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High-field specific-heat and susceptibility measurements: Relevance to the spin-Peierls phase diagram and the validity of a soliton picture

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(Received 23 June 1986)

We discuss recent high-field specific-heat measurements on the spin-Peierls compound tetrathiafulvalinium bis-*cis*-(1,2-perfluoromethylethylene-1-2-dithiolato)—gold [TTF-BDT(Au)]. An ordering anomaly can clearly be detected which defines a high-field phase boundary, despite some extraneous structure in the data apparently reflecting experimental limitations. The high-field phase boundary is in good quantitative agreement with the theory of Cross and Fisher. Further, the specific-heat data are in good agreement with earlier ac susceptibility data, the reliability of which as indicators of a phase transition has been somewhat open to doubt because pronounced relaxation effects in the high-field regime result in striking differences between χ_{ac} and χ_{dc}. Some observations are made concerning the extent of hysteresis associated with the phase boundary between dimerized and high-field phases. Finally, the extensive experimental data are employed in several tests to determine the applicability of recent soliton theories.

I. INTRODUCTION

The compound tetrathiafulvalinium bis-*cis*-(1,2-perfluoromethylethylene-1-2-dithiolato)—gold [TTF-AuS$_4$C$_4$(CF$_3$)$_4$, denoted TTF-BDT(Au)] is one of the very few experimental examples of a spin-Peierls (SP) system. Such systems show a zero-field transition in which an assembly of spin-$\frac{1}{2}$ Heisenberg antiferromagnetic uniform chains experience a progressive dimerization as the temperature is lowered through the spin-Peierls transition temperature, $T_{SP}(0)$. This transition is a consequence of magnetoelastic coupling of the spin chains to the three-dimensional (3D) lattice. The three compounds that have received extensive experimental investigation are TTF-BDT(Au), where $T_{SP}(0) \sim 2$ K; its sister compound TTF-BDT(Cu), where $T_{SP}(0) \sim 11$ K; and the compound methylethylmorpholinium ditetracyanoquinodimethane [MEM-(TCNQ)$_2$], where $T_{SP}(0) \sim 18$ K.[1]

The preparation of good samples is very difficult in the case of the TTF-BDT compounds, and for all three compounds experimental difficulties preclude a precise location of $T_{SP}(0)$. Hence, at present, the nature of the critical exponents characterizing the novel spin-Peierls transition cannot be determined. However, the global phase diagram is of great interest. The ordering behavior of the SP compounds is the outcome of competition between a spin-phonon interaction (which gives rise to an SP transition) and spin-spin interchain coupling (which would result in regular 3D antiferromagnetic ordering). An applied magnetic field will influence the relative importance of these two competing phase mechanisms,[2-4] and hence novel field-induced phase transitions are expected.

The majority of extant theoretical approaches qualitatively predict an (H,T) phase diagram as shown in Fig.

1.[1] The major features of this sketch include a dimerized phase region denoted D, extending in field up to a special value H^*, a paramagnetic region, denoted U, where the system behaves as an assembly of noninteracting uniform Heisenberg antiferromagnetic chains, and a high-field phase denoted I. The DU and IU phase boundaries are predicted to be higher order (second order) but there are conflicting predictions for the DI phase boundary. Those theories predicting first-order character suggest also that the DI transition line will be characterized by a notable amount of hysteresis extending over an appreciable range
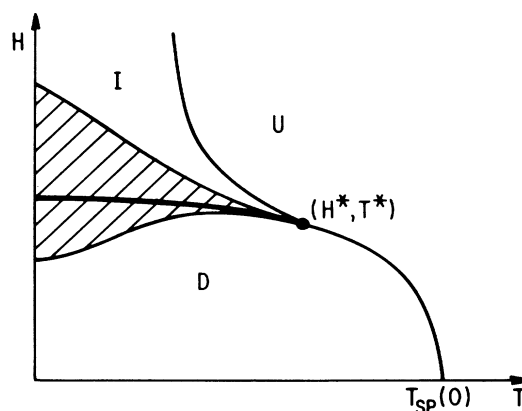

FIG. 1. Schematic $(H-T)$ phase diagram of a spin-Peierls system indicating dimerized (D), uniform (U), and intermediate (incommensurate) (I) phases. The DU and IU phase boundaries are second order and (H^*,T^*) is a Lifshitz point. The DI line, believed to be first order, is shown with an associated region of hysteresis (shaded) (after de Lima and Tsallis, Ref. 23).

in the (H,T) plane. The DU, DI, and IU phase boundaries meet at a special multicritical point (H^*,T^*), which is expected to be a Lifshitz point.

