Electron-Spin-Resonance Study of the High-Field Phase of the Spin-Peierls System Tetrathiafulvalene-Au-*bis*-dithiolene

T. W. Hijmans and W. P. Beyermann

Department of Physics and Solid State Science Center, University of California, Los Angeles, California 90024

(Received 2 March 1987)

We present ESR data obtained in the high-field phase of the spin-Peierls system tetrathiafulvalene-$AuS_4C_4(CF_3)_4$ (TTF-AuBDT). The measurements were performed on single crystals, and are the first ESR measurements performed in the high-field phase of this system. Our results demonstrate for the first time a marked effect of the magnetic structure of the high-field phase of a spin-Peierls system on the ESR spectrum. The data are analyzed in terms of the available theories for spin-Peierls systems. The results are in good agreement with the predictions of the theory.

PACS numbers: 75.30.Kz, 75.10.Jm, 75.80.+q, 76.30.Pk

Spin-Peierls (henceforth SP) systems are quasi one-dimensional (1D) magnetic systems with antiferromagnetically coupled spins of $S=\frac{1}{2}$, that undergo a magnetoelastic phase transition[1] which is analogous to the Peierls metal-insulator transition occurring in 1D metals. Like regular (electronic) Peierls systems, SP systems spontaneously dimerize, thereby forming a state with a lowered magnetic energy. However, there is one important difference: Unlike their electronic counterpart, SP systems have an additional parameter that determines their properties, namely, the applied magnetic field. The effect of applying a field is analogous to changing the chemical potential and hence, indirectly, the band filling of the electronic system. It has been argued (see, e.g., Cross,[2] Bulaevskii, Buzdin, and Khomskii,[3] and Nakano and Fukuyama[4]) that this may lead to an incommensurate high-field phase in which the wave vector describing the lattice distortion differs slightly from the value $k=\pi/a$ of the dimerized phase (a is the atomic separation along the chain direction in the undistorted phase). To date, there are only three compounds which have been characterized beyond doubt to display SP behavior: tetrathiafulvalene-Au-*bis*-dithiolene (TTF-AuBDT), tetrathiafulvalene-Cu-*bis*-dithiolene (TTF-CuBDT), and N-methyl- N-ethyl- morpholine- di(tetracyanoquinodimethane) [MEM-$(TCNQ)_2$]. All three compounds show a high-field phase that is different from the dimerized phase. Moreover, the fields at which the transitions to this phase occur scale with the transition temperatures of the systems and the phase diagrams show remarkable agreement with the theoretical prediction of Cross[2] (see de Jongh and co-workers[5-9] for experimental data concerning the determination of the phase diagram of TTF-AuBDT). Although the existence of a field induced phase transition is thus firmly established in the three SP systems, there is only a limited amount of direct experimental evidence that the high-field phase is indeed the predicted incommensurate phase. Recent NMR investigations of TTF-AuBDT,[8,9] the first experiments in which a microscopic probe was used to investigate the high-field phase of an SP system, yielded results that are in good agreement with the theoretical predictions. The purpose of the present investigation was to examine the properties of the high-field phase of TTF-AuBDT by looking at the resonance behavior of the magnetic moments themselves. TTF-AuBDT was chosen, rather than one of the other SP systems, because of the relatively low critical field ($B_c=2.25$ T).[8] In contrast to a recent study of the high-field phase of MEM-$(TCNQ)_2$ with far-infrared ESR,[10] we find pronounced shifts of the resonance line in the high-field phase. We shall comment on the possible cause of this discrepancy at the end of the paper.

