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Soliton Formation at the Neutral-to-Ionic Phase Transition in the Mixed-Stack Charge-Transfer Crystal Tetrathiafulvalene-*p*-Chloranil

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Intrinsic paramagnetic defects have been detected by ESR measurements in tetrathiafulvalene-*p*-chloranil single crystals, associated with the neutral-to-ionic phase transition at $T_c = 84$ K. Two kinds of paramagnetic species are identified with delocalized spins propagating on either donor or acceptor sites. Total spin density and electric conductivity were found to increase discontinuously as temperature is lowered across T_c. These features are attributed to the formation of mobile solitonlike (and antisolitonlike) paramagnetic defects induced in the dimerized lattice at the phase transition.

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The existence of neutral-to-ionic (NI) phase separation in the mixed-stack donor-acceptor (DA) crystals has been the subject of prolonged interest.[1,2] Specifically, considerable efforts have been focused recently on the tetrathiafulvalene (TTF)-*p*-chloranil (CA) crystal for its unique property for showing a temperature-induced NI transition under atmospheric pressure.[3] The infrared and Raman measurements[3,4] have shown that the transition occurs through an intermediate region where both quasineutral and ionic molecules coexist, while the visible reflectivity spectra in single crystals were found to exhibit a very sharp change at $T_c = 84$ K, indicating a first-order-like transition.[5] Since the mechanism of this particular transition in TTF-CA has a significant bearing on the study of charge-transfer (CT) complex crystals, more detailed experimental information is required by using well-qualified single-crystal samples. This Letter reports the results of electron-spin-resonance (ESR) measurements on pure TTF-CA single crystals. The results provide experimental evidence for the formation of solitonlike states at the NI transition. In contrast to the chemically induced solitons previously reported in the conducting segregated-stack CT crystal $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}\mathrm{TCNQ}$,[6] the paramagnetic spin solitons presently detected in the semiconducting mixed-stack CT crystal TTF-CA are of an intrinsic origin inherent in the dimerized ionic phase, and are utilized as a unique microscopic probe for the study of lattice dynamics of the NI transition.

Single crystals of TTF-CA were prepared by a plate cosublimation method from carefully purified polycrystals of TTF and *p*-chloranil.[5] The ESR measurements were made on single crystals with a standard Varian *X*-band spectrometer. The microwave power was less than 2 mW and the amplitude of 100-kHz modulation field was about 0.1 G. Figure 1 represents the typical ESR lines in TTF-CA observed at 80 K (slightly below T_c) for the static magnetic field H in the ac' plane, making an angle of 20° to the c' axis which is perpendicular to the stacking axis (a) and the b axis (cf. the inset of Fig. 1).

When H is rotated within three planes spanned by the a, b, and c' axes, the ESR lines show characteristic angular dependences as shown in Figs. 2 (a) and 2(b). The experimental points shown by large open circles represent the major strong lines, and smaller open circles the weaker lines. The important features of this result are summarized as follows: (1) The spectra exhibit only doublet lines (marked 1 and 2 in Figs. 1 and 2) for all directions

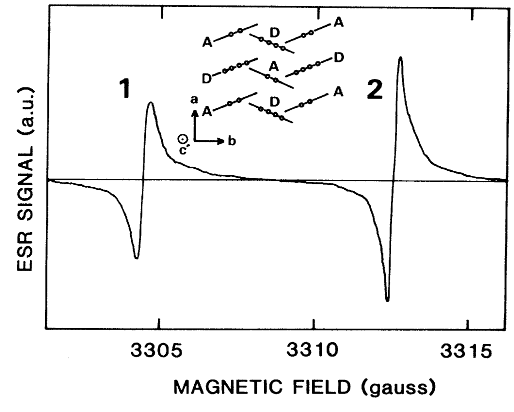

FIG. 1. The ESR signals in TTF-CA single crystal at 80 K for H parallel to the ac' plane making angle of 20° to the c' axis (schematic molecular arrays in the inset).

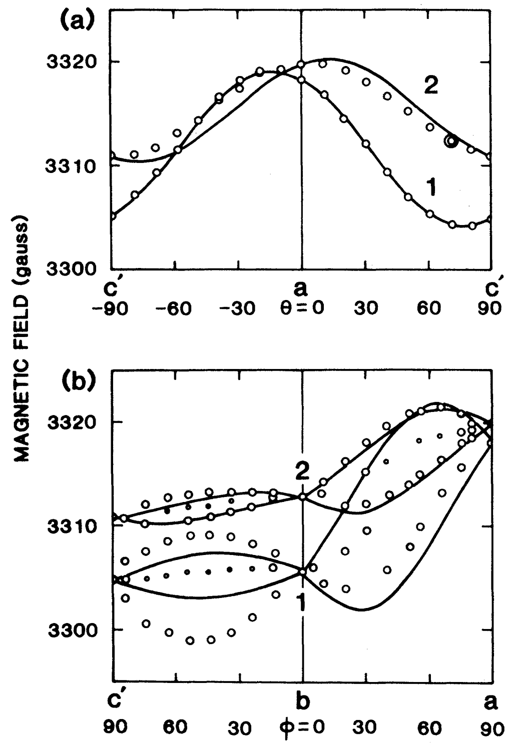

FIG. 2. Angular dependence of the ESR lines in TTF-CA single crystal (open circles for experimental points at 80 K, solid curves for calculated results).

of H lying on the ac' plane. (2) The same doublet lines are also observed for $H \parallel b$ axis. (3) For all other directions of H, each of the doublet lines is split into two or, sometimes, more lines.

