Field-dependent differential susceptibility studies on tetrathiafulvalene-$AuS_4C_4(CF_3)_4$: Universal aspects of the spin-Peierls phase diagram

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An applied magnetic field is known to produce novel effects in the phase behavior of magnetoelastic spin-Peierls systems. Hence we report measurements of the differential susceptibility (χ) and magnetization (M) in fields up to 40 kOe (4 T) on the spin-Peierls compound tetrathiafulvalene (TTF)-$AuS_4C_4(CF_3)_4$ in the temperature region (1.1 K $\leq T \leq 4.2$ K). This range of field and temperature encompasses an interesting phase region, including the zero-field spin-Peierls transition temperature $T_c(0) = 2.03$ K. The measurements of the differential (ac) susceptibility provide a more sensitive probe of the transition behavior than magnetization measurements. The first definitive evidence for significant deviations from mean-field critical behavior appear in these measurements, and the appropriate criteria for determining the precise location of the transitions are thus provided by the thermodynamic theory of λ transitions. Using the new criteria, qualitative and even quantitative agreement is obtained with current theories of the field dependence of spin-Peierls transitions. A novel contour plot of χ_{ac} in the H-T plane is shown to be useful for the delineation of the global phase-transition behavior. An investigation of the role of relaxation effects in χ_{ac} relative to the nature of the phase boundaries is conducted. A major feature is the observation of a striking degree of "universality" in the phase behavior of three spin-Peierls systems, TTF-$AuS_4C_4(CF_3)_4$, TTF-$CuS_4C_4(CF_3)_4$, and methylethylmorpholinium di-tetracyanoquinodimethane [MEM-$(TCNQ)_2$]. These universal features are preserved through considerable differences in lattice structure and a variation in $T_c(0)$ of a factor of 10.

I. INTRODUCTION

The spin-Peierls (SP) transition is a topic of high current interest which brings together many subfields of solid-state physics.[1-4] This transition marks the onset, as the temperature is lowered, of a progressive spin-lattice dimerization in a system of quasi-one-dimensional (quasi-1D) quantum antiferromagnetic (AFM) chains embedded in the 3D phonon field of the lattice. Theoretically the transition is observable in its simplest form when the magnetic chains are nonclassical; e.g., Heisenberg or XY in type. In practice it has been observed experimentally only in good Heisenberg, spin-$\frac{1}{2}$, systems characterized by g factors close to the free electron value. By analogy with the well-known Peierls instability in a 1D metal, it may be shown that a uniform AFM quantum chain is unstable with respect to an underlying lattice distortion which dimerizes it into an alternating chain AFM. A quantum alternating chain AFM is characterized by an energy gap between the nondegenerate

singlet ground state and (a band of) triplet excited states.[5] The gap is dependent on the degree of alternation and vanishes in the uniform chain limit. As observed experimentally, in zero field, the transition is second order, and the degree of alternation increases as the temperature is lowered, reaching a maximum at $T = 0$.

The effect of a magnetic field on an SP system is quite dramatic and has been the subject of a number of theoretical papers.[6-11] In simple terms, the magnetic field lowers the energy of the magnetic excited levels below the $S = 0$ zero-field ground state, destroying the energy gap and altering the character of the phase behavior. On the experimental side, neutron studies up to about 70 kOe have shown that $T_c(H)$ is depressed by application of a magnetic field.[12] Magnetization studies have been performed in significantly higher magnetic fields (up to about 200 kOe) on tetrathiafulvalene (TTF)-$CuS_4C_4(CF_3)_4$ ($T_c \simeq 11$ K)[13] and on methylethylmorpholinium di-tetracyanoquinodimethane [MEM-$(TCNQ)_2$]

$(T_c \simeq 18 \text{ K})$.[14] The data indicate the existence of interesting new phase boundaries in the high-field region, the nature of which is not yet fully understood. This is in addition to the second-order phase boundary separating dimerized phase from uniform nonordered phase at lower fields.

In this paper we present and discuss both magnetization and also extensive differential susceptibility data on (deuterated) TTF-AuS$_4$C$_4$(CF$_3$)$_4$ ($T_c = 2.03$ K). As a consequence of the much lower value of T_c in this SP material,[2] correspondingly lower applied fields are needed to bring about the field-dependent transitions from the dimerized phase. It is therefore easier to carry out a study of the differential susceptibility (χ) over a large range of relative field. Since $\chi(H)$ measures the derivative with respect to the field of the $M(H)$ magnetization curve, it is a much more sensitive probe for studying the nature of the field-dependent transitions. As will be discussed in detail below, the differential χ data give interesting new information on the nature of the phase transitions in SP systems, and, in conjunction with a thermodynamic theory of second-order (λ-type) transitions, provide precise criteria for the location of the magnetic phase boundaries in these materials. Novel relaxation effects are observed which throw new light on the character of SP phases. Last, but not least, the χ data are instructive in an analysis of phase behavior which reveals some "universal" character to the H-T phase diagrams of TTF-AuS$_4$C$_4$(CF$_3$)$_4$, TTF-CuS$_4$C$_4$(CF$_3$)$_4$ and MEM-(TCNQ)$_2$.

II. EXPERIMENTAL ASPECTS

The experiments were performed on a powdered sample of 0.5 g of deuterated TTF-AuS$_4$C$_4$(CF$_3$)$_4$ prepared at General Electric R and D, Schenectady. The differential susceptibility was measured at Leiden by means of a mutual inductance technique. The coil system consists of a primary and two secondary coils. The latter are identical but oppositely wound and are placed one above the other. Moving the sample from the center of one of the secondary coils to the center of the other produces a change of the output voltage directly proportional to χ. A steady field up to 40 kOe (4 T) parallel to the ac field is provided by a superconducting solenoid. Temperatures were measured by a calibrated carbon resistance thermometer. This apparatus, in principle, enables simultaneous measurements to be made of the in-phase (χ') and out-of-phase (χ'') components of the complex susceptibility. However, due to the low density of spins in the sample, the magnetic signals were very weak. Hence only χ' could be studied (denoted by χ in what follows) since the χ'' signals were too small. The signal-to-noise ratio also inhibited studies of the frequency dependence of χ. All experiments reported below were performed at 1.88 kHz. For one field

sweep (at $T = 1.250$ K) an additional experiment at 0.94 kHz was performed which showed no detectable differences from the higher-frequency data. For measurements of the static magnetization (M) the same coil system may be used, in which case the primary coil is disconnected and the induction voltages in the secondary arising from sample movement are integrated electronically to yield the magnetization.