In order to analyze our experimental results, we shall mainly focus on the theory of Nakano and Fukuyama[4] (henceforth NF). This theory has been criticized in the literature for predicting a value for the transition temperature which is more than 2 times lower than is experimentally observed. This is partly due to a trivial calculational error of a factor of 2 in the expression for the critical field in that paper. The discrepancy with experiment is thus less serious than the critics maintain. The reason why we resort to the theory of NF is that their treatment makes explicit predictions for the microscopic spin-density distribution in the incommensurate state. The microscopic spin density determines the resonance properties. The theory of NF gives the following picture for the incommensurate state. Unlike the dimerized phase, the incommensurate phase has a nonzero magnetization, even at $T=0$. The Zeeman energy associated with this nonzero magnetization is the very reason for the stability of this phase in high magnetic fields. The modulation of the order parameter is not necessarily sinusoidal, but can be in the form of a "soliton lattice" consisting of regions that are almost perfectly dimerized, separated by kinks.[11] Associated with each of these kinks is a net spin of $\frac{1}{2}$. The latter property, which follows from topological considerations, is sometimes called the "counting rule for solitons." This spin is distributed around the center of the kink; we shall denote the spin density by S. Even in the case of a sinusoidal modulation, the topological constraint relates the period of the modulation to the

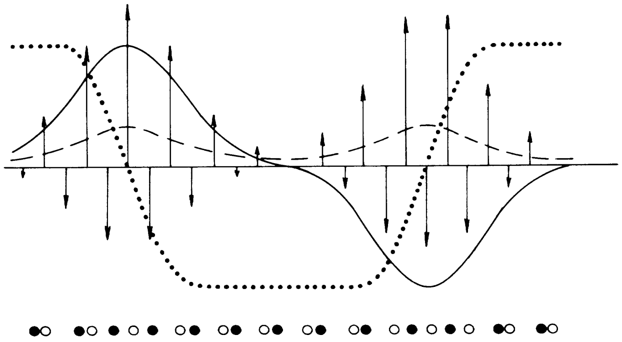

FIG. 1. Theoretical structure of a section of an SP chain containing two kinks. The dotted line represents the lattice distortion. The local magnetization on each site (denoted by arrows) consists of a staggered part S_s (full line) and a nonstaggered part S (dashed line). The open and filled dots at the bottom of the figure represent the positions of the TTF molecules on odd and even sites.

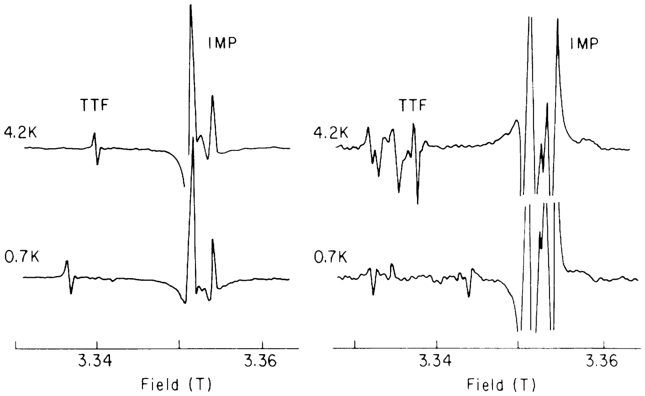

FIG. 2. Spectra of two different samples at $T=4.2$ K and $T=0.7$ K. TTF and IMP are the TTF and the impurity lines, respectively.

magnetization M. This period (in units of the lattice constant) is $2M/M_{\rm sat}$ ($M_{\rm sat}$ is the saturation magnetization). Alternatively, the magnetization is given by χB, where χ is the susceptibility of the system in the paramagnetic (undistorted) phase. When applied to TTF-AuBDT at the field used in the present experiment ($B=3.35$ T), this magnetization is found to be about 1.3% of the saturation value. This low value is due to the large exchange constant of TTF-AuBDT ($J/k=68$ K).[12]

It has been argued[8] that in addition to the net spin of $\frac{1}{2}$ associated with each half period of the modulation, there is a modulated staggered magnetization. The presence of this (modulated) antiferromagneticlike spin density (henceforth denoted by S_s) is a direct consequence of the theory of NF. It is important to note that the maximum amplitude of S_s can be significantly larger than the magnitude of S. Applying the theory to TTF-AuBDT, one estimates[8] the maximum amplitude of S_s at $T=0$ to be about 0.1. In Fig. 1 we schematically depict the variation along the chain of the quantities of interest: the lattice distortion, S, and S_s. We should remark that the only nonzero component of S and S_s is the one along the direction of the magnetic field, quite unlike antiferromagnets where the staggered magnetization is nonzero only along a direction perpendicular to the magnetic field (spin-flop phase). We now turn to the experiments.

