

# The intermediate state of the spin-Peierls system tetrathiafulvalene bis(dithiolene)aurate (TTF-AuBDT): a magnetic and specific heat study

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## THE INTERMEDIATE STATE OF THE SPIN-PEIERLS SYSTEM TTF–AuBDT: A MAGNETIC AND SPECIFIC HEAT STUDY

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We report measurements of the differential susceptibility, magnetization and specific heat on the field dependent spin-Peierls transition in tetrathiafulvalene-gold-bisdithiolene (TTF–AuBDT). Temperature-, field- and frequency ranges are extended in comparison with previous studies. The data confirm the incommensurate nature of the high field, low temperature phase in spin-Peierls systems.

Theoretical calculations, based on the mean-field Pytte Hamiltonian and using the soliton lattice solution for the incommensurate state prove to be in satisfactory agreement with the experiments. In the incommensurate state relaxation times, associated with the formation of discommensurations are found to be in the order of seconds.

### 1. Introduction

The spin-Peierls (SP) transition is an intrinsic lattice instability in a system of quantum-mechanical antiferromagnetic chains where the spins are interacting via a Heisenberg or *XY* exchange interaction and the chains are coupled to a 3-dimensional (3-d) phonon lattice. At the critical temperature,  $T_{SP}$ , a second order transition occurs to a state where the chains become dimerized. The dimerization increases progressively as the temperature is lowered and reaches a maximum at zero temperature.

The SP transition is the magnetic analogue of the regular Peierls instability in a quasi 1-d metal, where dimerization of the lattice introduces a gap in the electronic spectrum, thereby lowering the electronic energy and turning the metal into a semiconductor. One of the most interesting aspects of the SP transition is the correspondence between the applied magnetic field in the SP problem and the chemical potential in the Peierls problem. Hence, changing the magnetic field corresponds to the reduction of the number of fermions, that is the band filling of the Peierls system.

An applied magnetic field will lower the gain in magnetic energy upon dimerization and reduce the critical temperature. Due to Umklapp processes the wavevector describing the dimerization will remain fixed, up to a critical field  $B_c$ . Above this value an intermediate phase is predicted at sufficiently low temperatures, separating the dimerized and uniform phases. Several proposals for the nature of the intermediate state have been made. Recent theories conclude that it is incommensurate with the underlying lattice and will be in the form of a soliton lattice, i.e. the envelope of the ion displacements has a soliton lattice character. The associated wave vector will change continuously as a function of field. Literature on the theory of the SP transition is already quite vast. We mention two earlier review articles by Bray et al. [1] and by Buzdin et al. [2] as extensive introductions. The concept of a soliton lattice is discussed by several authors, either with emphasis on the Peierls [3–8] or the spin-Peierls [9–14] problem.

Experimental samples are thus far very few, the best known compounds in which the SP transition is well established being TTF–AuBDT, TTF–CuBDT [15, 16] and MEM–

(TCNQ)<sub>2</sub> [17], with critical temperatures  $T_{sp}$  of 2 K, 11 K and 18 K, respectively. The earliest reported high-field experiments were on the last two compounds [18–21]. Only a small part of the predicted intermediate phase could be covered and definite conclusions about its existence and character could not be drawn [22].

Similar measurements on the gold compound appeared later in the literature [23]. Here the experimental situation is much more favourable to probe the nature of the intermediate phase. The low zero-field critical temperature of 2 K implies a critical field of only 2 T, hence large values of  $B/B_c$  are within experimental reach.

In this article magnetization, differential susceptibility and specific heat data on TTF–AuBDT are presented. Temperature-, field- and frequency ranges are extended in comparison with previous studies. The data support the soliton lattice picture of the intermediate state and are compared with theoretical calculations by Fujita and Machida [14] which prove to be in satisfactory agreement with experiment. Also unusually long relaxation times, found in the intermediate phase and reflected in the difference between static and differential susceptibility, find a natural explanation within the soliton lattice concept.

We note that in an earlier publication by Hijmans et al. [24] convincing evidence for the existence of a soliton lattice state in TTF–AuBDT was obtained by comparing NMR data with the theory of Nakano and Fukayama [10, 11]. Brief reports on the results presented here have also appeared elsewhere [25, 26].

## 2. Experimental details

Magnetization data were obtained in a <sup>3</sup>He refrigerator. The sample could be moved between two oppositely wound coils placed in the homogenous part of the magnet. Integration of the output voltage yields the magnetization. A different coil system was used to measure the differential susceptibility as a function of field. Here rigidity of the construction is of prime

importance in keeping the signal-to-noise ratio at an acceptable level when the field increases, especially when measurements at frequencies lower than 100 Hz are made. This contrasts with a magnetization experiment where the signal is increasing with the applied field, so that data taking becomes the easier, the larger is the field. Changes in the sample susceptibility were measured by means of the mutual induction technique.

To measure the specific heat the heat-pulse technique was used [27]. The calorimeter was cooled in a <sup>3</sup>He refrigerator. Experimental problems arose from the heat contact inside the sampleholder. Since we did not want to mix the sample with grease, which is the normal procedure below 1 K to ensure a good heat contact, the sampleholder was filled with <sup>3</sup>He gas. However the very fine powder adsorbed such large amounts of gas that to ensure sufficient thermal contact down to 0.5 K we had to introduce 0.5 atm of gas (at room temperature). The earlier mentioned relaxation effects in the specific heat below 2 K are therefore likely due to a lack of heat contact and not intrinsic to the sample [28].

