where $d\ln R/dT^{-1}$ is diminished by about a factor of 2. Deviations found at low frequencies are probably caused by film inhomogeneity and those at high frequency by pinning forces. The resistance at $T_{\rm KT}$ varies with frequency as ω^{α}, with $\alpha \approx 0.9$, and is smaller than the prediction of the dynamical theory[7]: $R = 2\pi^3\omega L_K l_\omega^{-2}$. This discrepancy between the theory and experiment is perhaps due to pinning effects, which were not taken into account in the theory. Apart from the deviations noted above, our results generally confirm the fundamental physical ideas of Kosterlitz and Thouless.

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New High-Field Phase in the Spin-Peierls System, Tetrathiafulvalene-$CuS_4C_4(CF_3)_4$

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New magnetization data on the spin-Peierls system tetrathiafulvalene-$CuS_4C_4(CF_3)_4$ for $h \leq 155$ kOe and $T \geq 1.5$ K provide evidence for a new phase above $h \sim 115$ kOe. Considerable hysteresis in the field-induced transitions is observed for $T \leq 5.5$ K. These results are discussed in the light of current theoretical ideas.

We report the first observation of a new phase in the spin-Peierls (SP) system tetrathiafulvalene-*bis-cis*-(1,2-perfluoromethylethylene-1,2-dithiolato)-copper [(TTF)-$CuS_4C_4(CF_3)_4$ or further abbreviated as TTF-BDT(Cu)] at high magnetic fields and low temperatures. The SP transition is a progressive spin-lattice dimerization in an assembly of quasi one-dimensional (1D) Heisenberg antiferromagnetic (AFM) chains coupled to a 3D phonon field.[1] For the class of insulating compounds (TTF)-$MS_4C_4(CF_3)_4$ [denoted as TTF-BDT(M)] the zero-field transition occurs at about 11.5–12 K for M = Cu and at 2.1 K for M = Au. More recently SP behavior has been established in (TTF)-$CuSe_4C_4(CF_3)_4$ [$T_c = 6$ K] (Ref. 2) and methylethylmorpholinium-(tetracyanoquinodimethanide)$_2$ [(MEM)(TCNQ)$_2$] [$T_c = 18$ K],[3] and perhaps in the alkali TCNQ's.[4] In the TTF-BDT(M)

systems, experimental measurements of susceptibility, EPR, NMR, specific heat, and lattice dimerization[5] are in good agreement with a simple mean-field theory based on work of Pytte.[6] A recent x-ray study has been made of specific molecular displacements.[7] The crucial role of a preexisting soft phonon[5] from 200–300 K down to T_c in these transitions was also elucidated.[8,9]

SP transitions are rare: They do not occur in the majority of quasi 1D AFM's. It is thus of considerable interest to study the behavior of SP systems in a magnetic field. Note that the SP transition can be mapped onto the regular Peierls transition,[6,10] in which case magnetic field maps onto chemical potential. Recently, neutron scattering and magnetization data showed[11] a depression of $T_c(H)$ in reasonable agreement with theoretical predictions,[9,10] strongly supporting the SP character of the TTF-BDT(Cu) system. We have noted[11] that, in contrast, for a quasi 1D AFM an initial increase in T_N for $H > 0$ is observed.[12]

We present new magnetization data on TTF-BDT(Cu) which reveal new and important results for the SP system. The measurements were carried out at the Service National des Champs Intenses, Centre National de la Recherche Scientifique, using the same equipment as before[11] but with greater precision and greater detail. The powder sample (0.43 g) was newly prepared and was larger by a factor of 2. The absolute value of the magnetization results is in close agreement (~10%) with our lower-field data.[1] (The measurements of magnetization in Ref. 11 were both less precise and rather low, possibly from an inadvertent dilution during a prior experiment.) The relative uncertainty of the measurement was improved to ± 5 emu/mole. Isotherms were taken up to 155 kOe at the following temperatures: 1.5, 4.2, 5.2, 6, 7, 8, 10, 12, and 24 K. Isofield curves were measured from either 1.5 or 4.2 K up to about 17 K for the following fields: 20, 40, 60, 75, 85, 90, 97.5, 105, 110, 115, 125, 134, 136, 140, 144, 148, and 155 kOe.