Existing magnetization,[2,5-7] susceptibility,[8] and specific-heat[9] data for TTF-BDT(Au), TTF-BDT(Cu), and MEM-(TCNQ)$_2$ are in agreement with Fig. 1, at least as far as the DU phase boundary is concerned. Experiment is in support of the first-order character predicted for the DI phase boundary. Further, if the H and T axes are both scaled by $T_{SP}(0)$, i.e., if the data are plotted as a function of $H/T_{SP}(0)$ and $T/T_{SP}(0)$, measurements on all three compounds closely superimpose. This indicates that the (H,T) spin-Peierls phase diagram has universal character,[8] as expected on the basis of standard spin-Peierls theory.[1] Furthermore, extensive hysteresis in the neighborhood of the DI line, particularly at low temperature, observed in TTF-BDT(Cu) (Refs. 4—6) and MEM-(TCNQ)$_2$ (Ref. 7) has very recently been observed also in TTF-BDT(Au).[10]

Important universal parameters for points in the phase diagram are found experimentally to be $H^*/T_{SP}(0) \sim 1.0$ (H in tesla and T in K), and $T^*/T_{SP}(0) \sim 0.75$. Data delineating the IU line in Ref. 8 were obtained from magnetization measurements (on all three compounds) and ac susceptibility measurements [TTF-BDT(Au) only]. We note that of the three compounds, measurements over a substantial field range above H^* are feasible only for TTF-BDT(Au). Since TTF-BDT(Au) has the lowest value for $T_{SP}(0)$ (taken to be 2.03 K), by the universal scaling properties, the corresponding value of H^* is expected to be about 2 T. Hence, the existence and nature of a high-field phase can be probed most easily in the case of TTF-BDT(Au), and with greater difficulty in the case of TTF-BDT(Cu) ($H^* \sim 11.5$ T) and MEM-(TCNQ)$_2$ ($H^* \sim 18$ T).

Experimental results on TTF-BDT(Au) for differential (ac) susceptibility have already been reported, which allowed determination of DU and DI phase boundaries and an appreciable portion of the IU phase boundary.[8] Subsequent specific-heat measurements at low fields[9] were in excellent agreement with the susceptibility data in defining the DU boundary. A notable feature of the susceptibility measurements was the pronounced relaxation effects in the high-field region. When the ac susceptibility results were compared with corresponding static, isothermal susceptibility results obtained by differentiating magnetization isotherms, the two quantities X_{ac} and $X_{dc}=X_T$, were equivalent along the DU boundary, indicating that relaxation effects were unimportant in the case of the dimerized-to-uniform transition. However, in the high-field phase region, including the DI and IU lines, X_{ac} and X_T differ considerably, indicating that relaxation effects are prominent in this region of the phase diagram. This situation is shown in the inset of Fig 2. Figure 2 features ac susceptibility curves as a function of temperature for various field values both below and above H^* (2.1 T). The X_{ac} data exhibit a peak except at the lowest field values. In the high-field phase region (data points denoted by open symbols), for $H > 2.1$ T, the peak in X_{ac} is not paralleled by a peak in $X_{dc}=X_T$, the latter quantity continuing to increase as T decreases. In consequence, the
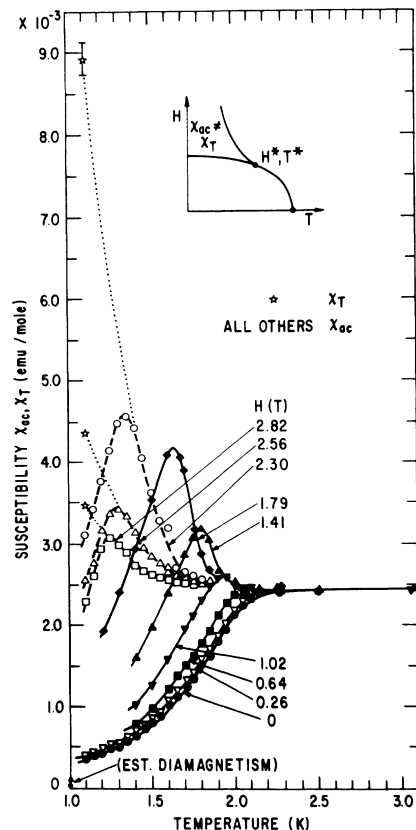

FIG. 2. Differential (ac) susceptibility curves, along with some isothermal susceptibility data, at various constant fields as a function of temperature for TTF-BDT(Au). Closed data points are for $H < H^*$ and open ones are for higher fields. The inset shows the (H,T) region in which ac and dc (isothermal) susceptibilities are unequal.

