Magnetic field effects on (TTF)$CuS_4C_4(CF_3)_4$, a spin-Peierls system

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(Received 29 March 1979)

We present neutron scattering data in magnetic fields up to 80 kG and magnetization data up to 150 kG for the spin-Peierls system (TTF)$CuS_4C_4(CF_3)_4$. The spin-Peierls transition temperature is depressed by the field, in reasonable agreement with mean-field theory, and the nonmagnetic spin-Peierls phase disappears above ~125 kG. We discuss details of the observed behavior in the light of existing theory. We show that the behavior is different from that of a quasi-one-dimensional magnetic system which orders antiferromagnetically, because of the contrasting role of fluctuations.

I INTRODUCTION

The donor-acceptor compound tetrathiafulvalenium *bis-cis*-(1,2-perfluoromethylethylene-1,2-dithiolato)-copper [or,(TTF) $CuS_4C_4(CF_3)_4$] has been demonstrated[1] to be the prototypical example of a spin-Peierls system in several respects. The magnetic susceptibility and EPR,[1] specific heat,[2] NMR,[3] and x-ray scattering[4] are all in basic agreement with behavior expected from theory.[1,5–8]

This material consists of stacks of alternating TTF^+ and $CuS_4C_4(CF_3)_4^-$ ions.[1] The TTF^+ ion alone carries a spin $\frac{1}{2}$, and these spins interact along a direction which is at an angle to the stacking axis. (More precisely, the stacking axis is $\vec{C}_F$ of the face-centered unit cell, and the magnetic axis is $\vec{C}_p$ of the primitive unit cell.[4]) The net result is a system of one-dimensional (1-D) Heisenberg spin-$\frac{1}{2}$ antiferromagnetic chains, which are coupled to a 3-D phonon field. The system can be described by the Hamiltonian[5] $\sum J\vec{S}_i\cdot\vec{S}_j$ + phonons, where the sum is over nearest-neighbor intrachain spins $\vec{S}_i$ and the (intrachain) exchange energy J is a function of the interspin separation. For the uniform chain, J is 77 K. Below a transition temperature ($\simeq$ 12 K in zero field), the coupled chains undergo a second-order, progressive spin-lattice dimerization. At zero temperature the spin system is in a singlet ground state with a magnetic gap. This transition appears to be crucially aided by a softness of the lattice[4] at the proper position in reciprocal space for dimerization, and the mean-field nature of the transition also may rely on this fact.[7,8]

In this paper, we examine the behavior of this system in high magnetic fields in order to gain further insight into the spin-Peierls phase behavior. We describe in Sec. II a neutron scattering study in fields up to 80 kG. In Sec. III, we report magnetization measurements up to 150 kG. In Sec. IV, we discuss these measurements in the context of what is expected theoretically of this system.

II. NEUTRON SCATTERING

We have carried out a neutron diffraction study of (TTF)$CuS_4C_4(CF_3)_4$ using a superconducting magnet capable of generating fields up to 80 kG. The experiment was performed on a triple-axis spectrometer set for elastic scattering (14 meV) at the Brookhaven National Laboratory High Flux Beam Reactor. Neutrons were monochromated and analyzed with the (002) reflection from a pyrolytic graphite crystal. Higher-order wavelengths were removed with a pyrolytic graphite filter.

For this study a small crystal ($9.1\times0.76\times0.5\text{mm}^3$) was oriented to study momentum transfers $\vec{Q}=(h,0,l)_p$, where p denotes the choice of primitive triclinic unit cell. Because the split coil magnet has very limited angular access it was necessary to align the crystal accurately before insertion in the magnet. This procedure was complicated by the large structural phase transition at $T=240$ K which results in considerable motion of the crystal.[9] It is only possible to predict the orientation of the crystal below this phase transition if it is held rigidly on a particular crystal face. We rejected this method of mounting to minimize the strain which would be developed below this transition. Instead, we chose to wrap the crystal in an Al foil envelope and monitor the crystal's motion down to 10 K in a preliminary diffraction study outside the magnet assembly. Following this examination we returned the sample to room temperature and oriented it such that if (i) the motion were reproducible and (ii) the crystal did not break, it would be aligned correctly at low temperature in the magnet cryostat. Rather unexpectedly, our first attempt worked satisfactorily and the data presented below were obtained.

