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Thermal and magnetic study of exchange in the quasi-1-D molecular compound, $\text{TTF}\cdot\text{PtS}_4\text{C}_4(\text{CF}_3)_4$

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ABSTRACT

Single crystal magnetic susceptibility results from 2.5K to 270K and specific heat results from 3K to 16K are reported for $\text{TTF} \cdot \text{PtS}_4\text{C}_4(\text{CF}_3)_4$ (TTF=tetra-thiafulvalene). The combined results are analyzed using a simple model which ignores differences between the two types of $S=1/2$ spin carriers and involves a system of ferromagnetic chains treated "exactly", with interchain antiferromagnetic interaction evaluated in a mean field approximation. Above an apparent ordering transition at 8K, the susceptibility is well described by the model irrespective of whether the ferromagnetic exchange is Heisenberg, Ising or intermediate to these. The magnetic contribution to the specific heat is obtained using earlier results for the isostructural Au compound. Comparison with specific heat calculations for the Heisenberg, Ising and intermediate cases successfully narrows the ambiguity to an intermediate anisotropic exchange close to the Heisenberg limit.

I. INTRODUCTION

Quasi-one-dimensional (1-D) systems have attracted much attention for their unique physical properties. We have prepared [1] a family of π -donor-acceptor compounds of the type $\text{TTF}^+ \cdot \text{MS}_4\text{C}_4(\text{CF}_3)_4^-$, where TTF^+ =tetra-thiafulvalinium and $\text{MS}_4\text{C}_4(\text{CF}_3)_4^-$ is a series of bis-dithiolene metal complex anions with $M=\text{Cu}, \text{Au}, \text{Pt}$ and Ni . They are magnetic insulators with much variety in magnetic properties [2]. The TTF^+ ions are spin-1/2 paramagnetic ($g \approx 2$) while the $\text{MS}_4\text{C}_4(\text{CF}_3)_4^-$ ions are diamagnetic for $M=\text{Au}, \text{Cu}$ but paramagnetic for $M=\text{Ni}, \text{Pt}$ ($S=1/2, g \approx 2$). In the $M=\text{Au}, \text{Cu}$ compounds, a system of antiferromagnetic (AF) chains of TTF^+ spins displays a spin-Peierls transition [3,4]. We examine the contrasting $M=\text{Pt}$ compound, whose powder susceptibility [5] indicates dominant ferromagnetic (FM) subsystems with residual AF coupling at low temperatures.

We report single crystal susceptibility (χ) and specific heat measurements (C_p). The magnetic contribution to the specific heat (C_m) is estimated using earlier results for the $M=\text{Au}$ compound [6]. We explore the limits of an analysis of the combined results for the $M=\text{Pt}$ compound using a simple model which ignores differences between the two types of spin carriers. A system of FM chains is treated with "exact" numerical models while the AF interchain exchange is evaluated in a mean field approximation. It proves possible to describe the properties within reasonable limits, in terms of a dominant FM exchange intermediate between the isotropic Heisenberg and the extreme uniaxially anisotropic Ising limits, but closer to the former.

II. EXPERIMENT AND RESULTS

The synthesis and structure of $\text{TTF} \cdot \text{PtS}_4\text{C}_4(\text{CF}_3)_4$ have been reported [1,7]. All of the compounds of the family crystallize to form stacks in which the planar TTF^+ and $\text{MS}_4\text{C}_4(\text{CF}_3)_4^-$ ions alternate. The $M=\text{Pt}, \text{Cu}$ and Au compounds are isostructural, with triclinic symmetry, resembling a distorted NaCl arrangement [4].

