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Comment on "Exchange Narrowing in One-Dimensional Systems"*

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Attention is drawn to the similarity in one-dimensional spin dynamics between the recently investigated inorganic salt $(CH_3)_4NMnCl_3$ (TMMC) [R. E. Dietz *et al.*, Phys. Rev. Letters 26, 1186 (1971)] and a variety of organic charge-transfer and free-radical crystals previously studied by electron paramagnetic resonance. The theoretical description developed for the organic crystals based on the linear Heisenberg antiferromagnet is applicable also to the inorganic systems.

The magnetic properties of lower-dimensional spin systems, especially of the Heisenberg linear antiferromagnet, have been intensively studied recently. The letter of Dietz *et al.*[1] examines the effects of one dimensionality on the spin dynamics in the inorganic system $(CH_3)_4NMnCl_3$ (TMMC) with chains of $S=\frac{5}{2}$ Mn^{++} ions. The magnetic properties of a variety of organic free-radical and charge-transfer crystals have also been analyzed in terms of Heisenberg linear antiferromagnets with chains of $S=\frac{1}{2}$ radicals.[2-4] The extreme one dimensionality of the exchange in organic crystals containing stacks of planar, aromatic free radicals[2,5] is dramatically demonstrated in crystals with magnetically inequivalent stacks of radicals, where EPR splittings of a few gauss are readily resolved in spite of intrachain exchange of 10^2–10^3 cm^{-1}.[3,6] The similarities between the magnetic properties of inorganic and organic linear antiferromagnets have been largely overlooked and are the reason for this comment. The two types of crystals are, in fact, complementary and illustrate the unusual spin dynamics of one-dimensional systems.

The planar aromatic molecules or ions in organic free-radical crystals stack face to face[5,2] to form linear chains in which the unpaired π electron, delocalized over each radical, overlaps with the π electrons of adjacent radicals in the stack. The magnetic one dimensionality is thus inherent in the crystal structure and does not depend on estimating various pathways for exchange or superexchange between paramagnetic atoms in inorganic salts. The g tensors in aromatic crystals are very close to the isotropic free-electron g value, as expected for radicals composed of light atoms with small spin-orbit coupling. Strong antiferromagnetic exchange (with J of the order of 10^3 cm^{-1} in some charge-transfer crystals[3,4]) between adjacent radicals in a stack reflects charge-transfer stabilization[2,7] rather than direct (Heisenberg) exchange. Strong antiferromagnetic exchange leads to EPR lines of a few gauss or less, in contrast to the many-gauss dipolar lines expected in any free-radical solid, and leads to uniform magnetic dilution, which is observed as a quenching of the paramagnetism when $kT \ll J$.[2] Strong short-range antiferromagnetic correlations lock the spins into a diamagnetic ground state. Only a thermal-equilibrium density ρ of spins is then reorientable by thermal fluctuations[8] and only these spins are observed in EPR or static susceptibility measurements. Temperature thus becomes a powerful experimental parameter.

The spin dynamics and relaxation in organic crystals are successfully described by models based on the Heisenberg linear antiferromagnet.[2-4] Once the uniform magnetic dilution due to strong exchange is included, the general, high-temperature theories[9] of magnetic resonance absorption are equally applicable to both inorganic and organic systems. Indeed, the differences in hyperfine, exchange, spin-orbit, and other contributions then emphasize the power of the general theories.

The theoretical analysis of the one dimensionality of spin correlations in TMMC[1] was anticipated[10] by the interpretation of the motional narrowing of the hyperfine interaction in Wurster's blue perchlorate (WBP) due to triplet exciton motion along molecular stacks. The EPR line shape was shown to be intermediate between Lorentzian and Gaussian, but the WBP data were insufficient to demonstrate the deviations from Lorentzian behavior observed in TMMC far from the center of the resonance. The anisotropy of electron dipolar interactions discussed quantitatively in TMMC have been observed in TMPD-TCNQ,[4] a 1:1 charge-transfer complex containing stacks of ion radicals. The

"10/3" effect in TMPD-TCNQ was observed by varying ω_0/ω_e through the temperature dependence of the effective exchange ω_e rather than by the usual[11] technique of varying the Larmor frequency ω_0. The temperature dependence of the linewidth in TMPD-TCNQ is consistent with a Lorentzian spectral function characteristic of a one-dimensional system,[12] rather than a Gaussian spectral function. However, the divergence in the spin correlation function expected for one-dimensional spin diffusion and observed in TMMC as deviations from a Lorentzian line shape does not dominate the almost Lorentzian EPR signal in either TMPD-TCNQ or $Cu(NH_3)_4SO_4 \cdot H_2O$, a spin-$\frac{1}{2}$ inorganic linear antiferromagnet.[13]

In summary, the stacking of planar aromatic free-radical molecules or molecular ions in crystals leads to highly one-dimensional spin systems which can be described as Heisenberg linear antiferromagnets. Strong one-dimensional antiferromagnetic exchange permits a continuous temperature variation of the thermally reorientable spin density. The spin dynamics and relaxation are given by the general theories applicable to inorganic crystals as well. We hope that comparison of experimental and theoretical results for organic and inorganic systems will result in greater understanding of the unusual properties of magnetically one-dimensional crystals.

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