In Fig. 1 we show representative χ and M data as a function of temperature taken at different constant fields. This figure clearly illustrates the power of the differential χ measurements. Whereas in the case of the high-field $M(T)$ curves significant features are not apparent, the corresponding $\chi(T)$ plots display pronounced maxima (anomalies) indicating the presence of transitions. Note that the amplitudes of these maxima are strongly field dependent and vanish as H tends to zero. As will be discussed in some detail below, the $H = 0$ transition is better defined as a maximum in the temperature derivative of χ than by a "kink" of "knee" in the χ vs T plot. In mean-field theory, the second-order SP transition both in zero and in nonzero field is given by a "knee" criterion, as calculated theoretically by Bulaevski *et al.*[7] and Tannous and Caillé.[10] Our differential χ measurements definitively demonstrate the breakdown of a mean-field picture very close to the transition.

The magnetization and susceptibility data measured as a function of field at different constant temperatures are given in Fig. 2. In this type of plot pronounced maxima in the χ isotherms are again observed, and their amplitudes are in this case seen to be strongly temperature dependent. In the magnetization curves the transitions out of the dimerized phase are marked by maxima in the slopes of the $M(H)$ curves. In fact, the $\chi(H)$ curves are the derivatives of the $M(H)$ curves (apart from a reservation to be discussed later). We remark, perhaps superfluously, that such a relationship is not the case in Fig. 1, as is apparent from the discussion in Sec. IV.

At this point we should point out that the low-field susceptibility measurements were affected by minor impurity effects, thought to be of ferromagnetic origin since the contribution is found to saturate in relatively low fields ($\simeq 3$ kOe) and is independent of temperature. This can be seen in Fig. 2 by the $H = 0$ intercepts of the $\chi(H)$ curves. A correction for this spurious signal (dotted curves in Fig. 2) was applied, and the same correction was, in fact, applied to the $H = 0$ data shown in Fig. 1. We believe that the impurity was not present in the sample itself, but that it arose from the sample holder (resulting, e.g., from machining the holder or from impurity oxygen in the He gas condensing on the holder). It was considered unnecessary to correct the data for diamagnetism. The estimated diamagnetic contribution is indicated in Fig. 1.

The values for the critical fields and temperatures
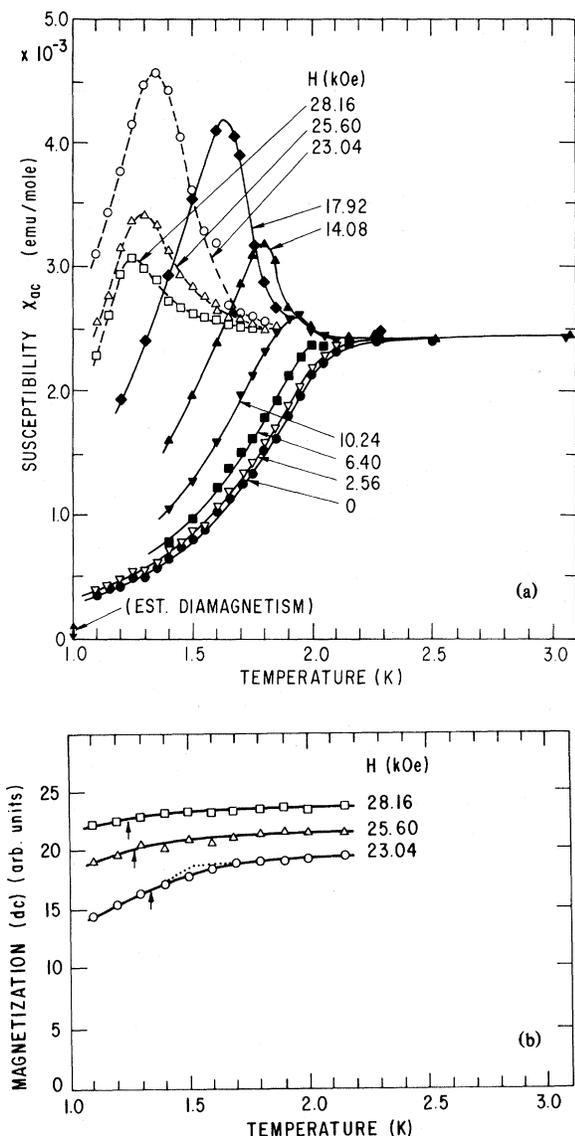
FIG. 1. (a) Differential susceptibility curves at various constant fields as a function of temperature for TTF-AuS$_4$C$_4$(CF$_3$)$_4$. The curves for the special high-field region are shown as dashed lines. (b) Magnetization (static) curves as a function of temperature at several fixed fields for TTF-AuS$_4$C$_4$(CF$_3$)$_4$. The arrows indicate the location of $X_H(T)$ maxima from Fig. 1(a). The dotted curve shows the location of the singularity using a mean-field knee criterion.

FIG. 2. (a) Differential susceptibility curves at constant temperatures as a function of field. Those curves belonging to the special low-temperature region are shown as dashed lines. At the lowest field, the dotted lines indicate a correction for an impurity effect. The arrow is discussed in Sec. III. (b) Magnetization (static) curves at constant temperatures as a function of field. The arrows indicate the location of $X_T(H)$ maxima from (a).

