Electron-Spin–Susceptibility Studies of Tetrathiafulvalene Tetracyanoquinodimethane (TTF-TCNQ)

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The temperature dependences of the spin susceptibility in TTF-TCNQ as measured by static and ESR techniques are in close agreement in the temperature region 30–300 K. This result indicates that the spin-resonance experiment interrogates *both* molecular chains, even at temperatures where at least one chain displays metalliclike properties.

Various studies on tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) led to the speculation that the two constituent molecular chains have different electronic properties. ESR[1] (electron spin resonance) and static-susceptibility studies have resulted in the conclusion that above 60 K the salt consists of weakly coupled chains, a metallic TTF stack and the TCNQ stack composed of localized spins. ESR of the TTF stack was reported to be unobservably broad while the nonmetallic TCNQ stack contributes to the ESR.

We report ESR in single-crystal TTF-TCNQ, and bulk static-susceptibility measurements on polycrystalline material. These two measurements are in good agreement throughout the temperature regime 30–300 K, indicating that if the TTF stack does not contribute to the ESR, its contribution to the total susceptibility is smaller than our experimental error (6–8%).

Polycrystalline TTF-TCNQ was prepared by rapidly adding an $8\times 10^{-3}M$ solution of gradient-sublimed TTF[2] to an equal volume of $8\times 10^{-3}M$ gradient-sublimed TCNQ in spectral-grade acetonitrile at room temperature under argon. The product was collected and dried under argon. Single crystals were prepared by allowing separate $6\times 10^{-3}M$ acetonitrile solutions of TTF and TCNQ to diffuse into $2\frac{1}{2}$ times their combined volume of pure acetonitrile at room temperature under argon. After one week the product was collected and dried under argon.

The static magnetic susceptibilities of powder specimens were measured by the conventional Faraday method using a Cahn RG microbalance, a field gradient $H\,\partial H/\partial x = \sim 4\times 10^{7}$ Oe^2/cm at 1.7×10^{4} Oe, and $HgCo(CNS)_4$ as calibrant. Curie-law paramagnetic- and ferromagnetic-impurity contributions were determined from the temperature dependence below ~ 15 K (χ versus $1/T$) and the field dependence (χ versus $1/H$), respectively.

The Curie constant for the paramagnetic impurities, which varied from 1.5×10^{-4} to 1.3×10^{-3} on a molar basis, corresponds to 3×10^{-5}–3×10^{-4} mole fraction of a high-spin Fe^{+3} ($S=\frac{5}{2}$) impurity *or* 4×10^{-4}–4×10^{-3} mole fraction of a $S=\frac{1}{2}$ impurity. Under the assumption of bulk iron as the ferromagnetic impurity the observed field-dependence contribution varied from 2 to 7 ppm on a mass basis. The estimated uncertainty in the susceptibility due to the paramagnetic and ferromagnetic impurities is ~ 7×10^{-6} emu/mole.

In Fig. 1, we display representative static-susceptibility data (designated by the asterisks) after correction for ferromagnetic and paramagnetic impurities.[3] All preparations exhibit the same susceptibility within the estimated error. The low-temperature corrected susceptibility is within 3% of that calculated from Pascal's constants for the normal diamagnetism of the closed-shell constituent atoms. The spin susceptibility

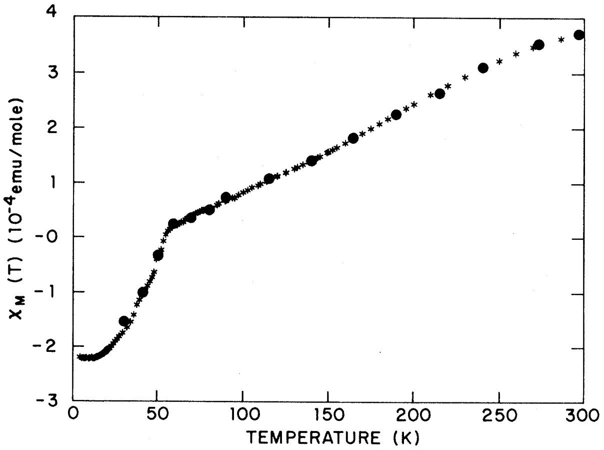

FIG. 1. Comparison of spin susceptibility determined by static methods (asterisks) and ESR (large dots). The ESR data are fitted to the static-χ_s data at $T=300$ K and shifted to account for χ_d.

is then obtained by subtraction of the temperature-independent diamagnetic contribution ($\chi_d = -2.22 \times 10^{-4}$ emu/mole). In this form, comparison can be made between the static and the ESR results.