question was raised whether the IU line determined from X_{ac} measurements corresponded to a "true" phase boundary, or was just an artifact of relaxation effects.[11,12] The relaxation effects were conjectured to result from a broad region in field of soliton nucleation processes associated with the (first-order) DI line.[11,12] Since the specific heat is intrinsically a static quantity, and, therefore, independent of relaxation effects, anomalies in the specific heat are arguably the most reliable indicators of the existence of a phase transition. Hence, low-field specific-heat measurements[9] were extended up to 4.0 T; i.e., well above the critical field $H^* \sim 2.1$ T.[13]

II. EXPERIMENTAL SITUATION

Specific-heat data obtained in zero field and in fields of 2.0, 2.3, 2.6, and 4.0 T are shown in Fig. 3.[13] The data for $H < 2.2$ T relate to the low-field DU phase boundary and the data for $H > 2.2$ T relate to the high-field IU phase boundary. In all cases a field-dependent, cusplike anomaly is observed, indicated by the arrows. The amplitude of the anomaly shows a steady decrease with increasing field as would be expected on theoretical grounds. The specific-heat peak for $H < H^*$ is in excellent agreement with earlier specific-heat studies.[9] In the data for $H > 0$,
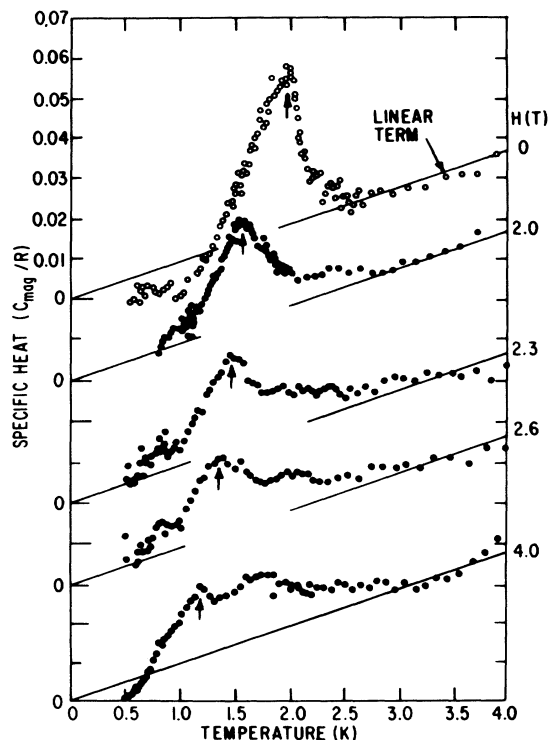
FIG. 3. Magnetic contributions to the specific heat in zero field and in various high fields $H \geq H^*$ for TTF-BDT(Au). The arrows indicate the field-dependent cusplike anomaly (after Hijmans et al., Ref. 13).
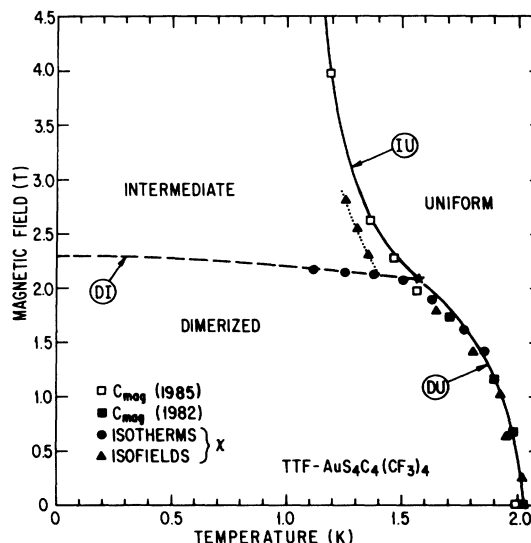

FIG. 4. Magnetic phase diagram for TTF-BDT(Au) conducted from susceptibility and specific-heat measurements (Refs. 8, 9, and 13) and the calculated phase boundaries (Ref. 16) scaled only by $T_{SP}(0)$.

anomalous structure is observed at about 2.4 K, independent of H. In the case of the low-field data, this anomalous structure does not affect the location of the specific-heat peak, and, hence, we conclude it may safely be ignored for all H. In the data for $H > H^*$, additional anomalous structure becomes evident at about 1.7 K, whose magnitude becomes comparable with the amplitude of the "true" specific-heat anomaly at the highest fields. In fact, this anomalous structure can also be discerned at the lower field of 2.0 T as a "shoulder" on the high-temperature side of the DU specific-heat peak. Both amplitude and location of this anomaly are approximately field independent and, hence, we again conclude this structure is a spurious artifact. Overall, therefore, we conclude that anomalous structure appearing above the "true" specific-heat peak in temperature is most likely of extraneous contributions resulting from experimental procedures and not a property of the spin-Peierls system TTF-BDT(Au). In particular, the fact that this extra structure is field independent implies that it does not result from, say, the effects of short-range order.