(H_c, T_c) obtained from the plot in Figs. 1 and 2 have been collected in Fig. 3, where they are shown in comparison with the theoretical predictions of Bray,[6] Bulaevskii et al.[7] and Cross.[8,9] All theoretical predictions give a second-order transition line extending from $T_c(0)$ to a special point (multicritical point) denoted (H_c^*, T_c^*). We shall call this boundary the

DU line in what follows, since it separates the (ordered) dimerized from the (nonordered) uniform phase regions. The Bray calculation[6] for the DU lines is equivalent to that of Bulaevskii et al.[7] Hence both theories, evaluated carefully,[15] give the same values for (H_c^*, T_c^*), namely, $\mu_B H_c^*/k_B = 0.75\,T_c(0)$ and $T_c^* = 0.54\,T_c(0)$. Above H_c^* and below T_c^* (high-field, low-temperature region) Bulaevskii et al. predict an intermediate (new) phase separating the
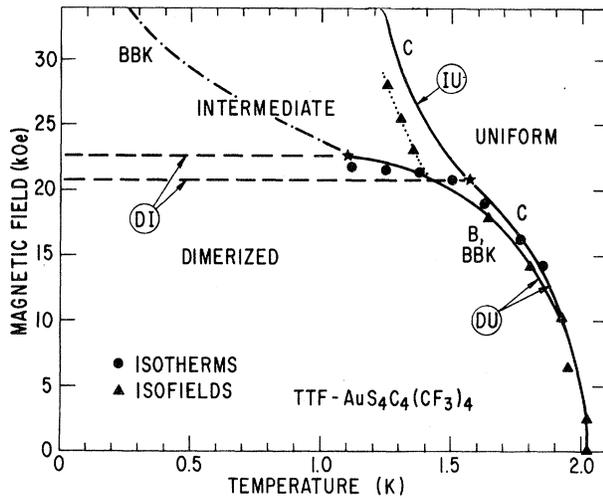
FIG. 3. Magnetic phase diagram for TTF-AuS$_4$C$_4$(CF$_3$)$_4$, constructed from susceptibility maxima of Figs. 1 and 2. Theoretical curves of Cross (C), Bray (B), and Bulaevskii *et al.* (BBK) are shown along with their respective multicritical points (starred).

dimerized and uniform phases. The calculated boundary between intermediate and uniform phases (*IU* line) is shown in Fig. 3 and is second order. Bulaevskii *et al.*[3,7] predict the boundary between dimerized and intermediate phases (*DI* line) to be first order, but are not able to present a precise calculation. This first-order boundary is therefore shown only schematically in Fig. 3. The Cross theoretical predictions (also shown in Fig. 3) show strong qualitative similarities to those of Bray-Bulaevskii. The location of the multicritical point is slightly different, occurring at $\mu_B H_c^*/k_B = 0.69 T_c(0)$ and $T_c^* = 0.77 T_c(0)$. The *DU* lines for both theories are very close, but the high-field *IU* transition lines show significant differences. In existing calculations the Cross line asymptotically approaches $0.5 T_c(0)$ as $H \to \infty$, whereas the Bulaevskii line asymptotically tends to a value close to $T = 0$. However there is some possibility of reconciliation, since the precise location of this line is sensitive to details of the assumed phonon spectrum. For the *DI* transition between dimerized and intermediate phases, Cross speculates on the order of the transition, but gives no calculated values. Hence, we again show the transition line schematically in Fig. 3.

Regarding the experimental data in Fig. 3 we can make a number of comments. First we note that, as regards the DU curve, the experimental data are in between the Bray-Bulaevskii and the Cross results. We conclude that, to present experimental accuracy, the data do not really favor either theory, but are in gratifying agreement with both, especially since the only adjustable parameter needed in fitting theory to

the experiment is $T_c(H = 0)$, taken to be 2.03 K (see below). Secondly, the experiment also shows a bifurcation of the *DU* line, emanating from a multicritical point located at $H_c^* = 21.4 \pm 0.2$ kOe and $T_c^* = (1.4 \pm 0.03)$ K or at $\mu_B H_c^*/k_B = 0.71 T_c(0)$ and $T_c^* = 0.69 T_c(0)$. (In later sections, we justify the precision of the determination of these parameters.) The experimental T_c^* lies midway between the two theoretical predictions, as also does the experimental H_c^*.

The *IU* line between intermediate and uniform regions needs special discussion. The experimental points shown are derived on the basis of the $H = 23.04$, 25.60 and 28.16 kOe χ curves in Fig. 1. Evidence for this phase line is not very apparent in the plots of Fig. 2. The reasons for this are interesting and will be discussed in a subsequent section (III). We do note that the experimental data points lie quite close to the Cross prediction, and the shape (curvature) of the line, to the extent that it is experimentally defined, is consistent with the shape of the Cross curve.

We conclude, therefore, that below $T = 1.4$ K and above $H = 21.4$ kOe two distinct phase boundaries (*IU* and *DI*) are present in the experimental (H_c, T_c) phase diagram which encompass a new intermediate phase such that magnetization and/or susceptibility are generally lower than in the immediately adjacent uniform chain or dimerized regions. The magnetic measurements, which have been carried out down to 1.1 K [$0.54 T_c(0)$], do not show explicit evidence of first-order character in the *DI* phase line, but this possibility is not ruled out, as will be discussed below.