Our principal results are summarized in Figs. 1–3. First, as shown in Fig. 1, we find no magnetic field dependence of the wave vector associated with the dimerization. Data taken at $T=5$ K are shown at 0 and 78 kG with no apparent change in the reduced wave vector $\vec{q}=(\frac{1}{2},0,\frac{1}{2})$. However, the intensity reduction indicated in this figure is a real effect which is a result of the suppression of the transition temperature as shown in Fig. 2. We measured the intensity of the (1.5, 0, 0.5) peak as a function of temperature at four different field values. Approximate transition temperatures T_c are obtained by extrapolating the linear region of these curves. The decrease in

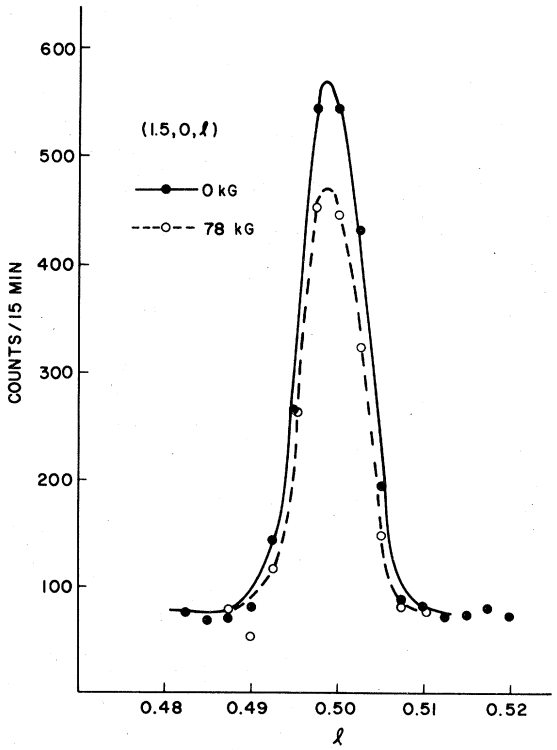

FIG. 1. Scans through the (1.5;0,0.5) dimerization Bragg peak at zero field and at the highest obtainable field, 78 kG ($T=5$ K).

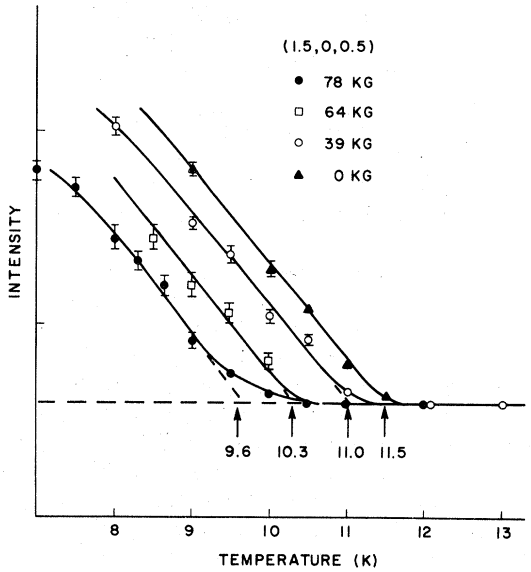

FIG. 2. Temperature dependence of the intensity of the (1.5,0,0.5) peak at a series of different applied magnetic fields.