ESR experiments were performed on single crystals, with use of a conventional ESR spectrometer operating at 9 GHz, at temperatures between 30 and 300 K. Two TTF-TCNQ crystals were mounted in symmetrical positions in a Varian V-4532 dual-sample cavity operating in the TE_{104} mode. With the rf magnetic field parallel to the crystal b axis (axis of highest electrical conductivity), and the static field approximately parallel to either the crystal a axis or c^* axis, the skin depth is large compared with sample thickness, yielding symmetrical ESR profiles. With one crystal field-modulated at 40 Hz and maintained at room temperature providing a reference signal, the second was inserted in a variable-temperature Dewar and cooled with a stream of helium gas for 30–100-K measurements and nitrogen gas for 90–300-K measurements.[4] This sample was field-modulated at 100 kHz so that after detection and narrow-banded amplification the signals from the two crystals did not interfere. The ESR cavity was maintained at room temperature at all times. By continuous monitoring of the signal from the reference crystal, changes in cavity Q, power level, or detector response are made readily apparent and appropriate corrections can be applied to the data.

For narrow lines, the spin susceptibility is directly proportional to the total resonance power absorption.[5] In these experiments, no attempt has been made to measure the absolute absorption; we have determined only the relative absorption as a function of temperature. The shape of this curve is then compared with that obtained from static-bulk-susceptibility measurements. Our procedure is as follows:

The ESR signal is an intense single line near $g = 2.0$ whose width increases with decreasing temperature, reaching a maximum at about 60 K and falling rapidly to a minimum at about 30 K.[1] The line is Lorentzian in shape to at least 7 linewidths into the wings at all temperatures. Data were taken at fixed frequency by scanning the field slowly through the resonance while recording the first derivative of both the reference crystal and the crystal under study. The derivative curves were automatically digitized and stored in a general-purpose computer for analysis. Analysis consists of a least-squares fitting of *analytical* Lorentzian-derivative curves to experimental data and computing the integrated area of the analytical curve from the fitting parameters. This procedure involves no numerical integration and is, we believe, the only reliable method of extracting reasonably accurate intensity information from experimental Lorentzian curves.[6] This fitting procedure was carried out for *both* crystals at *every* temperature studied. Representative experimental data with best-fit analytical curves are shown in Fig. 2. The integrated area normalized to room temperature was then determined as a function of temperature, and is shown in Fig. 1 by the large dots. The two data are in good agreement throughout the temperature region studied, including the 60-K transition.[7] The ESR data are independent of the static field orientation.

It was suggested[1] that in the region $T > 60$ K the resonance line from one molecular stack is unobservable by ESR. Accordingly, the spin susceptibility of that stack would not contribute to the intensity of the observed ESR, and a discrepancy between static and ESR measurements would exist. This "missing susceptibility" would be identifiable by assuming that there is a separate

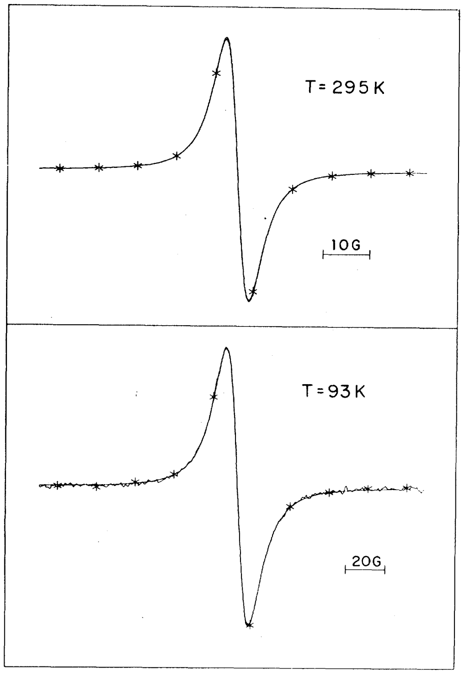

FIG. 2. Experimental resonance profiles. Data are identified by a solid line interrupted by asterisks. Best-fit analytical Lorentzian-derivative curves are also shown.