With such large amounts of gas its contribution to the heat capacity is certainly not negligible. Indeed, we observed contributions of the same form as the specific heat curves for <sup>3</sup>He adsorbed on a substrate, as published in the literature [29]. The heating-off of successive layers of <sup>3</sup>He covering the sample is thus responsible for a large background below 1 K, prohibiting reliable estimates of the sample specific heat in that temperature range.

All the experiments were performed on a powdered sample of 200 mg deuterated TTF–AuBDT, prepared by L.V. Interrante (General Electric, Schenectady). The crystallographic structure, shown in fig. 1 is triclinic. The linear stacks are mixed, i.e. they consist of alternating TTF<sup>+</sup> and AuBDT<sup>−</sup> molecules. The TTF<sup>+</sup> molecule possesses a spin  $S = \frac{1}{2}$  and a  $1 \mu_B$  magnetic moment. The  $\vec{c}_p$  direction, along which a close packing of TTF<sup>+</sup> molecules occurs, is the chain direction. The  $\vec{c}_p$  axis becomes considerably shorter at the first-order crystallographic transition at 200 K [30].

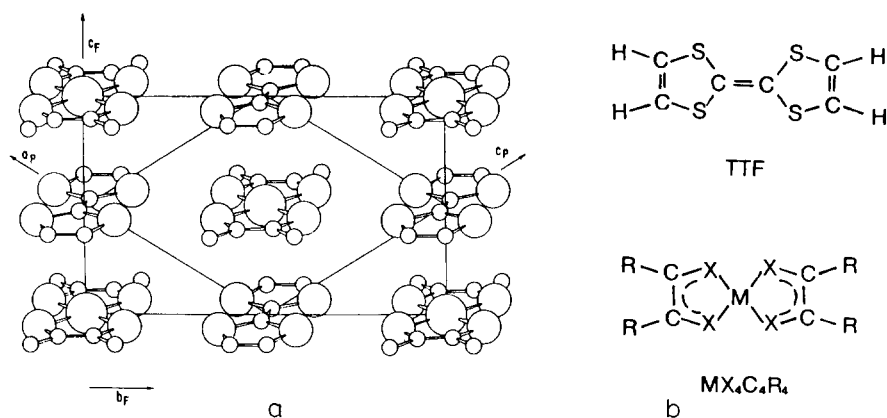


Fig. 1. Molecular structure for tetrathiafulvalene (TTF) and the metal bisdithiolene complex (M-BDT) with  $M=\text{Au}$ ,  $X=\text{S}$  and  $R=\text{CF}_3$  (a). Room temperature structure of TTF-AuBDT(b);  $a_f, b_f, c_f$  denote the primitive axes of the face centered unit cell and  $a_p, b_p, c_p$  those of the triclinic cell.

Unfortunately the magnetic measurements were further affected by contributions to the signal of paramagnetic origin, emanating probably from spins at finite chain ends. This “back-

ground” had appeared in the course of time, in which the same sample had been used in numerous experiments. We attribute it to the repeated crossing of the above mentioned transition at 200 K which is accompanied by drastic structural changes. Since no other sample could be made available, we had to accept this inconvenience. Fortunately in the temperature and field region of interest, i.e. below 2 K and above 2 T, this small paramagnetic background is rapidly saturated, whereafter it no longer contributes to the field variation of the signal. In fig. 2 we show raw data of an isothermal magnetization curve measured at 0.62 K, where the saturation effect in the low-field region can be clearly seen. After correcting for this background the obtained magnetic data were found to agree with the earlier published results [23], in so far as they overlap.

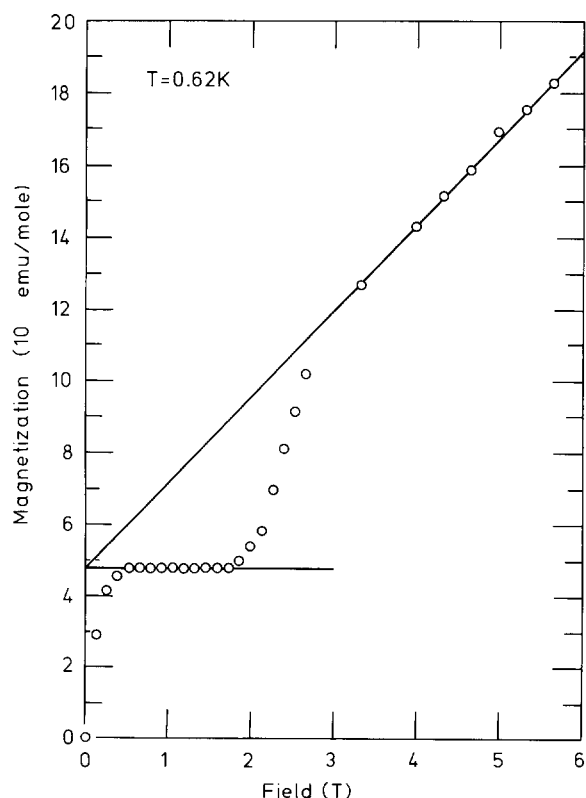


Fig. 2. Raw data of the isothermal magnetization curve at  $T=0.62$  K.