In our earlier work, the molecular stacking axis was suggested as the exchange path both for the AF

chains of the $M=\text{Cu}, \text{Au}$ compounds and for the FM chains of the $M=\text{Pt}$ compound. Each compound shows evidence [2] of an abrupt but magnetically undramatic change just below room temperature. Delker [8] studied its structural aspects for $M=\text{Cu}$. He showed that nearly equivalent diagonal directions of the room temperature face-centered "NaCl" structure became rather different below the transition. Its importance became apparent with the observation [9] that the predicted low temperature dimerization in the Cu compound occurs along the shorter of these diagonals. Thus, the AF interaction of the $M=\text{Cu}, \text{Au}$ compounds is along this diagonal and appears to result from direct exchange between TTF^+ spins.

No similar study of the $M=\text{Pt}$ compound has been carried out. It is, however, reasonable to assume that this structural feature persists and, with it, the AF exchange. The simplest assumption for the FM interaction is that it occurs along the molecular stacking axis.

Magnetic susceptibility measurements were carried out on a 3mg crystal using the Faraday method with techniques described elsewhere [4]. Measurements were made with the field along the stacking axis \vec{c} , and along two other principal directions, \vec{a}^* and \vec{b} , of the face-centered cell. In Fig. 1, we show these data. The solid line is calculated from the model as described in Section III. Results for the three directions have been normalized arbitrarily at 100K because of a variation (up to 19%) in magnetometer response when the sample is remounted for different orientations. The positive deviation from a Curie-law above 40K demonstrates the FM interaction, while the drop in χ_b below 12K indicates some AF coupling as well as magnetic anisotropy. In ref. [2] we raised questions as to the "completeness" of the apparent transition to a 3-D AF ordered state at the apparent inflection point in χ_b at 8K. These questions remain.

The specific heat was measured utilizing a calorimeter described elsewhere [10]. Data were taken on a compacted sample (464mg) using a heat-and-drift cycle time of 25 or 125 sec. In Fig. 2 we show the C_p data for the $M=\text{Pt}$ compound, along with the data for the isostructural $M=\text{Au}$ member [6]. A broad anomaly be-

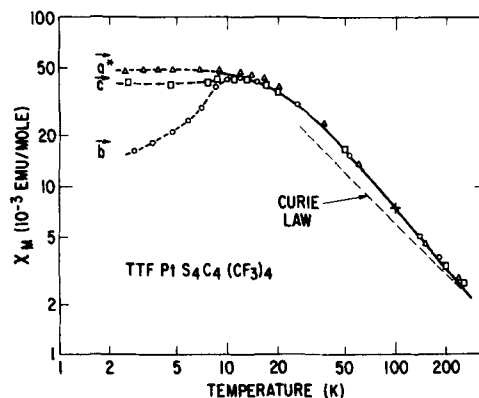


Fig. 1. Magnetic susceptibility for $\text{TTF} \cdot \text{PtS}_4\text{C}_4(\text{CF}_3)_4$, including a line calculated from the model.

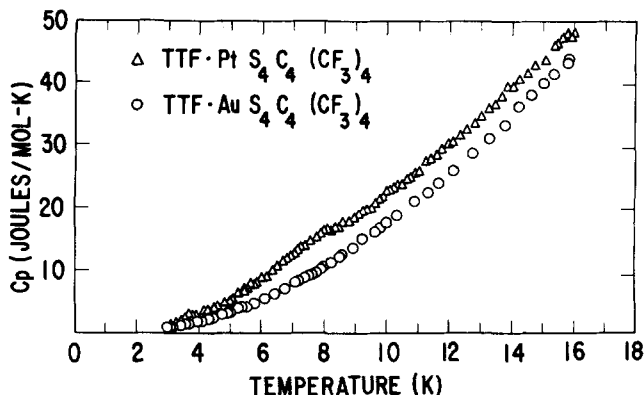


Fig. 2. Specific heat data for the M=Pt and M=Au Compounds

tween 5K and 9K is visible for the Pt compound.

