Evidence for an Incommensurate High-Field Phase in the Spin-Peierls System Tetrathiafulvalene-$AuS_4C_4(CF_3)_4$

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(Received 2 January 1985)

Frequency-dependent proton and fluorine NMR experiments have been performed on tetrathiafulvalene-$AuS_4C_4(CF_3)_4$, which give the first experimental evidence for the incommensurate nature of the high-field phase in spin-Peierls systems. The field-induced transition to this phase is found to be first order at low temperatures. The echo shape in the high-field phase is described in terms of a soliton-lattice model due to Nakano and Fukuyama.

PACS numbers: 75.10.Jm, 75.30.Kz, 75.40.Fa, 76.60.−k

The spin-Peierls (S-P) transition[1] is a phenomenon which occurs in a number of $S=\frac{1}{2}$ antiferromagnetic linear-chain compounds and is analogous to the more common regular Peierls transition. The analogy is seen by mapping the Hamiltonian of the magnetic chain onto one describing a system of interacting spinless fermions by means of the Jordan-Wigner transformation.[1] An important difference between the electronic and the magnetic case is the fact that in the latter system the number of particles is not conserved, but can in principle be varied at will by applying a magnetic field. S-P systems thus offer the possibility to investigate Peierls-type transitions as a function of band filling.

Among the very few materials for which convincing experimental evidence exists that they exhibit and S-P transition,[1] the compound tetrathiafulvalene-$AuC_4S_4(CF_3)_4$ (TTF-AuBDT) is unique because of its low transition temperature of 2.03 K.[2,3] Relatively moderate fields (≈ 2 T) are thus sufficient to make the electronic Zeeman energy comparable to the Peierls gap. This property makes the compound particularly suited for performing proton and fluorine NMR experiments in the field range where important effects associated with band filling are expected to occur.

Several models have been proposed for the phase diagram of S-P systems.[4] Most of these predict a field-induced transition from the dimerized to a modulated phase, which is characterized by a distortion wave vector q equal to twice the Fermi wave vector k_F. No direct experimental evidence has been obtained so far as to whether q indeed becomes incommensurate in S-P systems in high fields. It has been argued that odd harmonics of the fundamental are important (soliton lattice), if q is sufficiently close to π/a.[5,6]

The NMR measurements on powdered samples of TTF-AuBDT presented in this paper show that the earlier reported[2] field-induced phase transition becomes first order at temperatures of 1 K and lower. The data on the high-field phase clearly indicate this phase to be different from the paramagnetic one, and can indeed be excellently described in terms of an incommensurate state. Furthermore, the modulation of the dimerization order parameter appears to be in the form of a soliton lattice rather than sinusoidal.

In Fig. 1 we show the H-T phase diagram of TTF-AuBDT, as obtained from the spin-echo experiments described here and the observed changes in temperature dependence of the proton and fluorine relaxation rates (above T_c the relaxation rate is independent of T whereas below T_c it rapidly decreases), combined with previously published susceptibility and specific-heat data.[2,3]

Figure 2(a) shows the inverse half-width at half height of the spin echo as obtained in a pulsed NMR experiment as a function of field at $T=0.57$ K and $T=1.35$ K. The data at 0.57 K show a sharp rise occurring in a narrow field range (≈ 0.1 T) around 2.26 T and a hysteresis of about 40 mT. Similar jumps were seen at higher temperatures, up to 1.0 K. The inset shows the echo signal, measured at 1.0 K for fields around 2.25 T. This echo shape is the Fourier transform of the inhomogeneous part of the line shape, caused by the local fields of the electron spins on the TTF molecules as felt by the proton spins. In

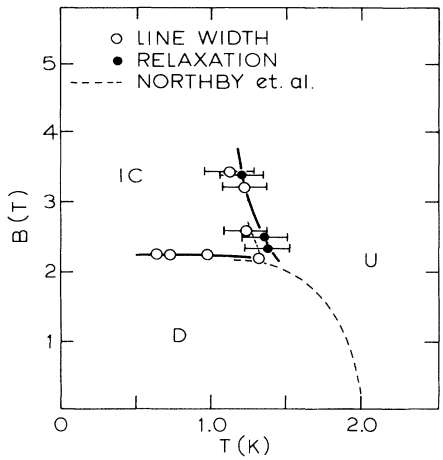

FIG. 1. Phase diagram. U, D, and IC, denote uniform, dimerized, and incommensurate phases. The D-IC phase boundary is first order.