The experiments were performed at a frequency of 94 GHz. The sample was placed near the end of a wave guide inserted in a ^{3}He cryostat. The field of 3.35 T was provided by a superconducting solenoid. The resonance was detected by sweeping and modulating the field with two smaller coils. The resonance position was calibrated with reference to a quinoline-di(tetracyanoquinodimethane) [Qn-(TCNQ)$_2$] marker sample. Several runs were made, during each of which a single crystal of TTF-AuBDT was mounted at a different, but random, orientation with respect to the magnetic field. The morphology of the crystals did not enable us to determine the orientation of crystal axes.

In Fig. 2 we show the spectra of two different samples (to be referred to as samples I and II) at $T=4.2$ K and $T=0.7$ K. The spectra show two distinct features, a line with a large intensity and a temperature-independent resonance field, and a smaller line, which shows temperature dependence. The large line is paramagnetic, and is due to impurities (presumably air) inside the wave guide. This impurity signal has a rather irregular shape, probably as a result of the fact that the impurities were distributed along a large section of the wave guide. Because of this signal it was difficult to distinguish the marker signal in some samples and as a result there is an uncertainty of about 30 G in the absolute determination of the resonance field of the sample. The relative uncertainty in the line position, that is, the shift from the value at 4.2 K, is much smaller (about 8 G). The smaller line is the TTF-AuBDT signal. In spectrum II this line is broadened as a result of twinning due to fragmentation of the crystal. Most spectra look similar to spectrum I. In Fig. 3 the resonance field of the TTF-AuBDT line is plotted, for four different crystal orientations. Lines a and b are the positions of the low-field and the high-field side of the twinned spectrum II. Line c is the resonance of sample I, and line d was obtained in a third sample (III). Lines a and d have the largest and the smallest g values, respectively, at $T=4.2$ K. These g values agree within experimental accuracy with the extremal g values reported for the resonance of the TTF$^+$ ion[12] in the analogous compound TTF-CuBDT. At temperatures below 1.5 K, the resonance fields shift. The magnitude and the direction of the shift depend on the crystal orientation. Spectra b and c show the largest shifts towards higher and lower field, respectively, of all samples mea-

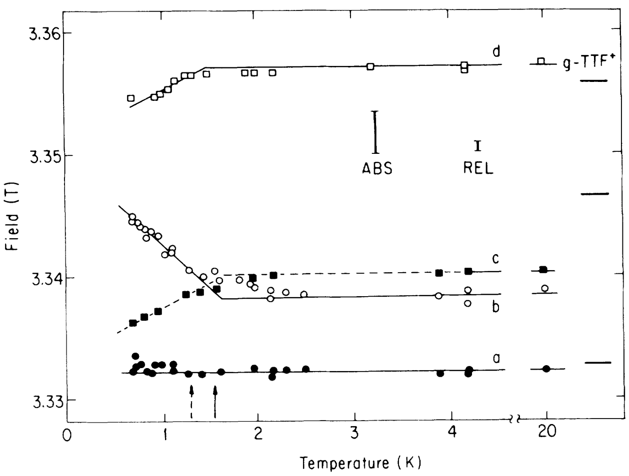

FIG. 3. The resonance field of the TTF line at four different crystal orientations. The solid and the dashed arrows correspond to the transition temperature according to different criteria (see text). The resonance fields of the TTF^+ ion in TTF-CuBDT (Ref. 11) corresponding to the principal axes of the g tensor are denoted at the right side of the figure. The error bars marked "abs" and "rel" refer to the absolute error in the resonance field and the error in the determination of the shift relative to the high-temperature value.

sured. Although we have investigated only six different samples, we assume that spectrum b corresponds to an orientation close to the one yielding a maximum shift, and we shall use this spectrum below in our analysis. We should finally remark that within experimental accuracy, the intensity of the TTF-AuBDT line remained constant over the entire temperature range, including the region below the transition temperature. This is quite contrary to what is observed at low fields where the intensity diminishes rapidly below the transition as a result of the nonmagnetic (singlet) ground state of the dimerized phase. We checked this behavior using an X-band spectrometer and indeed found the signal intensity to diminish below the limits of observability at low temperature. We do not further comment on these X-band measurements here as similar findings have been reported elsewhere.[12]