Some epr measurements ($f=20\text{GHz}$) were also performed, mainly at 20K. A single absorption line is seen with g -factors of 1.91 ± 0.05 along the \vec{c} -axis and extremes of 2.05 ± 0.05 and 2.10 ± 0.05 in the plane perpendicular to \vec{c} . The considerable width at half maximum of ~ 1800 Oe, is responsible for the large error limits on the g -factors. This 10% g -factor anisotropy is midway between the 20% anisotropy observed on the anion complex in a frozen glass [11] and the $<0.5\%$ anisotropy of the TTF^+ ion [4] indicating coupling between the different spin carriers. It has also been suggested [12] that anisotropic ionic g -factors can introduce anisotropy in exchange of order $\Delta g/g$ or $(\Delta g/g)^2$.

III. SUSCEPTIBILITY ANALYSIS

The reduced susceptibility χ_r for interacting chains may be written in standard mean field approximation

$$(\chi_r)^{-1} = (\chi_{O,r})^{-1} + \lambda_{AF}$$

where, $\chi_{O,r}$ is the isolated chain susceptibility and λ_{AF} is the mean field interaction parameter. The reduced susceptibility is dimensionless, i.e., $\chi_{O,r} = \chi_0 J_F / N g^2 \mu_B^2$, where J_F is the FM intrachain exchange, N is the number of spins per mole, and the other symbols have their usual meaning.

We compared two double log plots, one of the measured $(\chi_m)^{-1}$ vs. T and the other of $(\chi_r)^{-1}$ vs. reduced temperature kT/J_F . For given $\chi_{O,r}$ we construct curves with differing λ_{AF} and look for the best superposition of model and measurement. The "T" scaling yields J_F/k

and that of χ^{-1} determines g . The "best fit" λ_{AF} corresponds to an interchain coupling $J_{AF} = J_F \lambda_{AF} / 2z$,

where z is the number of significant neighbors.

Inasmuch as we are considering anisotropic exchange (for $S=1/2$, there can be no crystal field anisotropy), we compare the experimental χ_b with the theoretical $\chi_{||}$. If γ is the anisotropy parameter in the Heisenberg-Ising Hamiltonian [13], $\gamma=1$ defines the Heisenberg and $\gamma=0$ the Ising exchange. We have extended earlier calculations [14,15] to produce $\chi_{O,r}$ extrapolations for various γ values for infinite length systems based on rings up to 13 spins.

For each γ , we can narrow the graphical comparison to determine a "best fit" J_F and λ_{AF} pair, estimated to 10%. These are given in Table I. The resulting fit is, however, equally satisfactory irrespective of the γ value! The method is indeterminate. In most other studies, one of the limiting cases $\gamma=0$ or $\gamma=1$ is assumed, often without apparent justification. For the Pt compound the χ and g -factor anisotropy suggest some intermediate range of γ . The analysis of C_m restricts

TABLE I

"Best χ Fit" Exchange Parameters for Various Anisotropies, γ , in $\text{TTF}\cdot\text{PtS}_4\text{C}_4(\text{CF}_3)_4$

γ	1	.9	.85	.5	0
J_F/k	65	66	60	36	36
λ_{AF}	.52	.68	.80	1.40	1.40
g	1.69	1.67	1.71	1.82	1.77

the choice to the region close to $\gamma=0.9$. The solid line of Fig. 1 presents this case with the other parameters of Table I.

The g -factors of Table I are relatively independent of γ , but are low compared to the epr g -factors. Some of the discrepancy may reside in the experimental normalization which could raise values by about 0.17. Other possible sources are the crudeness of the mean-field approximation when $|J_{AF}|$ is not small in comparison with J_F , as well as the simplification of ignoring differences between the different spin carriers and their respective interactions.