### 3. Theory

The starting point for a theoretical description of the SP problem is the Hamiltonian for the  $S = \frac{1}{2}$  Heisenberg antiferromagnetic (AF) chain together with the phonon term.

$$\mathcal{H} = \sum_{i=1}^N J_{i,i+1} (\mathbf{S}_i \cdot \mathbf{S}_{i+1} - \frac{1}{4}) - g_e \mu_B B_{\text{ex}} \sum_i S_i^z + \sum_q \omega_q b_q^\dagger b_q, \quad (1)$$

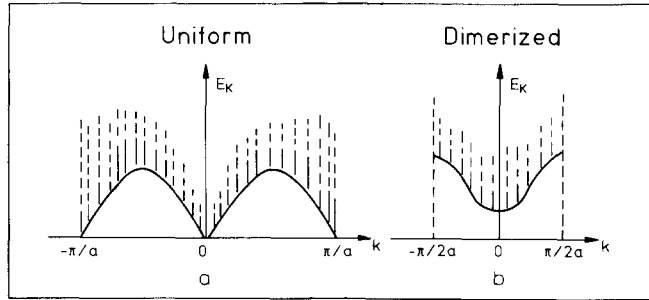


Fig. 3. Schematic excitation spectra for the uniform (a) and alternating (b) Heisenberg AF chain.

where  $\mathbf{S}_i$  is the spin operator at site  $i$ ,  $J_{i,i+1}$  the antiferromagnetic exchange integral,  $B_{ex}$  the magnetic field and  $b_q^\dagger(b_q)$  the phonon creation (destruction) operator with energy  $\omega_q$ . In order to obtain a non-zero transition temperature a 3-dimensional phonon field has to be considered. The spin value is taken as  $S = \frac{1}{2}$  as in the experimental SP compounds. The first term in Hamiltonian (1) has been extensively studied for both uniform and alternating exchange. The excitation spectra for the uniform and alternating Heisenberg AF chain are shown in fig. 3a and 3b, respectively. The essential feature is the lifting of the degeneracy between the singlet ground state and the band of triplet excitations upon dimerization of the chain.

To obtain a spin-phonon coupling the exchange integral is expanded to first order in terms of the displacements of the magnetic ions.

$$J_{i,i+1} = J + (\mathbf{u}_i - \mathbf{u}_{i+1}) \cdot \nabla_i J_{i,i+1}. \quad (2)$$

The spin operators are converted to pseudo-fermion operators via the Jordan-Wigner transformation

$$\begin{aligned} \psi_i^\pm &= 2^{l-1} S_1^z \cdots S_{i-1}^z S_i^\pm, \\ S^\pm &= S^x \pm iS^y, \\ S^z &= \frac{1}{2} - \psi_i^\dagger \psi_i. \end{aligned} \quad (3)$$

The XY part of the product  $\mathbf{S}_i \cdot \mathbf{S}_{i+1}$  gives rise to a two-fermion term, whereas the z part yields a four-fermion interaction term that is difficult to handle:

$$\mathcal{H}_{int} = \frac{1}{N} \sum_{k,k',q} v(q) c_{k+q}^\dagger c_{k'-q}^\dagger c_k c_k, \quad (4)$$

where  $v(q) = J \cos qa$ , with  $a$  the lattice constant and the  $c_k$ 's the Fourier-transformed pseudo-fermion operators  $\psi_i$ :  $c_k = (1/N^{1/2}) \sum_i e^{ikl} \psi_i$ .

A common approach to Hamiltonian (4) is to use the Hartree factorization

$$\langle c_k^\dagger c_q \rangle = \eta_k \delta_{kq}, \quad (5)$$

where

$$\eta_k = [\exp(\beta \epsilon_k) + 1]^{-1}, \quad \beta = 1/k_B T.$$

When we write the displacements  $\mathbf{u}_i$  in terms of phonon creation (destruction) operators, the following Pytte type Hamiltonian [31] is obtained:

$$\begin{aligned} \mathcal{H} &= \sum_k \epsilon_k c_k^\dagger c_k + \sum_{k,g} g c_k^\dagger c_k (b_q + b_{-q}^\dagger) \\ &+ \sum_q \omega_q b_q^\dagger b_q, \end{aligned} \quad (6)$$

where  $\epsilon_k = pJ \cos ka - g_c \mu_B B_{ex}$ , with the "renormalization" constant  $p = 1 - (2/N) \sum_k \eta_k \cos ka = 1.64$  at low temperatures  $k_B T \ll J$ . The fermion-phonon coupling parameter  $g(k, q) = g$ . Fig. 4 shows the excitation spectrum for the dimerized chain in the pseudo-fermion representation for different values of the magnetic field [32].

The above Hamiltonian can be regarded as a renormalized XY Hamiltonian and is equivalent to the regular Peierls Hamiltonian. For the SP system the number of pseudo-fermions is not conserved, as it is for the Peierls system.