In Fig. 4 we show an (H, T) phase diagram obtained on the basis of previous susceptibility and low-field specific-heat measurements[8,9] together with the new high-field specific-heat data.[13] The DU line and part of the DI line are clearly delineated although a small amount of data scatter, reflecting the difficult experimental situation, is present. Three experimental data points define the IU phase boundary out to $H \sim 2H^*$, and are in general agree-

ment with previous IU data points obtained from ac susceptibility experiments. The agreement of two different types of experimental measurements indicates to us (a) that previous concerns over the reliability of determining a phase boundary from X_{ac} peaks in a situation where $X_{ac} \neq X_T$ appear to be unfounded, and (b) that despite some spurious features apparently resulting from experimental artifacts, the new specific-heat data are reliably displaying an anomaly characterizing a phase transition from a paramagnetic (uniform) phase to a high-field phase (denoted "intermediate" on Fig. 4) of unspecified character.

It should be noted that our confidence in this interpretation of specific-heat and susceptibility data is strongly supported by very recent work consisting of frequency-dependent proton and fluorine nuclear magnetic resonance (NMR) experiments on TTF-BDT(Au).[10,13] Proton spin-echo linewidth and relaxation studies define the IU phase boundary up to fields of about 3.3 T, and the results are in excellent agreement with the specific-heat and ac susceptibility studies displayed in Fig. 4. The linewidth studies also extend the definition of the DI phase boundary from 1.1 K down to 0.57 K and reveal the presence of hysteresis below ~ 1 K, which confirms the first-order nature of the DI boundary.

III. DISCUSSION

A. High-field phase boundary

Let us examine the new experimental results in relation to theoretical calculations on spin-Peierls systems in a field. As noted in the Introduction, most theories predict a field-induced transition from a dimerized phase to an incommensurate[14-20] or modulated (higher-order commensurate) phase.[21-23] Such theories generally subdivide into

soliton- and non-soliton-based theories. Other extant cal-
culations predict that the high-field phase may correspond
to regular three-dimensional antiferromagnetic ordering
of either a spin-flop or antiferromagnetic (ordered Néel
ground state) type,[3,4] or even that no high-field phase is
present.[11,12] The experimental measurements reviewed
here[13] and obtained from other work[8,9] are in very good
agreement with the theory of Cross and Fisher,[16] ampli-
fied by Cross.[16] The DU and IU phase boundaries of
Cross are shown in Fig. 4, and very good quantitative
agreement with the experimental data is observed. In par-
ticular, it is noteworthy that the agreement extends to the
shape and location of the IU phase line (which is not the
case for other theories of the IU phase boundary,[15]) and
the location of the special multicritical point (H^*, T^*)
predicted by Cross to occur at $T^*/T_{SP}(0) \sim 0.77$ and
$\mu_B H^*/k_B T_{SP}(0) = 0.69$ ($g = 2.00$). Both leading theories,
that of Cross and Fisher,[16] and the related soliton-lattice
theory of Nakano and Fukuyama,[20] predict the high-field
phase to be incommensurate (but differ appreciably in
their predictions for characteristic parameters related to
the (H, T) phase diagram as discussed below). Bulk ther-
modynamic (susceptibility and specific-heat) studies are
not suited to determined whether the high-field phase is
indeed an incommensurate phase. We can only note that
the relatively weak IU specific-heat anomalies are con-
sistent with current theoretical predictions[24] concerning
incommensurate or Kosterlitz-Thouless phases. The re-
cent NMR work[10] leads to calculations which demon-
strate that the high-field phase is neither paramagnetic
nor three-dimensionally ordered, either antiferromagneti-
cally or in a spin-flop configuration. By these and other
arguments related to agreement of certain features of the
experiments with the Nakano-Fukuyama soliton-lattice
picture, it is concluded that the high-field phase is, in
fact, incommensurate. In the NMR work[10] no attempt is
made to compare the experimental data to a global phase
diagram based on the Nakano-Fukuyama theory. One
problem would be the fact that the field of the DI phase
boundary, essentially equivalent to H^*, is given by
$\mu_B H^*/k_B T_{SP} \cong 0.28$, a value considerably lower than that
resulting from the Cross theory and experiment.