III. SUSCEPTIBILITY CONTOUR PLOT

The extensive nature of the experimental χ vs T and χ vs H data allow us to present a new kind of plot for illustrating phase behavior generally, and for delineating phase boundaries. In Fig. 4 we show contour lines of constant susceptibility (solid curves) in the H-T plane. The plot extends only down to about $0.5 T_c(0)$ owing to present experimental limitations. A major feature of interest is an essentially flat "shelf" (shown shaded). In the H-T region of the shelf, transition (precursor) effects have disappeared and we are in a uniform chain region. Over the ranges of temperature and field studied the uniform chain susceptibility is constant since both $k_B T_c(H)$ and $g\mu_B H_c(T)$ are very small compared to J_{Au} (from Ref. 2, $J_{Au}/k_B = 68$ K). The dashed curve clearly corresponds to a "ridge" in the susceptibility contours. It is also equivalent to the *DU* transition line of Fig. 3 continued through the special point (H_c^*, T_c^*) into the *DI* line, down to 1.1 K. Thus phase boundaries are defined by ridges in the χ contour plot. The high-field *IU* phase boundary (see
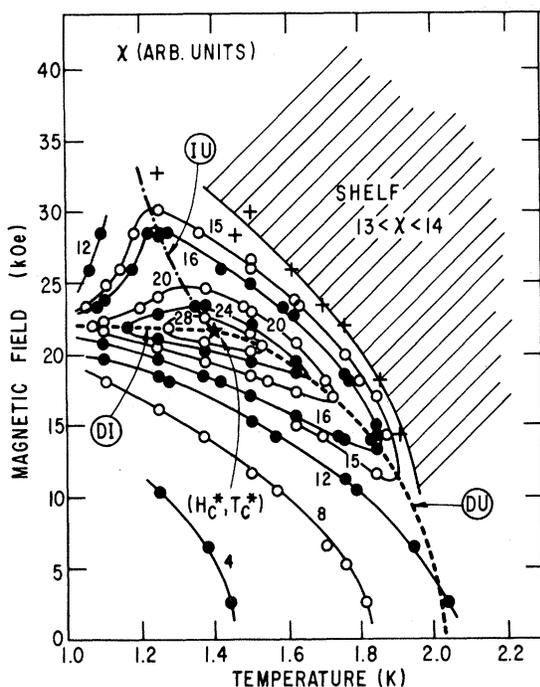
FIG. 4. Contour plot of ac differential susceptibility in the
H-T plane for TTF-AuS$_4$C$_4$(CF$_3$)$_4$ (solid lines). Ridges in
the contours are shown as dashed or dot-dashed lines and
correspond to phase boundaries. Values of χ are in (arbi-
trary units) such that 1 arb. unit corresponds to 1.89×10^{-4}
emu/mole.

Fig. 3) appears in Fig. 4 as a dash-dot line emanating
from (H_c^*, T_c^*). Note that again it is characterized by
a ridge in the susceptibility contours, although this
time the ridge is less sharply defined than for the DU
and DI branches. The special point (multicritical
point) H_c^*, T_c^*, shown by the star in Fig. 4, appears as
an overall peak of maximum susceptibility in the en-
tire H-T plane.

This contour plot illustrates why the high-field IU
phase line is visible only in the $\chi(T)$ plots of Fig. 1
and not in the $\chi(H)$ plots of Fig. 2. The constant
field plots of Fig. 1 cross the high-field IU phase
ridge at a pronounced angle (almost perpendicular)
and the effects of the ridge are clearly manifest. In
Fig. 2 the pronounced maxima observed correspond
to crossing the DU line and the DI line at high and
low relative temperatures, respectively. It can be in-
ferred from Fig. 2 that the IU line could only have
been crossed by the $\chi(H)$ field sweep at $T = 1.250$ K.
The crossing point is indicated by the small arrow
($\downarrow$). Although no separate peak is seen, there is a
substantial shoulder for $H > H_{DI}$ for this particular
isotherm (compare the curves for $T = 1.11$ and
$T = 1.50$ K). This may be attributed to the fact that

the isotherm crosses the IU line at a very small angle
in this case, in which case the peak will not be
resolved since substantial broadening will occur. A
similar phenomenon can be inferred from data re-
ported for the metamagnetic compound
CoBr$_2 \cdot$2H$_2$O.[16]

IV. THERMODYNAMIC DISCUSSION

The interesting question of the criteria to be used
in defining SP phase transitions over a range of tem-
perature and field, and the novel appearance of the χ
plots in general, is best discussed in terms of a ther-
modynamic theory of second-order phase transitions
(λ transitions).[17-19] The rationale for discussing our
experimental results in the light of such a theory ar-
ises from the fact that the $H = 0$ specific heat shows a
characteristic anomaly,[20] and the χ data do indicate
second-order (λ) transitions along the DU line.

Theoretically one assumes that the specific heat at
constant field $C_H \equiv T(\partial S/\partial T)_H$ has a singularity at
the field-dependent critical temperature, i.e., along
the DU line of the H-T phase diagram. By thermo-
dynamic arguments it then follows that the isother-
mal susceptibility $\chi_T \equiv (\partial M/\partial H)_S$ as well as the
quantity $(\partial M/\partial T)_H$ will display the same anomalous
behavior as C_H. By contrast, the adiabatic suscepti-
bility $\chi_S \equiv (\partial M/\partial H)_S$, the specific heat at constant
magnetization $C_M \equiv T(\partial S/\partial T)_M$, and the slope of
the DU line itself $(\partial H/\partial T)_\lambda = (\partial H/\partial T)_S$, will
remain finite (display a much weaker singularity)
along the DU line. From the thermodynamic theory
it follows that $(\partial \chi_S/\partial T)_H = -(C_H/T) (\partial^2 T/\partial H^2)_S$.
Thus, although χ_S shows only a weak anomaly along
the DU line, its temperature derivative will display a
strong singularity (since the quantity $(\partial^2 T/\partial H^2)_S$, as
well as C_H, diverges along the DU line). As H tends
to zero, $M \rightarrow 0$ and therefore $\chi_T \rightarrow \chi_S$ and takes on
its characteristics. It follows that the experimental
criterion for defining $T_c(H)$ at low fields should be
the temperature of the maximum slope of the $\chi(T)$
curves. If this criterion is followed, the value of
$T_c(0)$ obtained is (2.03 ± 0.02) K, which agrees with
specific-heat studies as a function of field underway
at Leiden. Within the errors there appears to be no
difference between our value for the deuterated com-
pound and that reported in the literature[2,20] for non-
deuterated TTF-AuS$_4$C$_4$(CF$_3$)$_4$ ($T_c = 2.06$ K). Note
that use of the mean-field "knee" criterion would
yield a value for $T_c(0)$ a few percent higher.