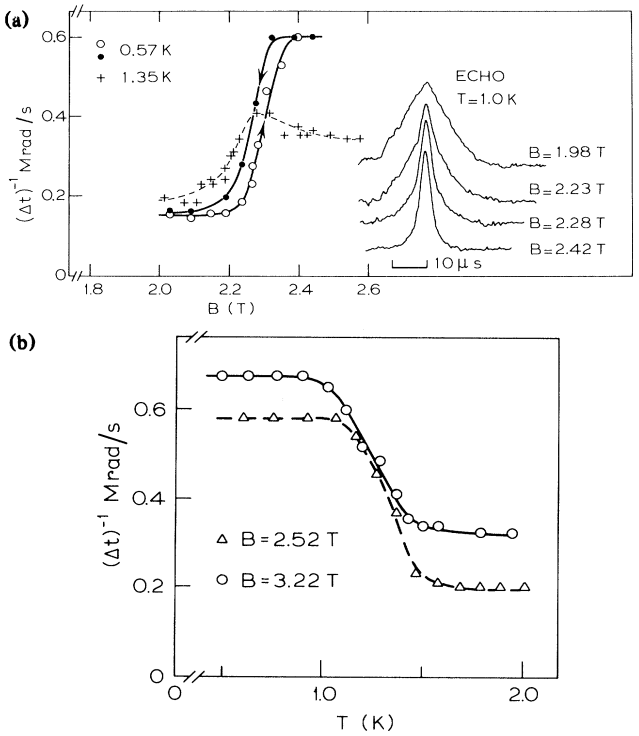

FIG. 2. The inverse half-width of the proton spin echo, vs (a) field and (b) temperature. The inset in (a) shows the echo shape.

this field range the echo signal apparently is a superposition of two components [see inset of Fig. 2(a)], suggesting coexistence of two phases. Combined with the hysteresis this is indicative of the occurrence of a first-order transition. Measurements performed at constant fields higher than 2.25 T [Fig. 2(b)] show a similar, but more gradual, increase as the temperature is lowered below a certain value (which was approximately 1.4 K at 2.5 T and 1.2 K at 3.3. T). The fluorine resonance displayed similar but less pronounced effects.

The echo width in the high-field phase corresponds to a half-linewidth of about 1.6 mT. This value is much larger than the linewidth calculated for the paramagnetic phase. Taking[1] $J/k_B = 68$ K and using an effective dipolar field d (coupling strength divided by $\hbar\gamma_H$) of -44 mT, as obtained in TTF-CuBDT,[7] we estimate the square root of the second moment $M_2^{1/2}$ to be 0.2 mT for fields of about 2.5 T. This clearly shows the high-field phase to be different from the paramagnetic one. The field inhomogeneity made the experimental paramagnetic linewidth somewhat larger. We shall now analyze our data in terms of the theory of Nakano and Fukuyama.[6] To facilitate discussion we briefly summarize their model here.

By taking the continuum limit, we can write the Hamiltonian of the spinless fermion system in terms of density-fluctuation operators $\rho_1(k)$ and $\rho_2(k)$ of fermions near $+k_F$ and $-k_F$, respectively,[8,9] so that it takes the form[6]

$$\mathcal{H} = \int dx \{A(d\theta/dx)^2 + Cp^2 - [Eu(x)/u_0]\cos\theta + D\cos 2\theta + 2Ku^2(x)/a - 2AQ\, d\theta/dx\}. \quad (1)$$

Here $A = \frac{1}{8}Ja$, $C = \frac{1}{2}\pi^2 Ja$, $E = J\lambda u_0/a^2$, $D = \pi^2 J/8a$, $Q = 2g\mu_B B/\pi Ja$, $\theta_\pm + \pi/2 = i\sum_{k\neq 0}[\rho_1(k) \pm \rho_2(k)] \times A(k)$, $A(k) = (2\pi/Lk)\exp(-\frac{1}{2}\alpha k - ikx)$, $\theta = \theta_+$, $p = -(4\pi)^{-1} d\theta_-/dx$; a, u_0, λ, and α denote the lattice constant, the staggered lattice displacement, spin phonon coupling constant, and a cutoff parameter. The third term in (1) gives the contribution to the energy of the fermion system which is due to the lattice distortion, allowing for a spatially varying dimerization order parameter as represented by $u(x)$. The fourth term is due to umklapp scattering; the fifth term represents the energy associated with the lattice distortion itself. K is the elastic constant. The last term represents the Zeeman energy. In (1) the Fermi wave vector is taken equal to π/a. θ is then related to the spin density at $x = ia$ by

$$S^z(x) = \frac{1}{2\pi}\frac{d\theta(x)}{dx} + \frac{(-1)^i}{a}\sin\theta(x). \quad (2)$$