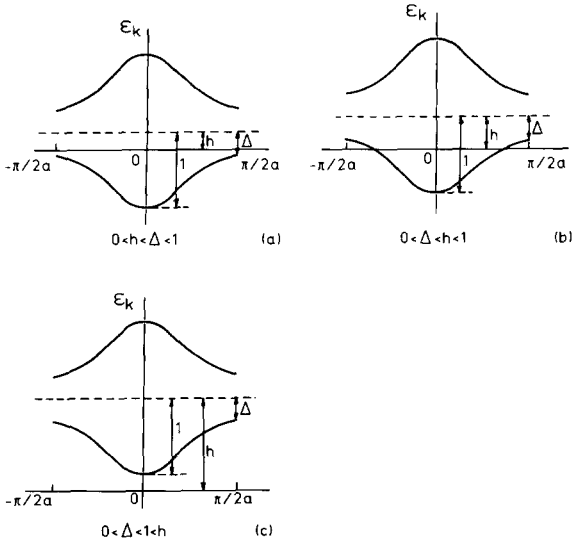


Fig. 4. Excitation spectra for the pseudo-fermion representation of the dimerized chain for different values of the scaled magnetic field  $h = \mu_B B / |J|$ , after [32]. Here  $2\Delta$  is the magnetic gap. In the figure all energies are normalized to  $|J|$ .

Cross and Fisher (CF) [33, 34] made use of a boson algebra to avoid the Hartree approximation of eq. (4). Their solution of the SP problem is based on the close relation between the pseudo-fermion representation of the Heisenberg chain and the exactly soluble Luttinger-Tomonaga model.

Nakano and Fukuyama [10, 11] have extended the CF approach with the inclusion of non-linear excitations. A sine-Gordon type equation is found after the transformation of boson variables to phase variables, which equation is solved for the soliton creation energy. However, the thermodynamic behaviour at non-zero temperatures is difficult to calculate on basis of these models.

On the other hand, the continuum version of Hamiltonian (6) does not suffer from the just mentioned restriction, so that the properties at non-zero temperatures can also be calculated. To arrive at the continuum version one writes the fermion eigenfunction as  $\psi(x) = u(x) \exp(i\pi x/2a) - v(x) \exp(-i\pi x/2a)$ , where  $u(x)$  and  $v(x)$  are slowly varying functions. The ion displacements are decomposed in a similar way and the fermion dispersion relation, i.e. the cosine bands, are linearized about  $k = \pm\pi/2a$ . Using a

spinor notation  $\psi(x) = \begin{pmatrix} u(x) \\ v(x) \end{pmatrix}$  for the fermion field, the continuum Hamiltonian reads

$$\mathcal{H} = \int_0^L dx \psi^\dagger(x) \left[ -i\hbar v_F \sigma_3 \frac{d}{dx} - \sigma_1 \Delta(x) - g_e \mu_B B_{ex} \right] \psi(x) + \frac{\omega}{4g^2 a} \int_0^L \Delta^2(x) dx, \quad (7)$$

where  $\sigma_i$  are the Pauli spin matrices,  $v_F = pJa/\hbar$  is the Fermi velocity and  $\Delta(x)$  the order parameter which describes the envelope of the spatial dependence of the spin lattice dimerization.

The self-consistent equation for  $\Delta(x)$  is given by

$$\Delta(x) = -\frac{2g^2 a}{\omega} \langle \psi^\dagger(x) \sigma_1 \psi(x) \rangle. \quad (8)$$

Several authors have solved the Hamiltonian (7) exactly [3, 4] at  $T=0$ . It was shown only recently that the solution

$$\Delta(x) = \Delta_2 \text{sn}(\Delta_1 x, k_1) \quad (9)$$

is also valid at finite temperatures [5]. Here  $\text{sn}(z, k)$  is a Jacobi elliptic function with modulus  $k$  and  $k_1 = \Delta_2/\Delta_1$  [35].

The commensurate (dimerized) state is described by  $k_1 = 1$ , while for  $0 < k_1 < 1$  the incommensurate state is found. This state is characterized by a snoidal modulation of the spin lattice dimerization. The thermodynamic behaviour may be numerically calculated and details of this procedure can be found in the paper by Fujita and Machida [14]. In the low-field regime ( $B \geq B_c$ ) the modulus of the sn function does not differ too much from one and we can visualize the soliton lattice as composed of regions of the (almost) dimerized phase, separated by walls over which the lattice is incommensurate. These walls each carry a net spin one-half. The solitons form a midband state as is shown in fig. 5. Thus the IC-phase has a double (energy) gap structure in contrast with the C-phase that has a single (energy) gap obeying the standard BCS relations.

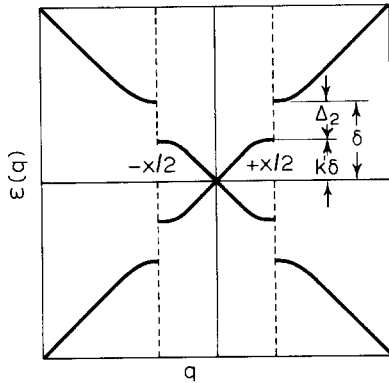


Fig. 5. Schematic excitation spectrum for the IC-phase in the pseudo-fermion representation. Here  $q = k - k_F$ . Details are to be found in ref. [5].