Let us further investigate the interesting situation
where $T_c(H)$ for low fields is derived from peaks in
$(\partial \chi_T/\partial T)$ whereas at higher fields, $T_c(H)$ is derived
from peaks in $\chi(T)$ itself. Consider the thermo-
dynamic relation

$$\chi_T - \chi_S = (C_H/T)(\partial T/\partial H)_S^2 .$$

Since both χ_S and $(\partial T/\partial H)_S$ are nonanomalous along the DU line, it follows that χ_T will display a peak similar to that in C_H. However, the amplitude of the peak in χ_T will decrease and eventually vanish for $H \rightarrow 0$. This is precisely what is observed experimentally. It is interesting to note that a similar situation arises in the case of ordered 3D antiferromagnets.[18] There the zero-field antiferromagnetic ordering temperature, T_N is defined as an inflection point in the plot of χ_T vs T, i.e., a singularity appears in $(\partial\chi_T/\partial T)_{H \rightarrow 0}$ rather than in χ_T itself. As the field increases, a peak progressively develops in χ_T. This has been observed by direct calculation as well as experimentally.[18,21] We therefore note that although the magnetoelastic SP antiferromagnetic chain and the regular 3D antiferromagnet represent two completely different physical systems, and accordingly have characteristically different forms for the χ curves, general aspects of the phase behavior are remarkably equivalent. This should indeed be expected, since it follows from basic thermodynamics and the shape of the phase boundary.[22]

We also point out that similar thermodynamic arguments yield the criteria to be used in defining the DU transition from the isothermal $M_T(H)$ or isofield $M_H(T)$ magnetization curves. Obviously, since $\chi_T \equiv (\partial M/\partial H)_T$, the transition in not too small fields is defined by the maximum slope of the isothermal magnetization curves. This is illustrated by the $M_T(H)$ curves in Fig. 2, where the arrows ($\uparrow$) indicate the temperatures at which the χ_T maxima are found to occur. Secondly, since $(\partial M/\partial T)_H = -(C_H/T)(\partial T/\partial H)_S$ it follows that for the isofield curves the transition is also defined to be the temperature of maximum slope. In Fig. 1 the vertical arrows ($\uparrow$) indicate the temperature of the $\chi_H(T)$ maxima. They are indeed seen to correspond to temperatures of maximum slope of the $M_H(T)$ curves.

Finally we note that since for not-too-small fields, the singularity in χ_T reflects the singularity in C_H, the reverse is also true. Previous experimental SP specific-heat data,[20,23] have been analyzed in terms of mean-field cusps, as theoretically calculated, for example, in Ref. 9. Specific-heat experiments on TTF-AuS$_4$C$_4$(CF$_3$)$_4$ at Leiden, at present in a preliminary stage, show anomalies which should be analyzed in terms of (rounded) λ anomalies. Conversely, the consistency of the form of the C_H and χ_T anomalies provides a test of experimental data.

V. RELAXATION PHENOMENA

In the preceding we have discussed the expected properties of $\chi_T(H)$, $\chi_H(T)$, $M_T(H)$, and $M_H(T)$ and we should now consider which of these quantities are in fact measured experimentally. Whereas the magnetization measurements are necessarily isother-

mal (dc), the susceptibility is measured with an ac technique and the result can yield either χ_T or χ_S, or indeed some intermediate quantity. The decisive factor in this problem is the ratio of the ac frequency to the relevant relaxation time. The latter will in general depend on both temperature and field, and may in fact show anomalies at the field-induced transitions.[18] Clearly, the nature of the susceptibility will be important for the interpretation of the χ-contour plot described above. In the absence of an extensive frequency study,[16,18] we resort to a direct test (for a limited set of experimental conditions). The dc magnetization measurements of Fig. 2 are sufficiently detailed to permit a direct evaluation of χ_T by differentiation of M with respect to H. χ_T evaluated this way may then be compared with the observed χ_{ac}. Alternatively, a new set of magnetization isotherms may be constructed by integrating $\chi_{ac}(H)$. The various sets of curves may then be examined for consistency with expected behavior.

Hence, in Fig. 5, we show the χ_{ac} vs H curve for $T = 1.759$ K in comparison with the $\chi_T(H)$ derived from the $M(H)$ curve at $T = 1.76$ K. The close agreement between these two curves demonstrates that for this temperature, χ_{ac} is in fact the isothermal susceptibility (χ_T). This tells us that the frequency ω of 1.88 kHz at which the χ_{ac} measurements were performed, is low with respect to the inverse relaxation times τ in this region, i.e., that the condition $\omega\tau \ll 1$ obtains. This region is therefore characterized by a very short ($\leq 10^{-5}$ s) relaxation time, even when the second-order DU phase boundary is crossed. This result is unusual in comparison with observed phenomena in 3D ordered antiferromagnets,[18] for which the relaxation time goes through a pronounced maximum at the second-order boundary and may reach values of the order of 10^{-1}–1 s. It may reflect the fact that in the ideal magnetoelastic
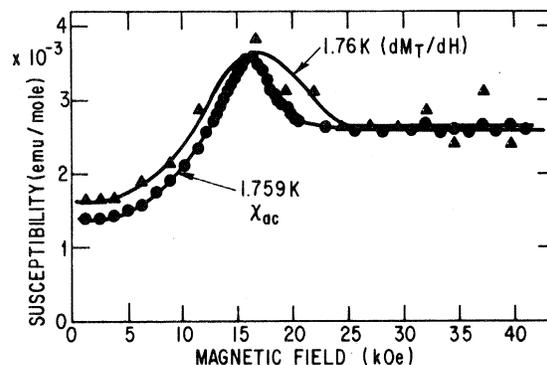
FIG. 5. Comparison of field dependence of differential susceptibility, χ_{ac}, at 1.759 K with the isothermal susceptibility, (dM_T/dH), obtained by differentiating the static magnetization data of 1.76 K.

SP system, the spins remain paramagnetically disordered in the dimerized phase, i.e., the ordering is manifested in the conformation of the lattice and not accompanied by long-range magnetic correlations.