In this section we shall analyze the behavior of the resonance line in terms of the theory outlined above. First we note that the resonance field starts to deviate from the high-temperature value below $T=1.5$ K. This temperature corresponds to the point where a marked change in the NMR linewidth was found to set in[8] (denoted by the solid arrow in Fig. 3). The value of the transition temperature in this field (3.35 T) as determined from the peak in the specific heat[7] is slightly lower (dashed arrow in Fig. 3). In the light of the above-mentioned theory, it is plausible to assume that the resonance shift is due to the dipolar fields caused by the modulated staggered alignment of the moments in the incommensurate phase. To test this hypothesis we have to estimate the order of magnitude of the dipolar coupling. In order to do so we treat the TTF molecules as point dipoles and assume that the dominant contribution to the dipolar field is due to nearest neighbors along the chain direction. This assumption is of course rather crude but a complete evaluation of the dipolar field is virtually impossible in view of the complicated magnetic structure which is to be anticipated and the smearing out of the spin density over the rather large TTF molecules. Using the fact[13] that the distance between adjacent TTF molecules along the chain direction is 6.7 Å (we neglect the very small and as yet unmeasured variation of this distance due to the SP distortion), we find that the dipolar field at a TTF site is given by the equation

$$B_{\mathrm{dip}}^{z}=246(3\cos^2\theta-1)\langle S_z\rangle\ \mathrm{G}. \tag{1}$$

Here θ is the angle between the field (z) and the chain direction, and $\langle S_z\rangle$ is the expectation value of the spin on each of the nearest-neighbor molecules. We now make the assumption that the dominant contribution to the signal stems from spins in the region where S_s is maximal, and that the resonance frequency for field directions along the principal axes of the dipolar tensor is given by the equation

$$\omega_{\mathrm{res}}=g\mu_{\mathrm{B}}[B+B_{\mathrm{dip}}^{z}-(B_{\mathrm{dip}}^{x}+B_{\mathrm{dip}}^{y})/2]. \tag{2}$$

Here x and y refer to dipolar fields due to spin alignments perpendicular to the field. Using Eq. (2), converting frequency shifts into field shifts, and identifying the maximum observed shift (about 70 G; spectrum b) with $\theta=90°$ in Eq. (1), we obtain an estimate for $\langle S_z\rangle$ ($=S_{s\,\max}$) of 0.1, or about 20% of the saturation value. In view of the fact that we may expect the resonance shift to level off to a constant value at some temperature below 0.7 K, this is in remarkable agreement with the above-mentioned theoretical value of the maximum amplitude of S_s at $T=0$ for TTF-AuBDT. We should mention that the fact that the maximum observed positive resonance shift (line b) is twice as large as the maximum negative shift (line c) is consistent with Eqs. (1) and (2), if we assume a staggered polarization along the field direction. However, this may be somewhat fortuitous. Although we believe that Eq. (1) gives a reasonable estimate of the magnitude of the dipolar field, the principal axes of the dipolar tensor may in reality be quite different. The main conclusion, however, is unquestionable: The resonance shifts clearly indicate the presence of a strong local spin polarization *in spite* of the fact that the overall magnetization is very small; there must be compensated (staggered) moments (for an experimental demonstration that the magnetization in the high-field phase is the same as in the undistorted paramagnetic phase, see Ref. 5). It can be seen from Fig. 3 that the shifts increase roughly linearly below 1.5 K. We have no explanation for this linear temperature dependence; the theory of NF applies to $T=0$. We note, however, that the variation with temperature of S_s is apparently quite different from that of the order parameter in antiferromagnets. Above 1.5 K, there is a slight deviation from the high-temperature value, presumably as a result of short-range order. Similar short-range order effects were observed in the specific heat,[7] up to temperatures of 2.5 K.