An overview of the data is given in Fig. 1 and the lowest-temperature results are shown in Fig. 2. The features of major interest are the evi-

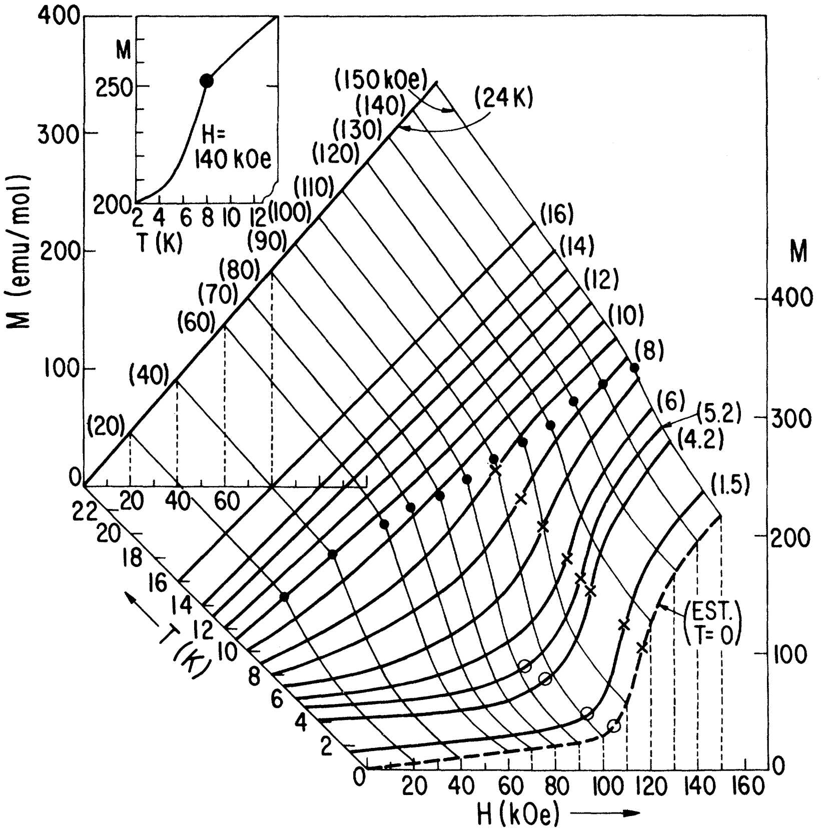

FIG. 1. Composite M, H, T plot of high-field magnetization data. The crosses are isotherm inflection points, the solid circles are isofield "knees" (example in inset), and the open circles represent the onset of hysteresis.

dence for the existence of a new phase at high fields and the substantial low-temperature hysteresis. In Fig. 1 the interpolated isotherms are shown as heavier lines and the quasiorthogonal isofield curves as lighter lines. Starting from high temperatures and low fields, the "knees" of the isofield curves (shown by solid circles) reveal the (initially quadratic) decrease of the SP transition.[11] Moreover, the "knees" persist up to the highest fields (see the inset of Fig. 1). The crosses, which mark the inflection points of the isotherms, form a locus which separates the region where $M(T=0)\approx 0$ from the region where $M(T=0)>0$. These features, a consequence of the improved precision, strongly suggest the existence of one or more new phases in (H,T) space. In the inset of Fig. 2 the magnitude of the low-temperature hysteresis is given. It is seen to decrease in a well-characterized manner and to vanish at about 5.5 K. The phase transitions for $T<5.5$ K are thus of first order as suspected earlier,[9,10] while at higher temperature (up to about 9 K) it appears, but is not proven, that they are of second order. Below $T=5.5$ K, the averages of rising- and falling-field-magnetization measurements are shown in Fig. 1. By extrapolation we arrive at an estimated $T=0$ isotherm. Its low-field susceptibility should be negligibly small; the small finite value may arise from an inadequate holder correction and/or possible "impurity" contributions.[1] The lines of solid circles and crosses are a guide to the eye suggesting an approximate H-T phase diagram for this system.