(1) is solved by separating θ into its mean value θ_s and a fluctuating part $\hat{\theta}$ which is treated in the self-consistent harmonic approximation (SCHA).[6] One obtains

$$\sin\theta = R[\sin\theta_s\left(1 - \frac{\hat{\theta}^2 - \langle\hat{\theta}^2\rangle}{2}\right) + \cos\theta_s\hat{\theta}], \quad (3)$$

where R is the quantity $\exp(-\langle\hat{\theta}^2\rangle/2)$, which is calculated in the ground state to be $R = (\Delta/\pi^2 J)^{1/2}$. Here Δ is the gap in the excitation spectrum of (1) due to the dimerization. Application of the SCHA to (1) yields a sine-Gordon equation for θ_s together with the condition $u(x) = u_0\cos[\theta_s(x)]$. This equation has soliton solutions. The Zeeman term has the tendency to stabilize a modulated structure with wave vector $Q + \pi/a$, which will have the form of a soliton lattice when Q is small [$u(x) \sim \mathrm{sn}(x/\xi k, \kappa)$ with sn a Jacobi elliptic function with parameter κ]. The soliton creation energy E_s becomes approximately[6] $E_s(B) = E_s(0) - g\mu_B B/2$. When $g\mu_B B > 2E_s(0) \equiv g\mu_B B_c$, the soliton lattice becomes stable and a commensurate-incommensurate (C-IC) transition occurs. For $B > B_c$, k_F shifts to $\pi/a + Q$, which can be incorporated in (1) and (2) by adding Q to θ, yielding an equivalent set of expressions. For the critical field B_c and the soliton half-width ξ the following relations[6] hold: $g\mu_B B_c = 0.56\Delta$ and $\xi = \pi Ja/2\Delta$.

From the first term of the right-hand side of (2) one finds that a net spin of $\frac{1}{2}$ is present on each soliton, while the second term gives rise to a modulated stag-

gered magnetization which equals $Rg\mu_B S$ at the centers of the solitons [with R the renormalization factor occurring in Eq. (3)], and is zero exactly in between. We calculated the echo shape at $T=0$ K and $B=2.5$ T using the contributions to the local magnetization density associated with these two terms, which give rise to inhomogeneous broadening of the NMR line. The applicability of a $T=0$ treatment to describe the low-temperature data is justified by the fact that the echo shapes did not change significantly as a function of temperature below 1 K. From the exact zero-field relation $M=g^2\mu_B^2 NB/\pi^2 J$, the magnetization at 2.5 T is calculated to be $5\times10^{-3}g\mu_B$, yielding a distance l between the solitons of 100 lattice sites. By substitution of the experimental value of 2.25 T in the above relation between the critical field and the gap, we estimate Δ/k to be 5.4 K, from which we obtain $\xi=19a$ and $R=0.09$. The gap value is slightly higher than the mean-field prediction $\Delta=3.5$ K.[10] In view of the ambiguities in the numerical constants used in the continuum-limit calculations, the obtained values for ξ and Δ should be considered as estimates. In a powder sample of TTF-AuBDT in the paramagnetic phase, the isotropic hyperfine field a and the effective dipolar field d (the corresponding coupling strengths divided by $\hbar\gamma_H$) give rise respectively to a shift and a broadening of the NMR line, which are both proportional to the magnetic moment of the TTF molecules to which the proton spins are coupled. The line shape due to the soliton lattice is thus found by multiplying the appropriately normalized paramagnetic line-shape profile with the calculated density of sites with a given spin. Here the magnetization scale has to be multiplied by an adjustable constant R_{exp} to account for the effect of the renormalization factor R. For the paramagnetic line shape we used both a point dipolar shape as well as a Gaussian. The latter choice should not be considered inferior as the spin is delocalized over the TTF molecule. The first and second moments of the paramagnetic line shape were adjusted to the values for a and d of 79 and -44 mT, respectively.[7] Figure 3 shows the line shape and echo shape obtained after a Fourier transformation for the Gaussian case, for $\xi/a=16$ and $l/a=100$. In the calculation we approximated $u(x)$ by a superposition of single soliton solutions, separated by a distance l. This is appropriate if l is appreciably larger than ξ. To fit the experimental echo shape, R_{exp} was taken equal to 0.1, which is in remarkable agreement with the value of 0.09 for R, calculated above. The lower curve in Fig. 3 results if a sinusoidal modulation of the dimerization parameter is assumed. If the point-dipolar model is used, a similar line shape as shown in Fig. 3 is found differing mainly by a sharp cutoff in the wings. This leads to a slightly wiggling structure imposed on the echo shape. The slight asymmetry in the line shape is due to the nonstaggered part of the magnetization density and should