On the other hand, the equivalent comparison X_{ac} at $T = 1.11$ K and X_T derived from $M(H)$ at $T = 1.10$ K, as shown in Fig. 6, presents a strong contrast. Clearly X_{ac} is no longer isothermal when the DI line is crossed, as well as for a substantial region of higher field. We make a preliminary observation that the field region where $X_{ac} < X_T$ corresponds roughly to the estimated field region spanned by the intermediate phase at this temperature. The experimental limitation in detecting X'' signals does not allow us to establish whether fully adiabatic conditions have been attained. Nevertheless, it is important to emphasize here that the most striking feature of this field region, namely, the DI phase boundary, is unambiguously indicated as an anomaly in both susceptibilities X_T and X_{ac}.

These two comparisons (at 1.76 and 1.1 K) do not tell us where, i.e., at what temperature, the cross over from isothermal to nonisothermal behavior in X_{ac} takes place. Some information on this effect may be obtained by examining a family of magnetization curves derived by integrating $X_{ac}(H)$. Curves are

available at four temperatures and are shown in Fig. 7. By comparison with the directly measured magnetization curves of Fig. 2, we might expect that these curves should converge to a common line at the highest fields of these experiments. This condition is met satisfactorily for $T = 2.1$, 1.759, and 1.50 K, but fails notably for the curve for $T = 1.250$ K. The "missing magnetization" is attributed to a failure of the condition $X_{ac} = X_T$. The onset of the inequality $X_{ac} < X_T$ must thus occur between 1.5 and 1.250 K. It is particularly tempting to associate it with the special point T_c^* at 1.4 K.

We have already noted that our X-contour plot has the special feature that the special point (H_c^*, T_c^*) is an absolute maximum, and further it is observed to occur at the junction of the three ridges defining the DU, DI and IU phase boundaries. We deduce that the onset of the inequality $X_{ac} < X_T$ with decreasing T or increasing H beyond (H_c^*, T_c^*) could explain the observed decreasing X_{max}. This feature is of great utility for a precise determination of the location of T_c^* (and also H_c^*). Figure 8 shows a plot of the amplitude of the susceptibility peak versus the temperature along the DU and DI phase boundary lines. Along the DU line, X_{max} increases as T decreases, in agreement with our previous thermodynamic arguments. Along the DI line, however, X_{max} progressively decreases with decreasing temperature, attributable to an increasingly longer relaxation time along this boundary. The intersection of the loci of X_{max} along the DU and DI lines presumably locates

FIG. 6. Same as Fig. 5, for $T \approx 1.1$ K.
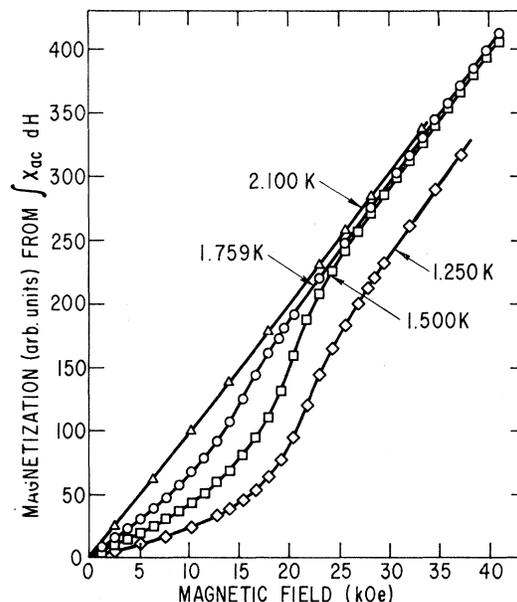
FIG. 7. Field dependence of magnetization as derived by integration of differential susceptibility curves for various temperatures.
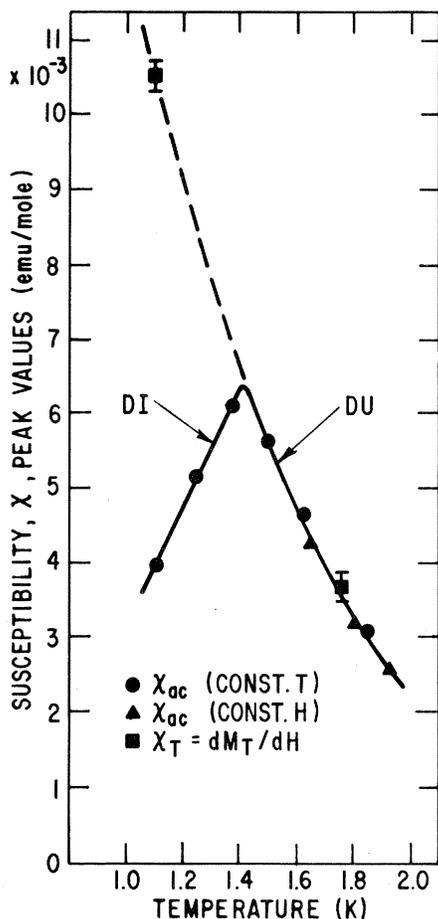
FIG. 8. Magnitude of susceptibility peaks, X_{ac}, along the *DU* and *DI* phase boundary lines. Also shown are two X_{dc} peak points which agree with X_{ac} above T_c^* and depart below T_c^*. The discrepancy leaves questions which are difficult to resolve owing to the sparseness of X_{dc} data.

the onset of $X_{ac} < X_T$ and hence locates (H_c^*, T_c^*) at $T_c^* = 1.4 \pm 0.03$ K, corresponding to $H_c = 21.4 \pm 0.2$ kOe, in agreement with, but more accurately than, the determinations from Fig. 3 and 4.