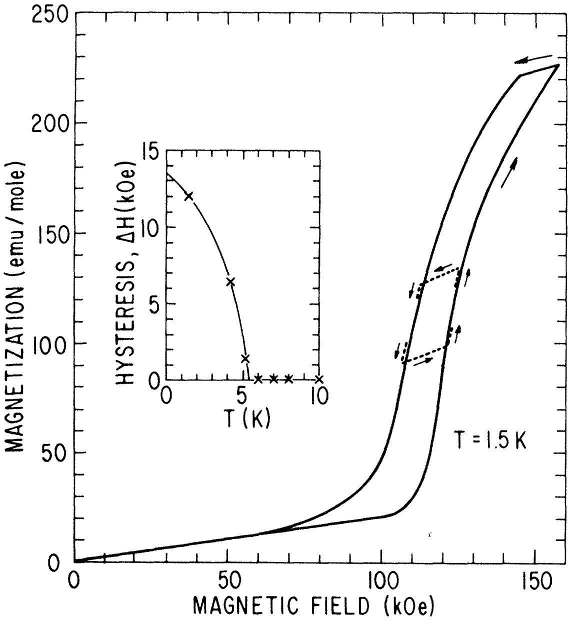

FIG. 2. Magnetization vs field at 1.5 K. Inset shows width of hysteresis "loop" vs temperature.

The isotherm at 1.5 K (Fig. 1) has peculiar features. From the isotropic EPR g factors ($\Delta g \leq 0.015$), one would expect a first-order transition for this powder to exhibit a steep rise of magnetization with increasing field by analogy with familiar metamagnetic transitions in single crystals. Our transition curve is sheared in field and curved so that it extends over at least 50 kOe, as demonstrated by the persistence of hysteresis over this region. Random impurities are unlikely to cause significant hysteresis in this essentially homogeneous compound, but the role of strain is much less certain due to the powder nature of the sample and the large structural phase transition at ~230 K. The intrinsic isotropy of g and χ) *should* distinguish this system from those in which precise crystalline orientation is required for a refined study of the H-T phase behavior.

A clearer view of the H-T phase behavior is presented in Fig. 3, along with boundaries corresponding to some models presented below. Inflection points (crosses) from isotherms are retained as boundary criteria, along with knees (solid circles) from isofield curves. Two of the latter (8.6 and 8.8 K) are shown open and appear to be less sharp. The boundary of the region designated I agrees within experimental error with our earlier data.[11] The point B at 5.5 K marks the end of the hysteretic transitions as noted above. In its simplest outlines (Figs. 1 and 3),

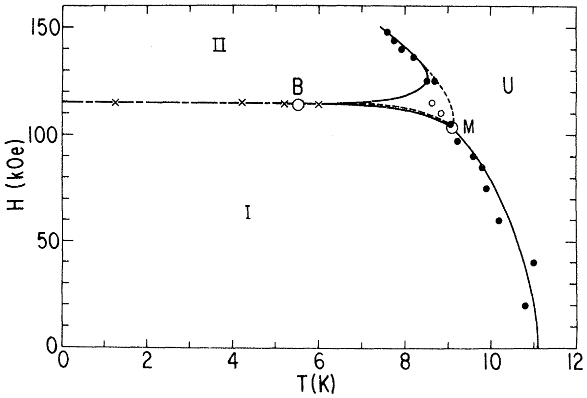

FIG. 3. SP H-T phase diagram. The boundary separating phases I and II and lying between points B and M may possibly be described by the dashed lines or by the solid ones. The region U corresponds to uniform chain behavior.

the present approximate phase diagram for this SP system draws attention to a variety of suggestions for its phase behavior and will undoubtedly stimulate further experiments. In what follows we focus on possible models for the phase transitions, for the new phase region(s), and for the special (multicritical) points of the phase diagram.

The simplest possibility can be immediately discarded, viz., an elastic distortive transition not involving spin-phonon coupling. Its transition temperature would not appreciably depend upon magnetic field, in contradiction to experiment.