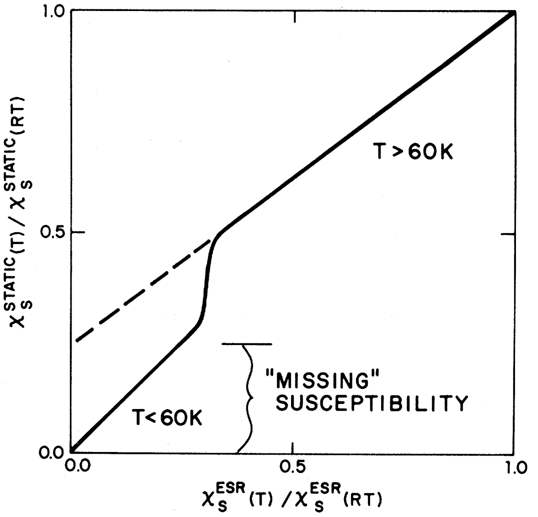

FIG. 3. Hypothetical diagram indicating how a "missing" susceptibility would be expected to appear.

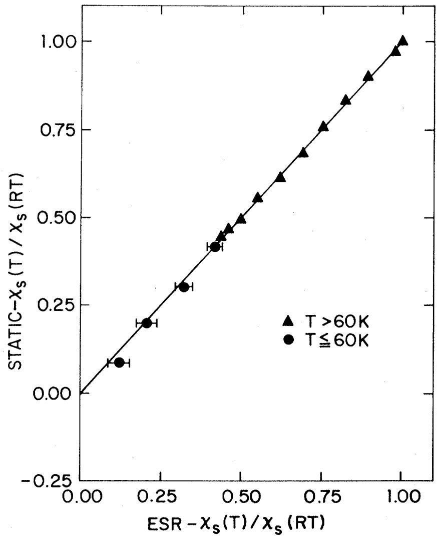

FIG. 4. Comparison of spin-susceptibility ratios as determined by static and ESR means. Data are identified by discrete points. The solid line is a linear least-squares fit to the $T > 60$-K data.

contribution to the susceptibility from the TTF and TCNQ chains,

$$\chi_s^{\text{static}}(T) = \chi_s^{\text{TTF}}(T) + \chi_s^{\text{TCNQ}}(T).$$

Below the 60-K transition temperature, where neither chain exhibits metallic behavior, it is reasonable to expect the ESR and static susceptibility measurements to agree with each other:

$$\chi_s^{\text{ESR}}(T) = \chi_s^{\text{static}}(t), \quad T < 60 \text{ K}.$$

A plot of $\chi_s^{\text{ESR}}(T)/\chi_s^{\text{ESR}}(\text{RT})$ versus $\chi_s^{\text{static}}(T)/\chi_s^{\text{static}}(\text{RT})$ would yield a straight line with unit slope through the origin for this temperature region (RT denotes room temperature).

If the TTF stack (for example) were metallic and unobservable via ESR above 60 K, then

$$\chi_s^{\text{ESR}}(T) = \chi_s^{\text{static}}(T) - \chi_s^{\text{TTF}}(T), \quad T > 60 \text{ K},$$

and we would observe, as shown in Fig. 3, a straight line with slope less than unity for the χ_s^{ESR}-versus-χ_s^{static} curve above 60 K, the extrapolated intercept being a direct measure of any "missing" component of χ_s. In Fig. 4, we plot our data in a similar manner, $T > 60$ K and $T < 60$ K being represented by different symbols. The solid line which is a linear least-squares fit to the data points above 60 K has unit slope and intersects the χ^{static} axis at the origin (slope $= 1.00 \pm 0.01$, intercept $= 0.00 \pm 0.01$) as expected if the two susceptibility curves obey the same functional form. These results demonstrate that there is little, if any, systematic deviation in the shape of the spin-susceptibility curve as measured via ESR as compared with that obtained by static measurements in the region $T > 60$ K. Obviously, a difference of a temperature-independent multiplicative constant would not be detected in our experiment. We believe that our overall accuracy above 60 K is such that an upper limit of 6–8% may be placed on a "missing" component of χ_s.

The data in Fig. 4 for $T < 60$ K are also completely consistent with a linear relationship with unit slope as would be expected for TTF-TCNQ in the nonmetallic region. However, because of the rapid variation of susceptibility with temperature in this region, the ESR results are less accurate as a result of temperature drift. We emphasize that the region of concern is $T > 60$ K, and the conclusions do not require data below 60 K. The low-temperature points are included for completeness.