It is often difficult to understand the magnitudes and microscopic mechanisms of relaxation processes. The existing literature for ordered as opposed to paramagnetic systems does not appear to be as well developed. However, the dramatic change occurring over a narrow range of parameters in this experiment suggests a reasonably simple explanation. Theory suggests that the *DI* line is a line of first-order phase transitions. We might therefore expect to see hysteresis phenomena in the magnetic measurements. Such phenomena have, indeed, been observed in the magnetization measurements on the SP sister compounds TTF-CuS$_4$C$_4$(CF$_3$)$_4$ (Ref. 13) and MEM-(TCNQ)$_2$,[14] but not in TTF-AuS$_4$C$_4$(CF$_3$)$_4$, at least down to ~ 1.1 K [$\sim 0.54 T_c(0)$]. If the *DI* line is,

nevertheless, first order, we may[18] well associate with it a new, rather slow, relaxation mechanism associated with transfer processes or nucleation effects between the two coexisting phases. This mechanism could explain the rather abrupt onset of the condition $X_{ac} < X_T$ and the "missing magnetization" (see Fig. 7) would correspond to the typical magnetization discontinuity associated with the first-order transitions, which would not be observable in X_{ac}. It could equally well be attributable to a continuing series of small jumps or discontinuities in magnetization as the field increases through the intermediate phase region. Such a phenomenon may be closely related to current theoretical ideas on multiphase phenomena[24] and "staircase" phenomena.[9,13,25]

VI. UNIVERSAL PHASE DIAGRAM

The precision susceptibility measurements on TTF-AuC$_4$S$_4$(CF$_3$)$_4$, which reveal non-mean-field characteristics of the SP transitions, have led us to re-examine previous experimental phase boundary data on TTF-CuS$_4$C$_4$(CF$_3$)$_4$ (Ref. 13) and MEM-(TCNQ)$_2$.[14] The data, reanalyzed along the lines discussed in the section on thermodynamics, are plotted in Fig. 9, along with the new "Au" data, in terms of reduced variables $H/T_c(0)$ and $T/T_c(0)$. The phase boundaries for "Cu" and "MEM" differ quite considerably (up to a 15% maximum) from those previously published, in consequence of the new criteria used in defining the transition points. The mutual and individual consistency of the data on the three materials is greatly improved. For instance, for
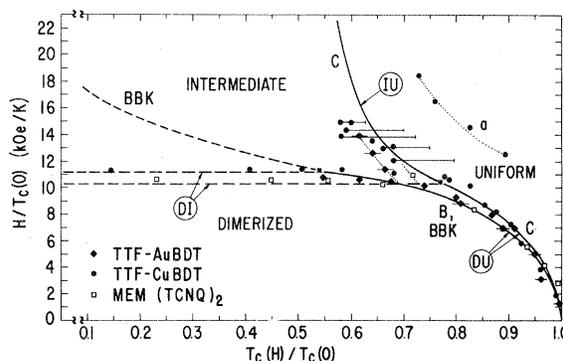
FIG. 9. Composite normalized phase diagram for TTF-AuS$_4$C$_4$(CF$_3$)$_4$, TTF-CuS$_4$C$_4$(CF$_3$)$_4$, and (MEM-TCNQ)$_2$ powders. The normalized scales are $H/T_c(0)$ and $T_c(H)/T_c(0)$. Where possible, transitions are located by peak values of $(\partial M/\partial T)_H$ or $(\partial M/\partial H)_T$ (or X_{ac}). For normalization, the values chosen for $T_c(0)$ are 2.03, 10.3, and 18.0 K for the compounds as listed. The line designated (a) represents mean-field estimates for the high-field phase boundary (for Cu) from data using a 10-MW solenoid ($H_{max} = 200$ kOe). The solid and dashed lines represent theoretical curves as in Fig. 3.

MEM-$(TCNQ)_2$ we now deduce $T_c(H \rightarrow 0) \simeq 18$ K, in much better agreement with the heat-capacity result $T_c(0) = 17.7$ K[23] than the value of 19 K previously deduced using the "knee" criterion and the $M_H(T)$ plots.[14] Most importantly, one observes that the three materials now show a universal behavior for the DU line, which, as discussed in Sec. II for Au, is in very good agreement with the two major theories of Bray-Bulaevskii,[6,7] and Cross-Fisher.[9] A similar conclusion of universality is obtained from data along the DI line (but note that the "theoretical" lines for this boundary are schematic as in Fig. 3). The greatest interest and challenge to current theory lies in data for the high-field IU phase line. A reanalysis of the high-field magnetization data on TTF-$CuS_4C_4(CF_3)_4$ in terms of (imprecisely located) inflection points in the $M_H(T)$ vs H curves for fields up to 155 kOe yields an IU boundary which is suggestively in agreement with the IU transition data for the gold member of the family. We note that there is considerable scatter because only magnetization, not susceptibility, measurements are available for TTF-$CuS_4C_4(CF_3)_4$ at this time. [For MEM-$(TCNQ)_2$, only a single high-field data point is at present available, but that also is not inconsistent, within experimental accuracy, with "gold" and "copper."] The curve marked (a) on Fig. 9, for copper, was derived from high-field data at 10 MW dissipation, using the "knee criterion." This criterion essentially locates the boundary of the susceptibility "shelf" (see Fig. 4).

One feature of the phase behavior of the three compounds that is definitely nonuniversal is the occurrence of hysteresis in the demagnetization curves for the "Cu" and "MEM" compounds. This hysteresis starts in the vicinity of the DI line and extends well into the new, intermediate phase. The hysteresis persists all the way up to (H_c^*, T_c^*) for MEM-$(TCNQ)_2$, up to $T/T_c(0) = 0.53$ for TTF-$CuS_4C_4(CF_3)_4$ and has not so far been observed in TTF-$AuS_4C_4(CF_3)_4$ down to a relative temperature $T/T_c(0) = 0.54$, the present experimental low-temperature limit. Further relaxation studies, as discussed in Sec. V, may throw light on the nature of the DI line and the hysteretic phenomenon.

So far we have not discussed the nature of the high-field intermediate phase. Current theories predict that the dimerized phase remains stable in nonzero applied field until the Zeeman energy overcomes the "pinning" energy associated with lattice Umklapp effects. At the appropriate critical field, H_c^*, therefore, the lattice is expected to enter (a) an incommensurate phase, i.e., such that the periodicity of the spin configuration bears no relation to the underlying lattice distortion[6,7,9] or, possibly, (b) a sequence of higher-order commensurate phases.[9,13,25] These current theories predict a universal character to the SP phase diagram, i.e., that there should be scaling of the phase diagram with respect to the single parameter $T_c(0)$.