B. Susceptibility in the high-field phase

A point of special interest is the striking difference be-
tween χ_{ac} and the corresponding $\chi_{dc} = \chi_T$ in the high-field
phase region. This feature is shown in Fig. 5, where χ_{ac}
and χ_T are compared as a function of field at a tempera-
ture of ~ 1.1 K.[8] The maximum in both susceptibility
curves occurs at the same field, $H \sim 2.2$ T, but the magni-
tude is considerably greater in the case of $\chi_T = dM_T/dH$.
It should also be noted that there is noticeable asymmetry
in the curves, particularly in the case of χ_T. The curve
rises sharply on the low-field side of the transition and
drops more gradually on the high-field side. In an at-
tempt to throw light on the high-field behavior of spin-
Peierls systems approximate calculations on a pure dimer-
ized Heisenberg antiferromagnetic chain (without cou-
pling to the lattice) were performed using the Bulaevski
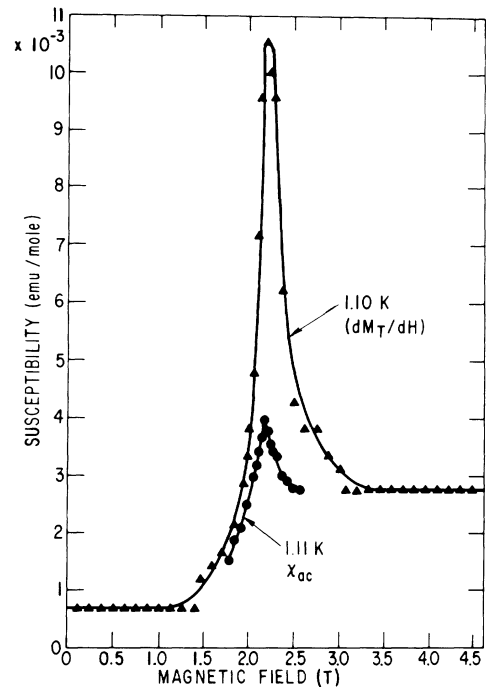Hartree-Fock and related approaches.[25] The qualitative

FIG. 5. Comparison of the field dependence of differential
susceptibility, χ_{ac}, with the isothermal susceptibility, χ_T, at
$T = 1.1$ K for TTF-BDT(Au) (after Ref. 8).

accuracy of the results was checked by finite-chain calcu-
lations.[26,27] In an alternating antiferromagnetic quantum
system, the lowest excited states are triplets, and cross the
zero-field singlet ground state as a result of Zeeman term
effects at a lower critical field H_{c1}. Results for the sus-
ceptibility, χ_T, as a function of field for various low tem-
peratures are shown as Fig. 2 of Ref. 25. The theoretical
results in the vicinity of H_{c1} only, are shown schematical-
ly in Fig. 6. A pronounced peak occurs in the vicinity of
H_{c1}, which sharpens as T is lowered, becoming divergent
at $T = 0$. (In the presence of interchain coupling, this
divergence will be suppressed, but a pronounced "peak-
ing" effect will remain.) Furthermore, an asymmetry of
the kind observed experimentally is seen at low tempera-
tures in the vicinity of H_{c1}. A large dc susceptibility
diverging as $T \rightarrow 0$ is characteristic of systems in which a
region characterized by an energy gap changes to a gap-
less region due to the effect of a field. The continuous
low-lying density of states gives rise to a power-law diver-
gence of the susceptibility at $H = H_{c1}$.[28] It also gives rise
to a finite, nonzero value for the susceptibility for
$H_{c1} < H < H_{c2}$, where H_{c2} is a second critical field at
which a gap opens up. Hence it seems reasonable to con-
clude that similar phenomena will occur also for magne-
toelastic systems where the spin-phonon coupling is weak
($T_{SP} \ll J$) and a dimerized phase with gaps shows a phase
transition to a gapless (incommensurate) phase. Moving
now from the vicinity of the DI phase boundary (Fig. 4),
we discuss the expected behavior of χ_{ac} and χ_T at con-
stant field as a function of temperature in the vicinity of
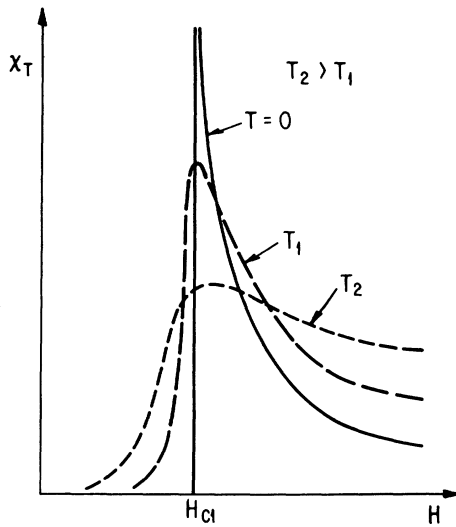the IU phase boundary (see Fig. 2, inset). The ac suscepti-