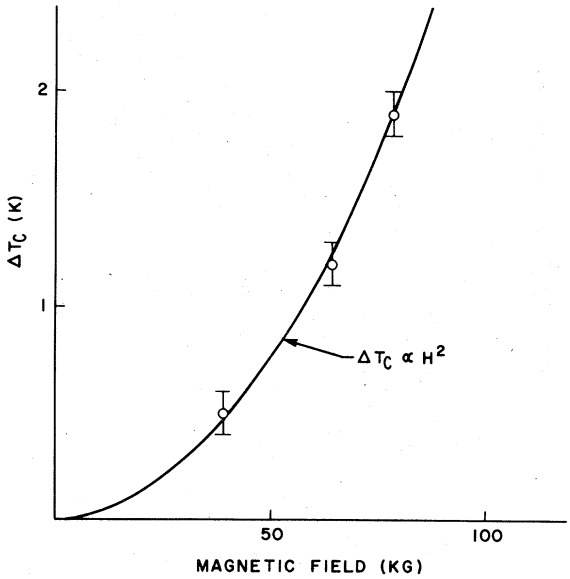

FIG. 3. Decrease in transition temperature vs applied field. Solid line is the relation $T=3.1\times10^{-4}H^2(\text{kG})$.

transition temperature, ΔT_c, is then plotted versus field H in Fig. 3. Note that $T_c(H=0) \equiv T_{c0}$ as determined by this method is 11.5 K. Sample-dependent variations of T_{c0} from 11.5 to 12 K with susceptibility and to 12.4 K with specific heat[2] have been observed.

III. HIGH-FIELD MAGNETIZATION

We have examined the high-field magnetization of (TTF)$CuS_4C_4(CF_3)_4$ at Service National des Champs Intenses–CNRS. The magnetic field is produced in a water-cooled Bitter-type solenoid. The maximum obtainable field is 155 kG at a power dissipation of 5 MW. Carbon and platinum resistors are used for temperature measurement and regulation. The magnetization is measured using an extraction technique at constant magnetic field on the sample. The signal produced by the sample displacement in measuring coils is integrated using a digital voltmeter. Sensitivity is 10^{-3} emu. A shift of 2.8×10^{-4} emu/mole has been made to correct for the intrinsic diamagnetism of the sample. A temperature- and field-dependent correction has been made for the Plexiglass holder. Because of the small amount of powder sample used (0.19 g), the error in the magnetization is almost ±20 emu/mole.

The results of the measurements are presented in Figs. 4–6. In Fig. 4, we present the magnetization M

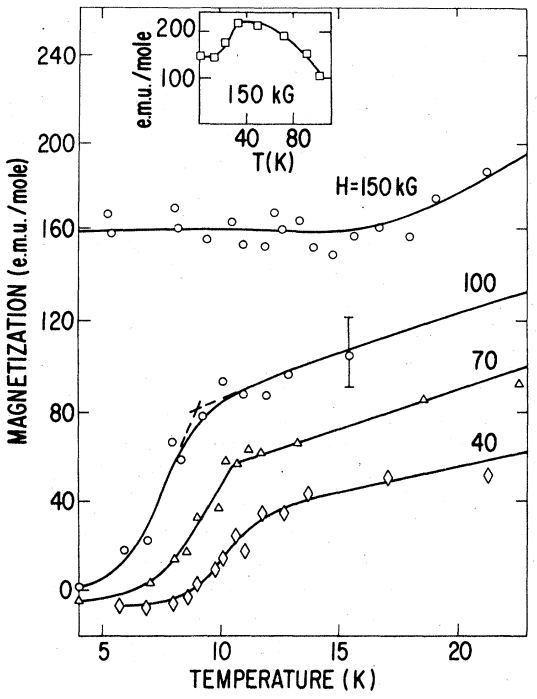

FIG. 5. Magnetization vs temperature in various fields. The dashed lines are an aid to determining T_c. The inset shows a broader temperature range at $H = 150$ kG.