These data, and also measurements of proton relaxation rates on partially deuterated TTF-TCNQ, suggest that the spin susceptibility should be viewed as a single entity arising from a coupled two-chain system with a sufficiently strong coupling to produce a single ESR resonance containing the spin moment of the entire system.

The authors are grateful to H. S. Jarrett for many helpful discussions. These experiments were made possible by the synthesis of high-

purity TTF-TCNQ by L. R. Melby.

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[1] Y. Tomkiewicz, B. A. Scott, L. J. Tao, and R. S. Title, Phys. Rev. Lett. 32, 1363 (1974).

[2] L. R. Melby, H. D. Hartzler, and W. A. Sheppard, J. Org. Chem. 39, 2456 (1974).

[3] The data of Fig. 1 report smaller values of χ, in the region near 60 K, than do previously published susceptibility curves. [See Ref. 1, and J. C. Scott, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 3131 (1974).] A series of ten runs on five separate preparations involving different synthesis procedures all gave results within the error limits discussed in the text. Our experience with susceptibility measurements has shown that a slight amount of oxygen contamination in the apparatus leads to anomalously high values of χ in the 60-K region.

[4] Temperatures are accurate to within 1 K with the nitrogen flow system and approximately 2.5 K with the helium flow system.

[5] See L. S. Singer and J. Kommandeur, J. Chem. Phys. 34, 133 (1969).

[6] This procedure involves the assumption that the profile is exactly Lorentzian for an arbitrary distance into the wings, which is, strictly speaking, impossible. However, the fact that the resonance is quite narrow, coupled with the observed Lorentz shape of the central portion, suggests that the profile is extensively motionally narrowed. Under these circumstances deviations from the Lorentz shape probably occur hundreds, or even thousands, of linewidths into the wings, and the error in the area as we compute it would be entirely negligible. If, for some reason, the profile deviated from Lorentzian *immediately* outside our experimentally accessible region, a maximum absolute error of 6–8% would occur in the integrated area. However, since we are interested only in the relative values of the areas, even this would not affect our results unless the shape of the curve only in the area outside of our experiment changed drastically as a function of temperature.

[7] These results are in approximate agreement with susceptibility data obtained from low-field ESR experiments. See Ref. 3.

ERRATA

QUADRUPOLE MOMENT OF THE DEUTERON. R. V. Reid, Jr., and M. L. Vaida [Phys. Rev. Lett. 29, 494 (1972)].

In checking integrals similar to matrix elements of the field gradient operator, it was found that earlier the computing machine gave several matrix elements incorrectly. After correcting these we obtain $Q = 0.2860 \pm 0.0015\ \text{fm}^2$ for the quadrupole moment of the deuteron. This is a revision of the value $0.2875 \pm 0.0020\ \text{fm}^2$ reported earlier. The estimated error assigned to Q was obtained as before and is intended to represent 1 standard deviation.

To four significant figures all nine values of Q obtained from the three wave functions and the three experimental quadrupole interaction constants are identical. That the high degree of convergence, which this indicates, is probably due to a fortuitous choice of bases for the wave functions will be shown elsewhere.

OBSERVATION OF THE $E2$ NUCLEAR RESONANCE EFFECT IN PIONIC CADMIUM. J. N. Bradbury, M. Leon, H. Daniel, and J. J. Reidy [Phys. Rev. Lett. 34, 303 (1975)].

Because of an error in the calculation of the nuclear resonance effect for ^{111}Cd, the quoted theoretical ratios are inaccurate; the corrected values for the comparison of ^{112}Cd and ^{111}Cd are

$$R_\alpha(\text{theory}) = 0.72^{+0.07}_{-0.13}, \tag{3}$$

$$R_\beta(\text{theory}) = 0.77^{+0.05}_{-0.10}, \tag{4}$$

and for ^{111}Cd and ^{110}Cd (*Note added*)

$$R_\alpha(\text{theory}) = 0.73 \pm 0.05,$$

$$R_\beta(\text{theory}) = 0.79 \pm 0.03.$$

The agreement with the experimental values for these ratios, already quite good, is improved by these changes.

Also, in the *Note added,* the 2^+ energy of ^{110}Cd should be given as 658 keV, not 257.9 keV.