The density of the walls is determined by the competition between the dimerization energy and the Zeeman energy associated with the net spins contained in the walls. It turns out that the magnetization in the incommensurate state re-

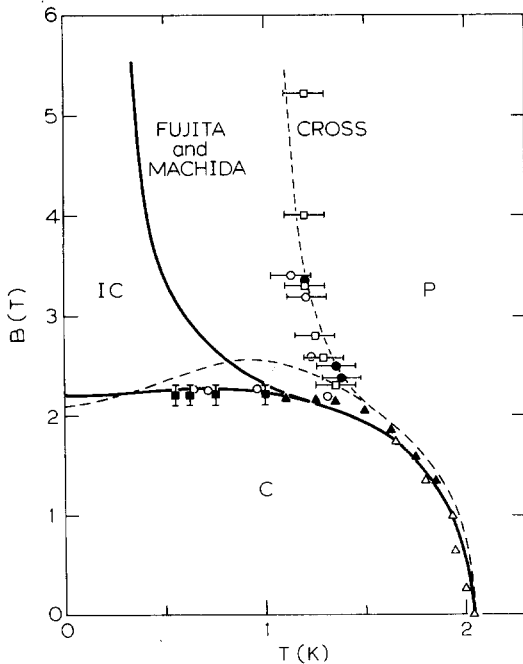


Fig. 6. Phase diagram of TTF-AuBDT. The theoretical predictions by Fujita and Machida (solid curve) and Cross (dashed curve) are scaled to the zero-field transition temperature. Experimental data are from the present work (squares), from ref. [24] (triangles) and ref. [23] (circles). A similar phase diagram is also obtained in other approaches, see e.g. [32].

sulting from the walls is almost the same as in the paramagnetic phase, except for values of  $B$  close to  $B_c$ . It is, in fact, this phenomenon which has hampered the determination from the uniform to the incommensurate phase by means of magnetization experiments, as will be further discussed below.

In fig. 6 we show the experimental phase diagram together with the theoretical predictions by Fujita and Machida (solid curve) and Cross [34] (dashed curve). The different phases in the diagram are the uniform or 1-d paramagnetic phase (P), the dimerized or commensurate phase (C) and the intermediate or incommensurate phase (IC). In addition to data points obtained in the present study the results from Northby et al. [23] and Hijmans et al. [24] have been included.

#### 4. Experimental results and discussion

In this section we present magnetization (figs. 7a, 8), static and differential susceptibility (figs. 7b, 9, 10) and specific heat data (fig. 11) on TTF-AuBDT. Magnetization and static susceptibility are compared with calculations by Fujita and Machida [14].

As regards the high-field IC-P phase boundary, the best prediction clearly is that of Cross. The IC-P phase boundary as calculated by Fujita and Machida falls off more rapidly as the temperature is lowered, presumably due to the Hartree approximation on eq. (4). However, as noted in the above, thermodynamic calculations at non-zero temperature can so far only be obtained within the framework of an effective XY Hamiltonian, so that we shall use the Fujita and Machida results in what follows.

To facilitate a comparison between this theory and the experiment also for the high-field regime, we have applied the following scaling procedure to the temperature at constant field:

$$t/t_c(b) = T/T_c(B),$$

where capitals denote experimental values of temperature and field and lower case refer to theory. A similar scaling procedure for data

taken at constant temperature was not necessary because of the flatness of the C-IC phase boundary. Magnetization and susceptibility data are further scaled by requiring that the paramagnetic value of the susceptibility is the same in theory and experiment.

Fig. 7a shows a set of isothermal magnetization curves. The magnetization in the commensurate phase vanishes quickly as the temperature is lowered. Only just below the critical field ( $\approx 2.25$  T) excitation across the dimerization gap becomes possible and an increase in the magnetization appears. At the critical field the transition

to the soliton lattice occurs and the magnetization rises quickly. At about 3.5 T a value already close to the paramagnetic one is reached and the magnetization becomes linear in the field. In both experiment and theory the field and temperature dependence of the magnetization in the incommensurate phase is quite similar to that in the paramagnetic phase. Thus the number of solitons each carrying a spin  $S = \frac{1}{2}$ , is just such that the magnetization has almost the same values as if the transition to the IC phase would not have occurred at all.