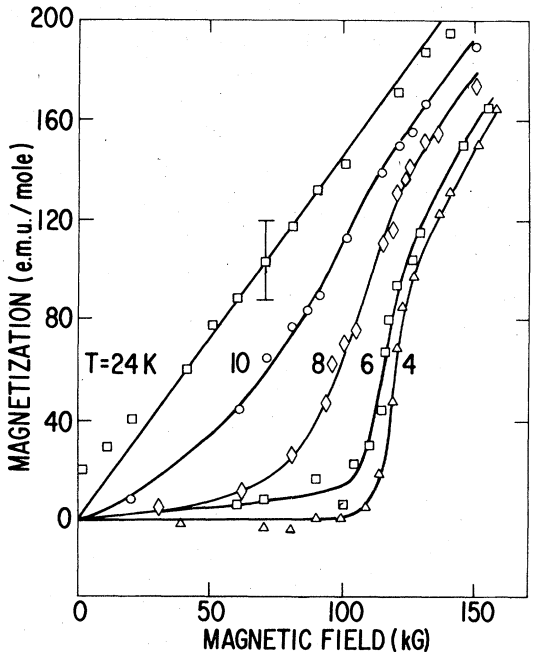

FIG. 4. Isothermal curves of magnetization vs field.

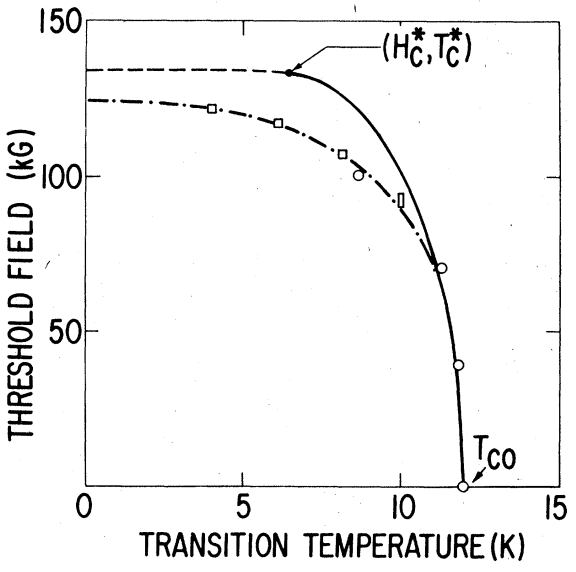

FIG. 6. Transition temperature vs magnetic field. The squares (circles) are obtained from Fig. 4 (Fig. 5). The dot-dashed curve is a guide to the eye and the solid curve is a theoretical prediction (see text).

versus field H at various temperatures. Figure 5 shows M versus temperature T in various fields. In Fig. 6, we show the threshold field versus transition temperature obtained from the inflection points of the isothermal curves (Fig. 4) for the squares; and from the "knees" of the isofield curves (Fig. 5) for the circles. Figures 3 and 6 are in agreement within experimental uncertainty. The $H=0$ point in Fig. 6 was determined previously by susceptibility measurements on other samples to be 12 K $= T_{c0}$.

The most notable single observation in the data is the disappearance of the nonmagnetic spin-Peierls phase above $H \simeq 125$ kG. The $M(T)$ curve at 150 kG (Fig. 5) shows that the state above 125 kG is no longer nonmagnetic, but its detailed nature requires more study. We looked for hysteresis at 4 K because M versus H gives some appearance of a first-order transition; none was observed.

IV. DISCUSSION

The variation of T_c with field, $T_c(H)$, has been predicted in mean-field theory[10,11] for a spin-Peierls system. For small values of $\mu_B H/k_B T_{c0}$ ($\mu_B \equiv$ Bohr magneton; $k_B \equiv$ Boltzmann constant), $T_c(H)$ is quadratic in H.

$$T_c(H)/T_{c0}=1-0.44(\mu_B H/k_B T_{c0})^2 - 0.2(\mu_B H/k_B T_{c0})^4+\cdots \quad (1)$$

as an expansion in H.[10] The solid curve in Fig. 3 depicts a quadratic decrease of $T_c(H)$,

$$T_c(H)-T_{c0}=-[(3.1\pm 0.2)10^{-4}\ \mathrm{K/kG^2}]H^2. \quad (2)$$

The corresponding coefficient from Eq. (1) is 1.66×10^{-4} K/kG^2, a discrepancy of almost a factor 2. This discrepancy may be due to inadequacies of mean-field theory. Cross and Fisher[8] have obtained both non-mean-field and mean-field results for $T_c(H)$. The former shows a more rapid decrease of T_c with H^2 than the latter, but both are less rapid than Eq. (1).