Let us finally compare the results of this paper with data on two other compounds: MEM(TCNQ)$_2$ and N,N-dimethyl- morpholine- di(tetracyanoquinodimethane) [DMM(TCNQ)$_2$)]. The first compound was the subject of a recent ESR study.[10] Unlike TTF-AuBDT, the position of resonance line of MEM(TCNQ)$_2$ does not deviate from the paramagnetic value at low temperature. An important reason for this may be the fact that the magnetic field at which those experiments were performed ($B=25.5$ T) is almost an order of magnitude higher. Similar dipolar fields produce a much smaller relative field shift. If the effect is there, it is likely to be buried in the broadening caused by the inhomogeneity of the applied field. Furthermore, the effect will be obscured by the fact that in high fields the difference between the magnitude of the S_s and the overall magnetization χB is less dramatic. Finally, the fact that pulsed magnetic fields were used in the measurements of Ref. 10 might have influenced the results. DMM-(TCNQ)$_2$ is a compound that shows a phase transition at $T=1.6$ K.[14] The nature of this transition is not yet completely clarified. In an attempt to explain the peculiar nature of the ESR in the low-temperature phase, it was assumed that this system is an incommensurate SP system. It was suggested that in this compound the modulation could be linked to the known presence of an incommensurate anion structure. Although the assumption of the SP nature of this compound was somewhat *ad hoc*, we would like to point out that there are strong similarities between the data of Ref. 14 and the present results—-notably, the apparent linear increase of the resonance shifts below T_c. The resemblance tends to support the interpretation of Ref. 14.

We wish to thank Dr. I. S. Jacobs and Dr. L. V. Interrante for supplying the samples, and Professor W. G. Clark, Professor G. Gruner, Professor H. B. Brom, and Professor L. J. de Jongh for helpful discussions and comments. This research was supported by the U.S. National Science Foundation under Grant No. DMR-84-09390 for one of us (T.W.H.) and Grant No. DMR-86-20340 for the other (W.P.B.).

---

[1] J. W. Bray, L. V. Interrante, I. S. Jacobs, and J. C. Bonner, in *Extended Linear Chain Compounds,* edited by J. C. Miller (Plenum, New York, 1982), p. 353.

[2] M. C. Cross, Phys. Rev. B **20**, 4606 (1979).

[3] L. N. Bulaevskii, A. I. Buzdin, and D. I. Khomskii, Solid State Commun. **27**, 5 (1978).

[4] T. Nakano and H. Fukuyama, J. Phys. Soc. Jpn. **49**, 1679 (1980), and **50**, 2489 (1981).

[5] J. A. Northby, H. A. Groenendijk, L. J. de Jongh, J. C. Bonner, I. S. Jacobs, and L. V. Interrante, Phys. Rev. B **25**, 3215 (1982).

[6] J. A. Northby, F. J. A. M. Greidanus, W. J. Huiskamp, L. J. de Jongh, I. S. Jacobs, L. V. Interrante, and I. S. Jacobs, J. Appl. Phys. **53**, 8032 (1982).

[7] T. W. Hijmans, W. H. Korving, G. J. Kramer, H. B. Brom, and L. J. de Jongh, Mol. Cryst. Liq. Cryst. **120**, 251 (1985).

[8] T. W. Hijmans, H. B. Brom, and L. J. de Jongh, Phys. Rev. Lett. **54**, 1714 (1985).

[9] T. W. Hijmans, H. B. Brom, and L. J. de Jongh, J. Phys. C **19**, 1581 (1986).

[10] Y. Matsuda, T. Sakakibara, T. Goto, and Y. Ito, J. Phys. Soc. Jpn. **55**, 3225 (1986).

[11] For a recent theoretical discussion of solitons in related systems see, e.g., B. Horovitz, Phys. Rev. B **35**, 734 (1987).

[12] I. S. Jacobs, J. W. Bray, H. R. Hart, L. V. Interrante, J. S. Kaspar, G. D. Watkins, D. E. Prober, and J. C. Bonner, Phys. Rev. B **14**, 3036 (1976).

[13] W. A. C. Erkelens, L. P. Regnault, J. Laugier, J. Rossad-Mignod, and L. J. de Jongh, Solid State Commun. **55**, 209 (1985).

[14] T. W. Hijmans and H. B. Brom, J. Phys. C **19**, 5629 (1986).