FIG. 6. Schematic plot of isothermal susceptibility, X_T, as a function of field at various low temperatures in the vicinity of a critical field, H_{c1}. Note that the divergence at $T = 0$ becomes a rounded peak at higher temperatures (after Mohan and Bonner, Ref. 25).

bility shows the peak characterizing the IU phase transition, while X_T may show only a minimal anomaly,[29] rising to large values in the neighborhood of (H^*, T^*).

Recently a magnetoelastic calculation has indeed appeared,[30] where, starting from the mean-field magnetoelastic Hamiltonian of Pytte,[14] thermodynamic quantities such as magnetization, susceptibility, and specific heat have been calculated, using the soliton-lattice solution for the incommensurate state which takes into account infinite numbers of higher harmonics.[19–21] This calculation supports the comment above that the inclusion of magnetoelastic coupling will not significantly change conclusions drawn from the purely magnetic calculation of Ref. 25. A plot of calculated dc susceptibility versus field at low temperatures, for example, shows a sharp rise at the low-field side of the DI phase boundary, and a more gradual drop to a nonzero value in the incommensurate phase above the DI boundary, in qualitative agreement with Fig. 6. More generally, the magnetization, susceptibility, and specific heat are qualitatively in agreement with experiment.[8]

C. Hysteresis and the DI line

The question of hysteresis along the DI lines is also of interest. In all cases, TTF-BDT(Cu), MEM-(TCNQ)$_2$, and TTF-BDT(Au), the onset of hysteresis is observed not at the Lifshitz point (H^*, T^*) but at significantly lower temperatures. In the case of TTF-BDT(Cu) hysteresis is first observed in dc magnetization measurements at $T/T_{SP}(0) \cong 0.50$; in MEM-(TCNQ)$_2$, also for dc magnetization measurements, at $T/T_{SP}(0) \cong 0.6$; and in the case of TTF-BDT(Au), for $T/T_{SP}(0) \leq 0.5$ in spin-echo half-width measurements.[10] Existing theories[16,19,23] predict that the DI line is first order all the way up in temperature to the Lifshitz point. A situation where the DI line

changes from first order to second order as the Lifshitz point is approached would be surprising. A possible resolution of this rather anomalous feature lies in a calculation by de Lima and Tsallis on magnetostrictive XY spin chains.[23] They show that in their model the DI line is associated with considerable hysteresis, as indicated in Fig. 1. The hysteretic region starts out near the Lifshitz point so narrow as to be effectively experimentally unobservable, and then "flares out" midway down the line. Such a theoretical prediction is certainly in accordance with current experimental observations.

Also of interest concerning the DI line is the apparent slope (see Fig. 4), which is negative. This forms an interesting contrast to the first-order antiferromagnetic—spin-flop phase boundary of antiferromagnets with some uniaxial anisotropy whose (H, T) phase diagram is in some ways analogous to the (H, T) phase diagram obtained for spin-Peierls systems.

D. Validity of a soliton picture

Our discussions above have focused on physical concepts and theories of the global spin-Peierls phase diagram which largely ignore nonlinear excitations and fluctuation phenomena. A case in point is our discussion of the behavior of X_{ac} (X_T) in the vicinity of the critical field. However, calculations based on a soliton picture are growing in popularity in comparison with theories based on the more traditional spin-exciton (magnon) picture. The magnetic model at low temperatures in the dimerized phase is that of the familiar antiferromagnetic alternating chain with alternation parameter δ, where

$$\mathcal{H} = \sum_{i=1}^{N} [J(1+\delta)\mathbf{S}_{2i} \cdot \mathbf{S}_{2i+1} + J(1-\delta)\mathbf{S}_{2i-1} \cdot \mathbf{S}_{2i}] . \quad (1)$$