Figure 6 shows $T_c(H)$ with more uncertainty over a much larger range of H. Over this range, Eq. (1) for $T_c(H)$ is inadequate and instead one must use Eqs. (3) and (5) of Ref. 10. A computer solution of these equations is shown by the solid line, and again it deviates from the data somewhat at high fields. The new experimental feature is the disappearance of the low-magnetization phase at high field. The theory[10,11] predicts that at $H_c^* \simeq 0.75 k_B T_{c0}/\mu_B$ (for small $\mu_B H/J$), the character of the spin-Peierls phase will change markedly. (Note that H_c^* is the same as H_c in Refs. 10 and 11). Specifically, the wave vector of the distortion will change to a new (commensurate or incommensurate) value. The highest transition temperature where this occurs is given by $T_c^* \equiv T_c(H_c^*) = 0.54\ T_{c0}$ (by a more refined version of the computation in Ref. 10). For (TTF)$CuS_4C_4(CF_3)_4$, these values are

$$T_c^* \simeq 6.5\ \mathrm{K},\quad H_c^* \simeq 134\ \mathrm{kG}\ . \quad (3)$$

In Fig. 6, (H_c^*, T_c^*) is a multicritical point; the transition for $T < T_c^*$ is first order if the distortion wave vector changes to a new commensurate value. The dashed line indicates this behavior, and its exact path is uncertain (i.e., it need not be straight as shown). It is interesting that the highest experimental threshold is $\sim$ 125 kG, quite close to the predicted H_c^*. Note also that the $M(H)$ curves (Fig. 4) are suggestive of a first-order transition at low temperatures (6 and 4 K).

The (TTF)$CuS_4C_4(CF_3)_4$ system has an important complication with regard to high-field behavior. As noted before, the spin-Peierls distortion occurs where the lattice is soft.[4] This soft region has a narrow width in reciprocal space and, therefore, will act as an additional pinning force on the periodicity (wave vector) of the distortion. Cross and Fisher[8] believe that this force is relatively small and will hold the system in the dimerized phase only to $\sim$ 15% higher fields than calculated above [Eq. (3)]. If this is incorrect and the periodicity is totally clamped, then the system will behave differently. The transition as H increases from zero will be to the undimerized, uniform chain for all $T < T_{c0}$, instead of to a spin-Peierls phase with a different periodicity for $T < T_c^*$. The theoretical phase diagram for the clamped system has not yet been examined in detail, but the predicted transition at $T=0$ is first order.[12] Since $T_c(H)$ near T_{c0} is second order, this phase diagram will presumably exhibit a tricritical point. We have performed (non-mean-field) computer studies on the Heisenberg system which give a preliminary indication that the clamped Heisenberg spin-Peierls system has two stable values of the dimerization amplitude with a first-order transition from one to the other as field increases. The $M(H)$ curves (Fig. 4) give some hint of such an efffect, and this will be examined and reported on in detail later.