By numerical differentiation of these curves we

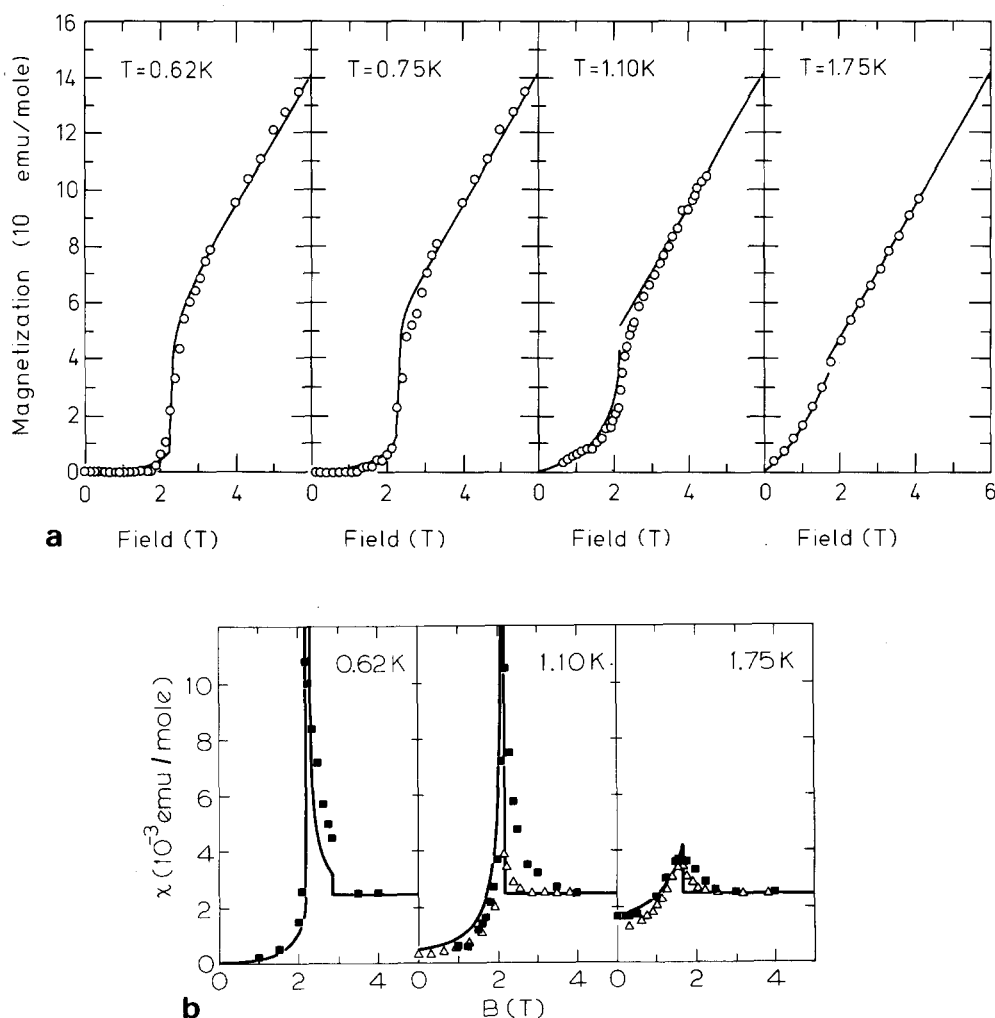


Fig. 7. (a) Isothermal magnetization data. The solid curves are fits to the theory of Fujita and Machida [14]. (b) Isothermal static (squares) and differential (triangles) susceptibility data. The solid curves are theoretical fits to the static susceptibility [14].



obtained the experimental static  $\chi$  at constant temperatures. In fig. 7b the experimental and theoretical static  $\chi$  are shown as well as the differential  $\chi$  at 1880 Hz for the two highest temperatures. Experimentally the 1.10 K curve has all the features of the C-IC transition, theoretically however only over a small field interval the IC phase will be found at this temperature (cf. fig. 6) as seen in fig. 7b where the theoretical static  $\chi$  drops almost instantly to the paramagnetic value. Clearly for the 0.62 K curve the scaling (4) of the theoretical to the experimental phase diagram works better, and a seemingly nicer fit results.

The general form of the curves is indicative of a second-order C-IC transition. The NMR experiments [24], however, showed a first-order character with hysteresis appearing at  $B_c$  for temperatures below 1 K. We did not observe hysteresis in the magnetization data, but it may have gone unnoticed since it was very small, (0.04 T) in the NMR experiment. The same smooth magnetization curves were found in the two other spin-Peierls compounds [19-22] but in those materials the hysteresis effects were much more pronounced. It has been argued [36] that hysteresis can occur because of pinning of the incommensurate wave vector due to lattice defects, impurities etc. Because of their higher transition temperatures, the amplitude of the dimerization is considerably larger in TTF-CuBDT and MEM-TCNQ<sub>2</sub> than in TTF-AuBDT. Pinning effects may then occur much more easily, leading to the observed larger hysteresis. The situation is somewhat analogous to domain-wall pinning in ferromagnets. Fujita and Machida as well as Nakano and Fukuyama predict the transition to be of second order, whereas Cross speculates it to be of first order assuming that the intermediate state can be described with a single Fourier component. However in real crystals, due to imperfections, the order can change from second to first, as is stressed in ref. [36].

In fig. 8 isofield runs of the magnetization are shown. As noted earlier, the magnetization and static susceptibility, are relatively insensitive to the IC-P transition in fields exceeding 3.5 T.

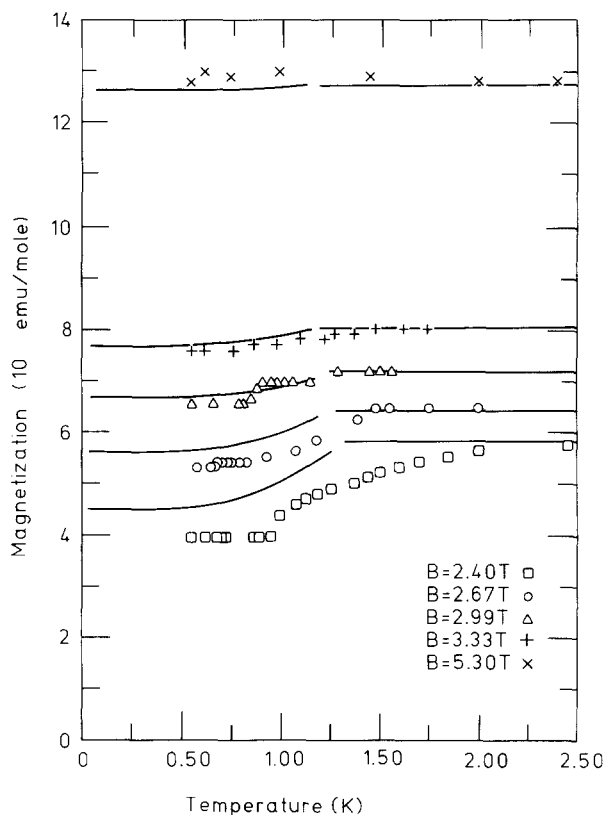


Fig. 8. Isofield magnetization data. The solid curves are theoretical fits [14].