The behavior of the transition in a field may be analyzed in terms of a pseudofermion representation of the Hamiltonian.[6,10] In zero field, the SP system can be mapped to a half-filled pseudofermion band system, where the dimerization wave vector $q = 2k_F = \pi/a$ ($a \equiv$ intrachain spacing, k_F $\equiv$ Fermi wave vector). As the magnetic field increases, k_F steadily decreases toward zero. This continuous tuning of k_F is a unique feature of the SP system in a field. Initially, although $2k_F$ is decreasing, q sticks at π/a on account of umklapp effects. Umklapp scattering produces a commensurability energy, which is the finite amount of energy required for q to switch to a new commensurate (or incommensurate) value.

For TTF-BDT(Cu), the experimental results[11] indicate that q remains fixed at π/a for $H \leq 120$ kOe. For $H \geq 120$ kOe, a variety of possibilities exists:

(1) The pinning energy of the preexisting soft phonon at the dimerization wave vector is so large that the system can exist only in a dimerized (SP) or a uniform phase. An XY-model calculation[13] displays a tricritical point where the SP phase boundary changes from second to first order at low temperatures. Our new magnetization data show definitively that this commensurate-uniform transition is not the correct picture for TTF-BDT(Cu). For the remaining models, the soft phonon can clamp the system at the dimerization wave vector only for a limited range of H.

(2) If the hysteresis is not due to powder-strain effects, the high-field portion of the phase diagram may correspond to a realization of the "devil's staircase".[14] As the field increases above ~120 kOe, a sequence of higher-order commensurate phases of very small width in H, or in commensurability energy, arises. Each step involves a small increase in magnetization from one commensurate phase to the next; i.e., a first-order transition. The steps are presumably too small to be resolved at our lowest temperature. The unusual spread in field of the hysteresis loop may be a feature of such a multiplicity of unresolved first-order transitions. A problem for the devil's-staircase picture comes from a mean-field calculation[15] of the commensurability energy associated with a commensurate phase of order m (dimer phase corresponds to $m = 2$) in the regular Peierls system. The commensurability energy decreases as $(\Delta/E_F)^m$, where Δ and E_F are the gap and Fermi energies, respectively, which implies that the energy difference between a commensurate (C) and an incommensurate (IC) state is insignificant for higher m and will not lead to observable staircase behavior (for $T > 0$).

(3) The final possibility, which has already received a preliminary discussion,[9,10] is a transition to an incommensurate phase. This could arise through the nucleation of solitons, small incommensurate regions in an otherwise commensurate lattice. A first-order transition results from attractive soliton interactions; otherwise the transition is second order (continuous). Horovitz[16] has shown that the dimerized-to-incommensurate transition in regular Peierls systems is first order because the Fock term leads to attractive soliton interactions. No Fock term occurs in the spinless pseudofermion SP model, and therefore the appearance of a first-order transition would depend on higher-order terms or perhaps on strain-induced interactions.[17]

There may be a problem, however, reconciling a simple C-IC transition with the data including the higher temperature range. As discussed already the hysteresis marking the first-order transition is found experimentally to disappear at ~5.5 K (Fig. 2, inset), whereas the data suggest that a multicritical point occurs at ~9 K. The implication (not proven) is that 5.5 K may be a special point where the phase boundary changes from first to second order, terminating at the multicritical point, M. This situation is shown by dashed lines in Fig. 3. It is anomalous from the viewpoint of conventional magnetic phase diagrams, since three second-order lines then meet at 9 K in a two-parameter space. One alternative is that the 5.5-K point is a bicritical point B from which two second-order (solid) lines emanate. Another is more exotic: A narrow intermediate phase may occur between 5.5 K and the multicritical point M at 9 K. B remains a bicritical point and M becomes a tetracritical point. A further intriguing possibility is that M may be a Lifshitz point[18,19] (and B a tricritical point) such that the I/II phase boundary marks a transition between a dimerized and an incommensurate phase.[20] Our SP systems should certainly be investigated in the light of these possible models.

Finally, we note that the saturation field for the AFM Heisenberg uniform linear chain corresponding to TTF-BDT(Cu) is 1140 kOe. The SP phase diagram could extend to this field but may be limited to fields of order of the gap energy (~ 220 kOe). It will depend sensitively on the interchain-coupling strengths whether the ordered phase at high fields remains magnetoelastic or becomes antiferromagnetic. The phonon field character is also crucial for determining how the distortion wave vector q will change, the softer phonons favoring distortion.

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