In the picture we have used, δ depends on temperature, $\delta = \delta(T)$, but at a given temperature, δ remains effectively constant along the chain. Soliton theories such as that of Nakano and Fukuyama[20] essentially allow for fluctuations in δ (kink solitons). The Nakano-Fukuyama theory starts from the Cross-Fisher theory, where the spin-phonon coupling is treated in the random-phase approximation (RPA) and the magnetic chains are the basis of a Luttinger bosonization approach.[16] The Hamiltonian is subsequently transcribed to phase variables and a sine-Gordon equation is obtained as a result of further approximations. The sine-Gordon equation is then solved for the lowest-lying excitations, which turn out to be solitons with effective spin $\frac{1}{2}$ instead of spin excitons (magnons) with effective spin 1. All existing formulations of soliton theory consistently predict that the soliton excitation energy, ΔE^{sol}, is considerably lower than the magnon (spin exciton) creation energy, ΔE^{mag}. The approximate relation

$$\Delta E^{sol} \sim 0.3 \Delta E^{mag} \quad (2)$$

is obtained.[31]

Our analysis of the extensive experimental data available not only for TTF-BDT(Au), but also for TTF-BDT(Cu) and MEM-(TCNQ)$_2$, favors the more traditional spin-exciton over the popular soliton excitation picture. Specifically, we have performed three tests to distinguish

between these two approaches:

(1) A comparison of theoretical predictions with experimental determinations of the characteristic features of the spin-Peierls (H,T) phase diagram. This would include, e.g., the location of H_c and the Lifshitz point (H^*,T^*).

(2) An examination of the magnetic thermodynamic properties, in particular the specific heat, for anomalies due to soliton states.

(3) A comparison of experimentally determined excitation energy gaps with theoretically predicted values, soliton and magnon.

An appreciation of the spectral excitations in a magnetic field should underlie our discussions of tests 1, 2, and 3. Let us consider $T=0$. The critical field H_c is determined from the dominant excitation gap which decreases in the presence of an applied magnetic field H. At $H=H_c$, the field-dependent excitation gap vanishes and the system passes from a phase with a gap to a gapless regime, as noted already above. The equation determining H_c is thus

$$\Delta E(H)=\Delta E(0)-g\mu_B H S_T^z, \quad H \leq H_c \tag{3a}$$

$$\Delta E(H)=0, \quad H=H_c . \tag{3b}$$

(g is the Landé g factor and μ_B the Bohr magneton. The quantity S_T^z is the effective spin of the excitation.) In the spin-exciton picture, in zero field, the ground state is a singlet with $S=0$ and the lowest excitations are $S=1$ triplets. In the presence of a field the relevant energy states are characterized by $S_T^z=0$ and 1, respectively. All soliton theories consistently predict that the spin of a soliton is given by $S(S_T^z)=\frac{1}{2}$. From Eqs. (2) and (3) we obtain the result

$$H_c^{sol} \sim 0.6 H_c^{mag} . \tag{4}$$

For a given zero-field excitation gap $\Delta E \equiv \Delta(T \rightarrow 0)$, therefore, the soliton picture predicts a critical field about 60% of the size of that predicted by the spin-exciton picture. The $T=0$ energetics scheme is summarized in Fig. 7. The spin-exciton (magnon) excitations form the lower boundary of a triplet excitation continuum above the gap ΔE^{mag}. By contrast, the soliton excitation is a localized excitation which has been split out of the triplet continuum; i.e., a localized midgap state. We now discuss tests 1–3 in light of Fig. 7.

(a) We have already observed above that experimental data on the three compounds, TTF-BDT(Au), TTF-BDT(Cu), and MEM-(TCNQ₂) give a very good quantitative fit to the phase diagram predicted by Cross and Fisher,[16] particularly as regards the variation of the Lifshitz point (H^*,T^*). The existing soliton theories are formulated in the vicinity of $T=0$ and thereby do not directly give predictions for H^* and T^*. However, we observe from Figs. 1 and 4 that $H_c \cong H^*$, since the first order DI phase boundary is almost horizontal. Hence we obtain a prediction for H^* for the soliton picture without having to construct a finite temperature development of the theories. We have already noted that the soliton value of $H_c \sim H^*$ is considerably lower than the value of Cross and Fisher. Since the Cross-Fisher value fits the experi-
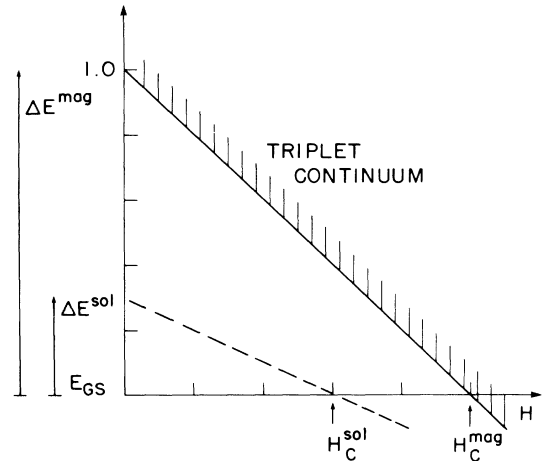