Only for fields just above the critical field an appreciable lowering of the magnetization in the IC-phase with respect to the P-phase is found.

Static susceptibility, theory and experiment, as well as the differential susceptibility are shown in fig. 9. The experimental static  $\chi$  was obtained by numerical differentiation of the magnetization data. The differential susceptibility covers the frequency range from 18 to 1880 Hz. A sharp rise in the static  $\chi$  is found only in the direct neighbourhood of the critical field. The experimental differential susceptibility, for  $B > B_c$ , goes through a broad maximum and then rapidly falls off to zero for all measured frequencies. This pronounced difference between the static and differential susceptibility indicates that relaxation effects are present even at very low frequencies. Since  $\chi(\nu)$  is the same for all  $\nu > 18$  Hz, we have to conclude that the associated

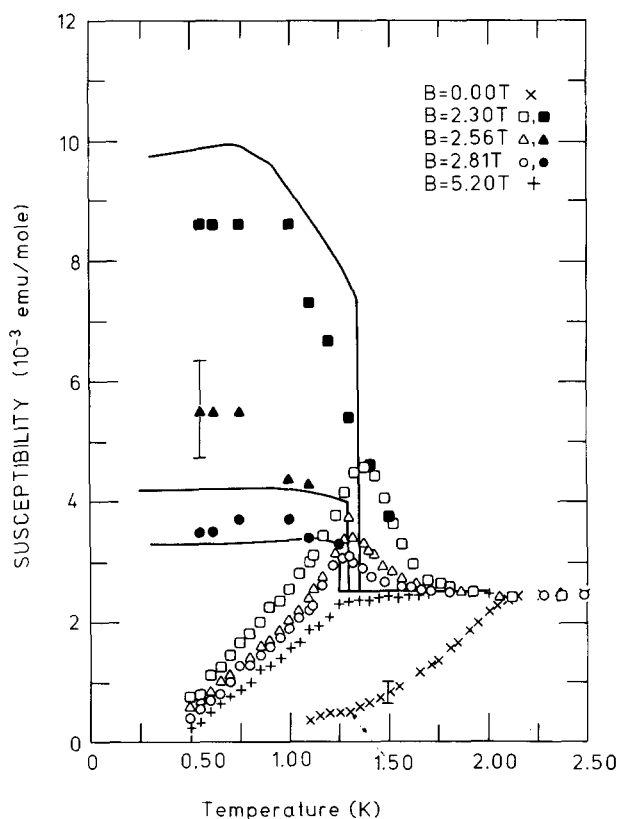


Fig. 9. Static (black symbols) and differential (other symbols) susceptibility. The solid curves are theoretical fits to the static susceptibility [14].

relaxation time  $\tau$  must correspond to a frequency lower than several Hz. Also, for  $\nu > 18$  Hz the measured  $\chi(\nu)$  apparently is the adiabatic susceptibility, as far as this relaxation mechanism is concerned. An upper limit to the relaxation time is obtained from the magnetization measurements, since if it would have been larger than 30 s it would have certainly interfered with the measurements. In fact we performed a measurement where the external field was raised very quickly, such that changing the field and registering a data point was reduced to a time interval of a few seconds. In these cases the variation in the magnetization was found to lag behind the field variation. Thus we can estimate the relaxation time to be of the order of a few seconds indeed.

Such long relaxation times are in fact quite compatible with the soliton lattice picture (see

also Buzdin, ref. [3]). The value of the magnetization determines the density of domain walls. Hence, to change the magnetization by means of a field variation, a change in the wall density is required. It is probable that the walls are coupled in adjacent chains to form planar domain walls, also the discommensurations associated with the wall width require the tilting of large organic molecules. Such a strong coupling between the electronic system and the lattice may lead to long relaxation times at the considered temperature.

In our opinion, therefore, the strong difference between the differential and the isothermal susceptibility in the incommensurate phase provides another important experimental indication of the existence of the magnetic soliton lattice, in addition to the earlier reported NMR spin-lattice and linewidth studies. We emphasize that at the transition from the uniform to the low-field dimerized phase such frequency effects are not

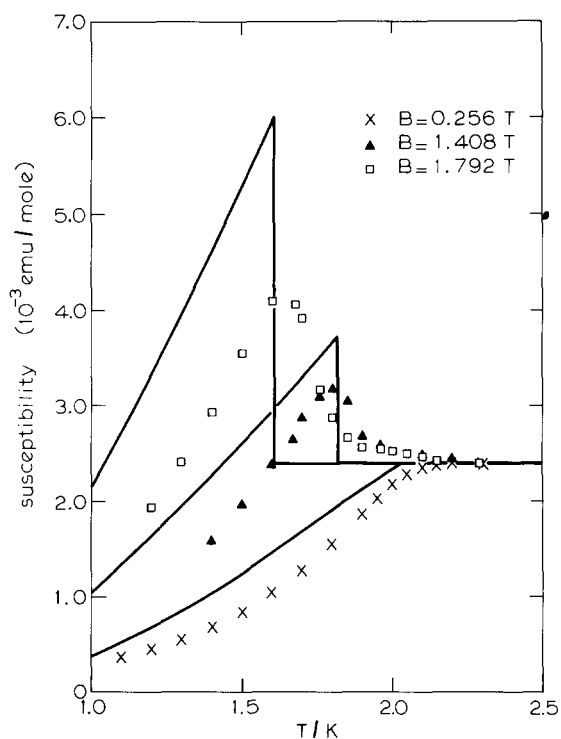


Fig. 10. Susceptibility in the C-phase. Here static and differential (1.88 kHz) susceptibility coincide. The solid curves are theoretical fits [14].

