strong frequency dependence at the convenient X- and Q-band frequencies. The magnitude $J' \sim 500$ G is also convenient, as it exceeds by more than a factor of 2 any of the local fields (hyperfine, intrachain dipolar, interchain dipolar) in CTP. As pointed out by Boucher[10] and by Reiter,[14] these local fields also limit the divergence and cannot be neglected in nearly one-dimensional[5] crystal. The occurrence of diamagnetic $PtCl_4^{--}$ units between $Cu(NH_3)_4^{++}$ sites in CTP is especially important in reducing the large intrachain dipolar fields typical of nearly one-dimensional systems.

We thank M. Blume for providing us with numerical results for two-spin correlation functions prior to publication, and for undertaking with B. Farrell to compute the intrachain four-spin correlation function.

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†Supported in part by NSF GP-9546

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