FIG. 7. Schematic view of the excited states of a spin-Peierls system in the presence of a magnetic field. The conventional picture of an alternating chain predicts an excitation gap ΔE^{mag}, from a singlet ground state E_{GS} to a triplet excited continuum. The gap ΔE^{mag} is field dependent, disappearing at H_c^{mag}. More recent soliton theories predict a gap ΔE^{sol} to a localized soliton state with spin $-\frac{1}{2}$. ΔE^{sol} also decreases linearly with field, disappearing at H_c^{sol}.

ment, it follows that the soliton picture does poorly on this particular test.

(b) The localized, low-lying soliton excitation gap given in Eq. (2) and sketched in Fig. 7 should manifest itself in low-temperature Schottky-like structure in the magnetic specific heat, followed at higher temperatures by a broad peak associated with the spin-1 magnon continuum. These features should be distinguished from the cooperative ordering anomaly at $T=T_{SP}$. No such structure is observed, not only in the case of TTF-BDT(Au) but also for TTF-BDT(Cu), and especially for MEM-(TCNQ₂), where data exist down to even lower relative temperatures.[32]

(c) The critical field has been rather accurately determined for all three spin-Peierls compounds. The $T \rightarrow 0$ excitation gaps inferred from Eq. (3), $\Delta^H(0)$, may be compared with values $\Delta^T(0)$ determined from an analysis of the low-temperature activation energies of the zero-field magnetic specific heat and susceptibilities. Determining the $\Delta^T(0)$ was difficult on the basis of existing data, and consistency of values for both $\Delta^H(0)$ and $\Delta^T(0)$ was not obtained. The zero-field excitation gaps derived for all existing spin-Peierls systems are consistently too large to agree with soliton or spin-exciton theory. The agreement with the soliton picture is, however, *worse* than with the spin-exciton picture. For the complete resolution of this complex situation, high-quality data on the magnetic thermodynamic properties for all three compounds down to even lower relative temperatures are required.

Hence, to conclude this section, we observe that in the case of all three validity tests, i.e., critical parameters of the global (H,T) phase diagram, low-temperature anomalous structure in the specific heat, and $T \sim 0$ excitation energy gap considerations, the experimental evidence

favors a spin-exciton picture over a soliton-excitation picture.

The reason for our failure to observe the characteristic features of soliton excitations may reflect the fact, long observed,[33] that spin-Peierls transitions in real systems show pronounced mean-field character. This could explain the apparent unimportance of nonlinear fluctuations (solitons) and the success of theories which do not include them.

IV. CONCLUSIONS

A considerable amount of specific heat and susceptibility data, both in zero and nonzero field, is now available for a variety of spin-Peierls compounds. Prominently featured here is the system TTF-BDT(Au), which permits detailed experimental study of all significant regions of the global (H,T) phase diagram. In particular, new high-field specific-heat data demonstrate conclusively the presence of a high-field phase predicted to be incommensurate. The specific-heat data define a high-field (IU) phase boundary in agreement with that derived previously from ac susceptibility measurements, and also are in excellent agreement with the theory of Cross and Fisher. The specific-heat data lay to rest doubts concerning the reliability of X_{ac} data in determining the IU boundary. The reason for doubt is that pronounced relaxation effects in the high-field phase result in striking differences between X_{ac} and X_{dc} in this region.

A theoretical explanation for these differences, and particularly the behavior of X_{dc}, is presented in the context of the behavior of an alternating chain as a function of field.[25] These remarks are fully supported by a mean-field magnetoelastic calculations.[30]

Some discussion is given of the nature of the DI phase boundary in comparison with the familiar first-order phase boundary of a spin-flop system. The unusual hysteretic behavior associated with the DI line is interpreted in terms of a recent theory.[23]

Soliton theories of the spin-Peierls transition have received much attention recently. The soliton predictions for the basic excitations and certain parameters of the (H,T) phase diagram differ greatly from the more traditional spin-exciton, mean-field picture on which our discussions here have essentially been based. These differences allow several experimental tests to determine the relative validity of each type of theory. All tests favor the traditional theories over the newer soliton theories, thus justifying the overall point of view of this paper.

Note: When this paper was in final preparation, we received a copy of work by de Jongh *et al.*,[34] in which measurements of X_{ac} and X_{dc} were extended to lower temperatures. The new results are consistent with both data and interpretation presented herein. However, the overall theoretical interpretation by de Jongh *et al.* differs considerably from that presented here.

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