Clearly, the existing experimental data on three compounds, two with essentially the same lattice structure, and one [MEM-$(TCNQ)_2$] with quite different lattice structure, are in rather dramatic agreement with current theories. However, magnetic studies do not unambiguously determine the microscopic nature of, say, the high-field phase. Microscopic probe techniques, e.g., neutron scattering, are required. Hence we briefly discuss two additional possibilities for the phase behavior of SP systems and, particularly, the nature of the high-field phase. The current theories so far discussed assume the phase behavior is completely determined by interchain spin-phonon interactions, and neglect interchain magnetic coupling entirely. In fact, the probable situation is that in SP systems the nature of the stable phase is determined by a competition between spin-spin and spin-phonon types of interaction. It is now known that for quasi-1D antiferromagnets the ordering temperature (to a 3D ordered spin array) is initially enhanced by an applied field,[26] whereas for SP systems the reverse is the case, as we see from Figs. 3 or 9. The possibility therefore exists[27] that at some nonzero field, the magnetic interchain coupling becomes dominant and the high-field intermediate phase may correspond to 3D AFM ordering. The appreciable hysteresis observed in TTF-$CuS_4C_4(CF_3)_4$ and MEM-$(TCNQ)_2$ is certainly consistent with a first-order transition between a lattice-dimerized, spin-disordered phase, and a uniform lattice, spin-ordered phase.[11] Further, it is reasonable that the onset of 3D AFM ordering should occur at H_c^* when the field has overcome the "pinning" or commensurability energy of the lattice, at which point the chains regain a substantial magnetization. Further experiments are now underway to test the apparent universality of T_c^* emerging from our current analysis. Universality of T_c^* is difficult to reconcile with the occurrence of a 3D ordered magnetic phase.

A very recent approach which takes account of nonlinear effects is a soliton picture.[28,29] By analogy with polyacetylene, where the spatial alternation has two possibilities for its location and solitons are domain walls separating the two types of bond alternation configuration, soliton excitations in SP systems may be regarded as boundaries between regions where the strong-weak exchange alternation reverses. More generally, solitons may be pictured as localized distortions away from the dimerized state. If solitons are reasonable for the DI transition and the I phase constitutes another periodicity (commensurate or incommensurate), then the relevant soliton is the transition region (domain wall) between portions which have these two periodicities. Using nonlinear solutions within the Cross-Fisher boson-algebra approach, it is observed that the soliton creation energy decreases linearly with applied field. Hence the field at

which the soliton energy goes to zero marks a transition from commensurate to incommensurate phases.[28] This Nakano-Fukuyama theory is therefore a modification of the basic Cross-Fisher picture. The soliton picture has its appealing features, but present calculations give a value of (H_c^*, T_c^*) which is low in comparison with experiment. However, it cannot be ruled out by present experiment; and subsequent, more microscopic techniques such as neutron scattering, NMR, or EPR experiments, are needed to distinguish between various theories.

VII. SUMMARY AND CONCLUSIONS

In this paper we have examined the effect of an applied magnetic field on the spin-Peierls compound TTF-AuS$_4$C$_4$(CF$_3$)$_4$, with emphasis on differential susceptibility in addition to magnetization measurements. Since the susceptibility is the derivative (in field) of the magnetization, it follows that differential susceptibility studies provide a much more sensitive probe of magnetic phase behavior than magnetization studies. The feasibility of accurate susceptibility measurements is greatly enhanced by the much lower zero-field transition temperature (and correspondingly lower transition fields) of TTF-AuS$_4$C$_4$(CF$_3$)$_4$ in comparison with the previously investigated compounds TTF-CuS$_4$C$_4$(CF$_3$)$_4$ and MEM-(TCNQ)$_2$. For these two compounds only magnetization measurements have been possible so far. Our new higher-sensitivity, measurements demonstrate deviations from mean-field behavior in terms of the form of critical singularities along the phase boundaries consistent with the Ginzburg criterion. This is in contrast with previous measurements on spin-Peierls systems where such deviations have not been unambiguously observed.

Using criteria for the definition of phase transitions in spin-Peierls systems in accordance with a theory of transitions more general than mean field, an extended phase diagram for TTF-AuS$_4$C$_4$(CF$_3$)$_4$ is obtained. It is striking that all aspects of this phase diagram, which includes low-field (dimerized) and high-field (intermediate) phases are in both qualitative and reasonable quantitative agreement with current theories, particularly that of Cross and Fisher, extended by Cross.

The precision of the differential susceptibility measurements, coupled with the extensive (high density of) available data points, have permitted us to construct a novel contour plot of susceptibility values in the H-T plane. This turns out to be a useful tool for delineating global phase behavior in a complex (e.g., multicritical) system and may well find application in other systems.

In general, in studies of the ac differential susceptibility, usually carried out at one or more frequencies, it is important to examine the role of relaxation effects on the susceptibility behavior. We have found that the vicinity of the DU phase boundary is characterized by rather short relaxation times, so that χ_{ac} is properly an isothermal susceptibility. On the other hand, DI transitions to the intermediate phase region are associated with much longer relaxation times, suggestive of first-order transitions.

The understanding developed from an examination in detail of the global phase behavior of TTF-AuS$_4$C$_4$(CF$_3$)$_4$ has proved fruitful in a reexamination of previous results in other compounds. This has led to the development of a composite phase diagram in (reduced) field-temperature space for three compounds; TTF-CuS$_4$C$_4$(CF$_3$)$_4$ and MEM-(TCNQ)$_2$, in addition to TTF-AuS$_4$C$_4$(CF$_3$)$_4$. These compounds belong to very different lattice structures and span a factor of 10 in zero-field transition temperature. The results demonstrate a significant degree of universality not only for the boundaries of the lower field dimerized region, and suggest universality also for the boundary of the intermediate and uniform phases. This finding lends weight to theories of spin-Peierls phase behavior which ignore spin-spin interchain coupling. Nevertheless, it is important and interesting to investigate the possibility of spin-spin (conventional) antiferromagnetic ordering at high fields in these systems. The possibility that a significant role is played by solitonic excitations has not yet been fully investigated theoretically or experimentally. Further, definitive, information is most likely to come from microscopic probe techniques, such as neutron scattering experiments, some of which are presently underway.

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