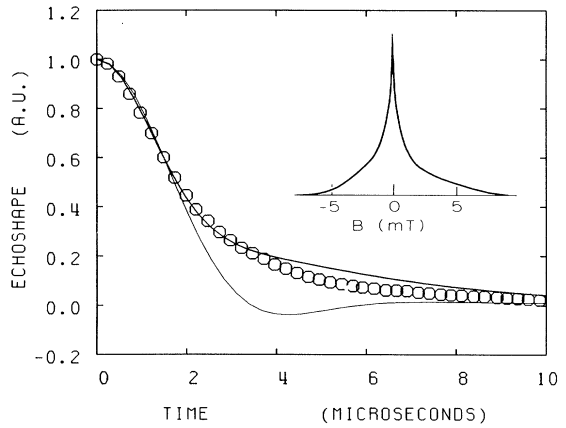

FIG. 3. Real part of the Fourier transform (upper solid line) of the proton NMR line shape (inset) calculated for the soliton lattice with $R_{exp}=0.1$, fitted to the experimental echo shape at $T=0.75$ K and $B=2.52$ T. The lower (thin) curve corresponds to a sinusoidal modulation.

give rise to an imaginary component in the echo signal. This component will be small and was not observed by us.

A final remark should be made concerning the possibility of ascribing the observed phenomena to conventional three-dimensional antiferromagnetic ordering. In the presence of a strong anisotropy, the sublattice magnetization M_s will be fixed with respect to the crystal irrespective of the applied field. If M_s is taken equal to $g\mu_B S$, the hyperfine interaction alone gives rise to a value of 23 mT for $M_2^{1/2}$. A zero-point spin reduction of more than 90% would thus have to be assumed to account for the observed linewidth. This seems unusually large even for so good a one-dimensional system. In the more likely case of weak anisotropy, the high-field phase would correspond to a spin-flop phase. Then the value of $M_2^{1/2}$ is mainly determined by the $M=\pm1$ terms in the dipole-dipole coupling and is equal to about 17 mT. Furthermore, in the latter case a split line shape and consequently an oscillatory structure in the echo signal is expected.

Some of our experimental NMR results have been presented elsewhere.[11] A more detailed account including a discussion of the relaxation data will be published later.

We wish to thank Dr. I. S. Jacobs and Dr. L. V. Interrante for supplying the samples and an enlightening stimulating correspondence during the course of the investigations.

[1]An extensive review of the spin-Peierls problem is given by J. W. Bray, L. V. Interrante, I. S. Jacobs, and J. C. Bonner, in *Extended Linear Chain Compounds,* edited by J. S.

Miller (Plenum, New York, 1982).

[2]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).

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

[4]See, e.g., M. C. Cross, Phys. Rev. B **20**, 4606 (1979); J. W. Bray, Solid State Commun. **26**, 771 (1978); L. N. Bulaevskii, A. I. Buzdin, and D. I. Khomskii, Solid State Commun. **27**, 5 (1978).

[5]A. Kotani, J. Phys. Soc. Jpn. **42**, 416 (1977); I. Harada and A. Kotani, J. Phys. Soc. Jpn. **51**, 1737 (1982).

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

[7]F. Devreux, C. Jeandrey, M. Nechtschein, J. M. Fabre, and L. Giral, J. Phys. (Paris) **40**, 671 (1979).

[8]A. Luther and I. Peschel, Phys. Rev. B **9**, 2911 (1974).

[9]M. C. Cross and D. S. Fisher, Phys. Rev. B **19**, 402 (1979).

[10]E. Pytte, Phys. Rev. B **10**, 4637 (1974).

[11]Proceedings of the International Conference on the Physics and Chemistry of Low Dimensional Synthetic Metals Abano Terme, Italy, 1984 (to be published).