IV. SPECIFIC HEAT ANALYSIS AND DISCUSSION

The usual problem with specific heat results is that of reliably separating the magnetic and lattice contributions, i.e., $C_p = C_m + C_L$. The lattice subtraction problem here is formidable in view of the large lattice contribution due to complexity of the structure and the relatively high transition temperatures [4,6]. In the case of atomic lattices that are not extremely anisotropic, a low temperature limiting form $C_L = \beta T^3$ (following, e.g., from a simple Debye model) is valid for a limited temperature range. With low symmetry lattices problems arise in formulating suitable extensions of the 3-D Debye model, and much effort has been expended in methods of analysis [16]. Further, in our case of molecular solids, low-temperature intramolecular excitations severely limit the range of validity of the basic T^3 approximation [17].

A second, and very successful empirical approach in applicable cases, is the use of a diamagnetic isostructural (nearly isomorphous) analog. A corresponding state procedure [18] is used to make a small modification of C_p of the diamagnetic analog, which then represents that of the magnetic system under investigation. This procedure consists of writing $C_m = f(T/b)$, where f is one unknown function for an isostructural family and b is a different scaling temperature for each compound.

In this family we lack a diamagnetic analog because the TTF^+ cation is always paramagnetic. However, the availability of C_p results for M=Au [6], the relatively

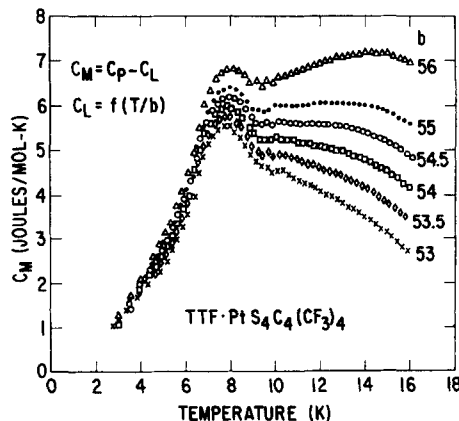


Fig. 3. A family of potential magnetic specific heat curves, C_m (Pt) for various values of the scaling factor b .

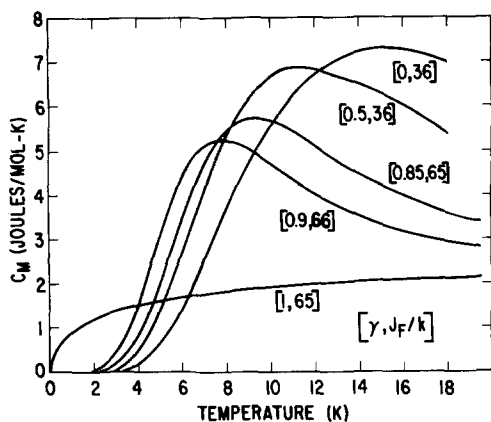


Fig. 4. Theoretical C_m curves for FM chains calculated with $[\gamma, J_F/k]$ values from Table I.

low temperature at which the second-order transition occurs [4], and our success in describing the magnetic properties above that transition, yield a very good approximation to the desired analog. We subtract the theoretical C_m for a system of AF $S=1/2$ Heisenberg chains [13-15] evaluated for $|J_{AF}|/k=34K$ appropriate to the Au compound, and thus obtain $C_L(Au)$ for $T > 4K$ which we then use to estimate $C_L(Pt)$.

The results for $C_m(Pt)$ are very sensitive to the scaling factor b , as shown in Fig. 3. A family of potential $C_m(Pt)$ curves is displayed which result from trying various possible $C_L(Pt)$ curves characterized by b values in the range 53-56. (Note that $b(Au)=55$ is the same as b_D in Ref. 6). The relative smoothness of these curves results from a polynomial fitting: the raw data show considerable scatter at temperatures above about 10K. Each curve shows a broad anomaly near 8K which corresponds in temperature to the apparent inflection point in χ_p . It appears to lack the sharpness which usually appears in transitions to ordered magnetic states. This rounding is not due to chemical impurity or lack of data points.