These data illustrate another important and definitive difference in our spin-Peierls system and a quasi-1-D magnetic system which orders in a 3-D antiferromagnetic state at low temperatures. In our spin-Peierls system, $T_c(H)$ is a monotonically decreasing function of H, whereas in a quasi-1-D magnetic system, the 3-D ordering temperature, $T_N(H)$, first increases as H increases, and then decreases, giving a maximum at $H \neq 0$.[13] This phenomenon can be restated in terms of the effect of a magnetic field on the number of spin components n of the order parameter[14] ($n = 1$ is an Ising-like, $n = 2$ is an XY,

and $n = 3$ is a Heisenberg system). The effect of H is to decrease n by one, and thus a Heisenberg system crosses over to an XY system, etc. In a magnetic system the relative ordering of transition temperatures is $T_N^{\text{Ising}} > T_N^{XY} > T_N^{\text{Heis}}$, other magnetic parameters being equal.[15] Therefore, a magnetic field will initially raise T_N, before this tendency is counteracted by the increasing Zeeman energy, which ultimately reduces T_N to zero. For a spin-Peierls system, a magnetic field will not directly affect the phonon degrees of freedom but will again decrease n. For spin-Peierls systems, however, the relative ordering of transition temperatures is in the opposite sense: $T_c^{\text{Ising}} < T_c^{XY} < T_c^{\text{Heis}}$, all other relevant parameters being equal.[1,5,8,16] Therefore, both the Zeeman energy and the n-reduction effect will act to reduce $T_c(H)$, as observed.

These contrasting changes of T_c and T_N with n (and, therefore, with H) may be understood in terms of the differing role of fluctuations in the two systems. As the spin dimensionality n increases, magnetic quantum fluctuation effects increase. These fluctuations decrease the intrachain spin coherence length and thereby depress T_N.[17] Thus a larger n means a lower T_N. In contrast, in a spin-Peierls system it is the quantum spin fluctuations (or spin zero-point energy, as defined with respect to the classical ground-state energy[18]) which provide the driving energy for the spin-Peierls transition, when the exchange J depends linearly on the intrachain spacing.[1] The dimerization of the chains introduces a gap in the magnetic excitation spectrum, gradually suppressing the quantum fluctuations until they vanish at the dimer limit, and thereby the magnetic energy of the system is lowered. Since the spin fluctuations decrease with decreasing n, the energy available to the spin-Peierls phase also decreases with n, and the ordering sequence of T_c with n noted above results. Since H reduces n, H must also reduce T_c.

It is important to note that there is another cause of the increase of T_N: thermal fluctuation effects.[19] Thermal fluctuations also increase as n increases[20] or indeed as any degrees of freedom increase. Thermal (like quantum) fluctuations reduce the intrachain spin coherence length and thereby contribute to the aforementioned decrease of T_N as n increases. These effects are evidently less important in a spin-Peierls system than quantum spin fluctuations, since T_c increases with increasing n. In the context of thermal effects, it is interesting to note that a classical system of Heisenberg chains cannot undergo a spin-Peierls transition (for J linear in intrachain spacing) but can easily undergo 3-D antiferromagnetic ordering with the discussed initial increase of $T_N(H)$.[13,19]

In conclusion, we have presented neutron scattering and magnetization data on the spin-Peierls system (TTF)$CuS_4C_4(CF_3)_4$ in high magnetic fields. The decrease of the transition temperature with increasing field is in reasonable agreement with theory. The detailed nature of the system when $T_c(H)$ vanishes is not known and will be the subject of further study. More refined theory and data are necessary to make certain of the agreement between theory and experiment. In particular, the consequences of the pre-existing soft lattice mode and its pinning effects must be studied further; the phase diagram depends crucially on the results. Finally, we showed that quantum fluctuations explain the marked difference between the field dependence of the transition temperatures of the spin-Peierls system and a quasi-1-D magnetic system which undergoes 3-D antiferromagnetic ordering.

ACKNOWLEDGMENTS

We acknowledge helpful discussions with W. P. Wolf. Work at GE was supported in part by the Air Force Office of Scientific Research under Contract No. F44620-76-C-0006. Research at Brookhaven was supported by the DOE under Contract NO. EY-76-C-02-0016. J. C. B. was supported by NSF Grant No. DMR 77-24136, NATO Grant 1338, and a Fellowship at Bunting Institute, Radcliffe College.

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