observed. Fig. 10 shows the susceptibility, in the C-phase as a function of temperature and field.

The differences between the theoretical and experimental values are due to the effects of short range order. In the theory, being mean-field, the susceptibility drops instantly to the paramagnetic value at the transition temperature. Experimentally, however, broad maxima are found with short-range order extending to about 0.5 K above  $T_c$ .

The above mentioned coupling between solitons has another important implication. As the creation energy of a soliton is smaller than that of a triplet excitation one would expect them to be visible in the C-phase as well. However the theoretical creation energy for a soliton, is for a single chain in a 3-d phonon lattice. For the creation of a single soliton in the commensurate phase we must add (elastic) energy due to the misfit with other chains. Alternatively we must

consider the simultaneous excitation of  $N$  solitons in  $N$  adjacent chains, which raises the required energy for the excitation  $N$  times. Also experimentally no evidence is found for the existence of thermally excited solitons in the C-phase. The isothermal magnetization curves and the static  $\chi$  below  $B_c$  can be explained with excitation across the dimerization gap only. At  $B_c$  the soliton lattice appears and  $M$  and  $\chi$  rise quickly, where after they drop gradually to the paramagnetic value. This results in the observed asymmetric form of the isothermal  $M$  and  $\chi$  curves, as seen in fig. 7b.

We note that the behaviour of the differential susceptibility for fields  $B > B_c$  is also incompatible with an antiferromagnetically ordered spin-flop phase, excluding this possibility to explain the experimental phase diagram.

As remarked in the above, the specific heat measurements were seriously affected by an un-

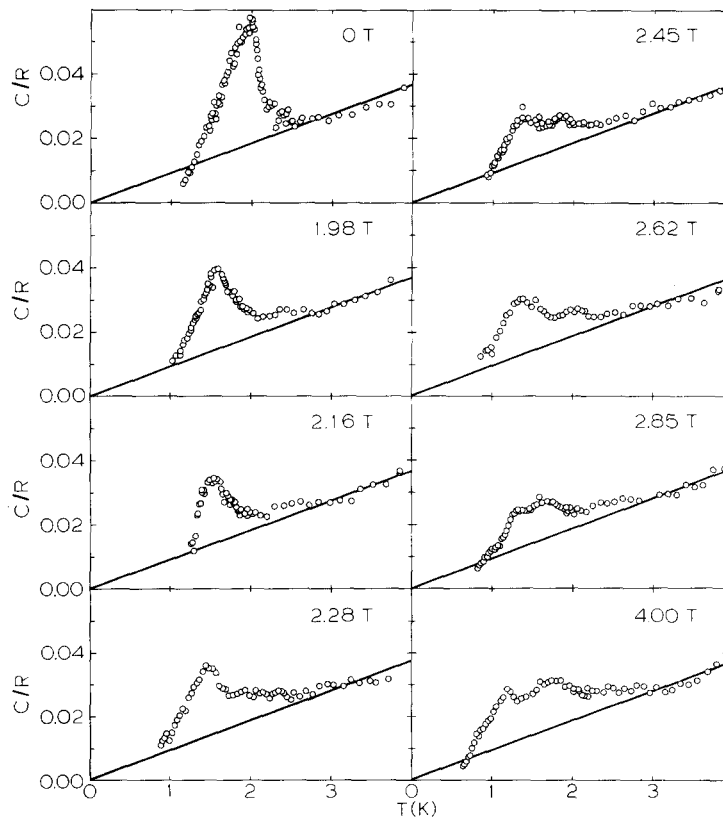


Fig. 11. Specific heat data for different field values, after subtraction of the lattice contribution. The straight line is the theoretical prediction for the uniform chain when  $T \ll |J|/k$ . In high fields the inaccuracy in the lower  $C/R$  values amounts to 0.005R.

certainty in the contribution of the  $^3\text{He}$  contact gas. Nevertheless the results obtained after correction are given in fig. 11, where the straight line is the prediction for the uniform AF  $S = \frac{1}{2}$  Heisenberg chain.

For field values  $B < B_c$  well defined maxima are found at the IC-P phase boundary. The location of these maxima agrees with the susceptibility results. Short-range order effects are seen in the specific heat up to 2.5 K. These effects remain present also for higher fields.

For field values  $B > B_c$  only broad maxima are found, so that the IC-P transition temperature cannot be located on basis of these measurements. In this respect we disagree with the interpretation of Bonner et al. [37] of our data. The error bars in the specific heat data are such that no conclusion regarding the presence or absence of peaks at the IC-P phase boundary can be drawn.

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