Theoretical curves for C_m obtained numerically by extrapolation techniques, similar to those used for χ , for a variety of anisotropy values between $\gamma=1$ (Heisenberg limit) and $\gamma=0$ (Ising limit) are shown in Fig. 4. The parameters are for the various " χ -acceptable" combinations $[\gamma, J_F]$ listed in Table I. In contrast to previous analyses, we concentrate on intermediate anisotropy. The form of the theoretical curves shows considerable variation with anisotropy, particularly for $\gamma \geq 0.85$. It is clear that fitting theoretical and experimental C_m curves can narrow down the acceptable ranges of $[\gamma, J_F]$ and thus remove the indeterminacy of the χ -analysis. An important restriction is that J_F be adjusted so that the low temperature results permit an entropy matching at high temperatures. This establishes a " C_m -acceptability" criterion which appears as an upper limit curve on the J_F - γ graph of Fig. 5, along with the χ -acceptable range. The crossing of these two sets of criteria in the region $0.85 < \gamma < 0.9$ indicates where our final best fit of theory to experiment must

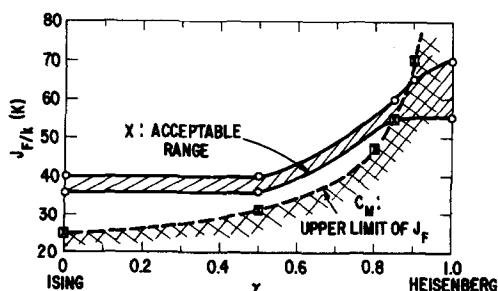


Fig. 5. Comparison of the χ -acceptable and C_m -acceptable ranges of $[\gamma, J_F]$ obtained from the model.

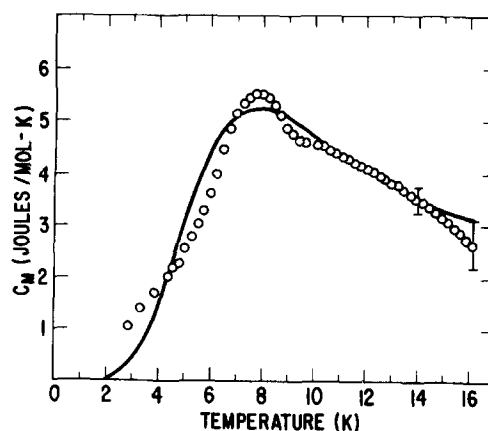


Fig. 6. Comparison of C_m (expt) with $b=53$ with C_m (theory) for $\gamma=0.9$, and $J_F/k=66K$ for $TTF \cdot PtS_4C_4(CF_3)_4$

lie. The "best" curve corresponds to $\gamma=0.9$, $J_F/k = 65K$ and is shown in Fig. 6 in comparison with $C_m(Pt)$ for $b=53$. Error bars arising from scatter in C_m data are indicated for the higher temperature region, while much smaller ones pertain at lower temperatures. The crossing of the theoretical and experimental curves down near 4K is not understood. It may be related to residual effects of the 2.K transition in the $M=Au$ compound.

From the relationship between λ_{AF} , J_{AF} , J_F and z , we roughly estimate $|J_{AF}|/k$ to be 11K (with $z=2$) or about one-third the value found in the isostructural $M=Au, Cu$ compounds. This may reflect a different degree of distortion for the Pt compound and/or the average of several (possible competing) interstack exchange interactions.

We have thus obtained estimates of the parameters describing both the susceptibility and magnetic specific heat of $TTF \cdot PtS_4C_4(CF_3)_4$, within the simple model proposed. While the numerical values cannot be considered to be very precise, they serve as guides until more sophisticated theoretical approaches can be developed in conjunction with future data using such microscopic probes as epr, nmr and neutron diffraction. The C_m measurements were undertaken because of uncertainties in the interpretation of the experimental χ . The C_m analysis has been highly successful in determining the degree of Heisenberg-Ising uniaxial anisotropy, and may prove valuable for examining similar systems.

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