These features of the anisotropic ESR lines can be successfully accounted for by assuming two kinds of paramagnetic spins having the same symmetries as the constituent TTF and CA molecules in the lattice: According to the x-ray measurements,[7] there are two inequivalent sites for both donor (TTF) and acceptor (CA) molecules as schematically illustrated in the inset of Fig. 1. If the paramagnetic spins are accommodated on either D (TTF) or A (CA) sites, there will be two inequivalent spins for the respective paramagnetic species in the general direction of H. But, for H lying in the ac' plane, these two spins become magnetically equivalent as evident from the crystal symmetry. The same situation is also realized for $H \parallel b$ axis. The observed features of the ESR lines are exactly in accord with these expectations.

The results of quantitative analysis of the experimental ESR spectra are shown by solid curves in Fig. 2. The principal g values of the two paramagnetic species have been determined from the best fit of the doublet lines at $H \parallel a$, b, and c' axes under the assumption that their principal axes are parallel to those of TTF and CA in the lattice. The species having the same symmetry as TTF have the g values of $g_x = 2.0110$, $g_y = 2.0154$ ($g_\parallel = 2.0132$), and $g_z = 2.0018$, and the species with the symmetry of CA have $g_x = 2.0096$, $g_y = 2.0076$ ($g_\parallel = 2.0086$), and $g_z = 2.0022$. The calculated curves reproduce the observed results fairly well, supporting the present model. In addition, the experimental g values are in good agreement with the reported principal g values of TTF$^+$ and CA$^-$: $g_x = 2.0069$, $g_y = 2.0151$ ($g_\parallel = 2.0110$), and $g_z = 2.0016$ for TTF$^+$ in TTF-CuS$_4$C$_4$(CF$_3$)$_4$,[8] and $g_x = g_y (= g_\parallel) = 2.0085$ and $g_z = 2.0024$ for CA$^-$ in p-phenylenediamine-CA.[9] The calculated curves for TTF (line 1) deviate from the experimental points in the bc' plane, indicating that TTF molecules are slightly tilted around the stacking axis (a), but the agreement as a whole may be regarded as rather satisfactory.

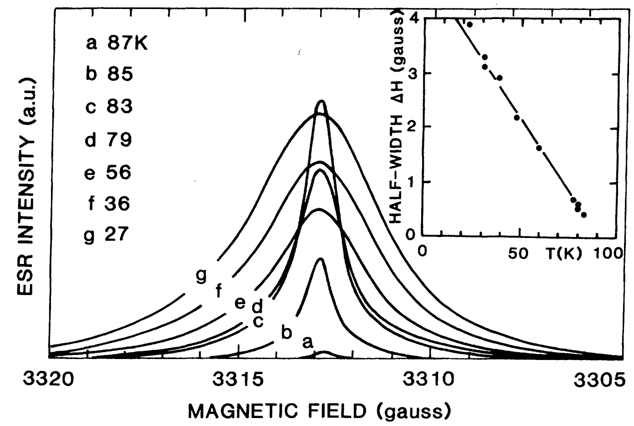

FIG. 3. The line shapes and the half-widths (inset) of TTF-p-CA single crystal near $T_c = 84$ K [the corresponding point is shown in Fig. 2(a) by a double open circle].

The salient features of these intrinsic spins located on the lattice sites are useful as a microscopic probe for the lattice dynamics at the NI transition. An example is demonstrated in Fig. 3 in which the temperature-dependent profiles of line 2 are shown. A weak and narrow ESR signal observed slightly above T_c (curves a and b) is significantly enhanced as the temperature is lowered across T_c (curve c), and then becomes considerably broadened below T_c (curves d–g). Meanwhile, the integrated intensity increases continuously with decreasing temperature. The thermal changes of the ESR spectra are reversible in a repeated cooling and warming process, provided that the rate of temperature change is slow enough. The observed shapes fit with Lorentzian curves quite well throughout the whole temperature range.

The half-width ΔH for line 2 is plotted in the inset of Fig. 3 as a function of temperature. The minimum linewidth is as narrow as 0.43 G near T_c. Similar features have also been observed for line 1, with a little larger half-width, ca. 0.6 G, above and near T_c. The linear dependence of ΔH on temperature as well as the Lorentzian line shape are most naturally attributed to the motional-narrowing effect on these ESR lines. This implies that the paramagnetic spins are not localized on fixed lattice sites but are moving on equivalent TTF (for line 1) or CA (for line 2) molecules in the lattice. The rate of transfer $(\Delta H - \Delta H_0)^{-1}$ shows a critical temperature dependence in the form of $(T_c - T)^{-1}$, with ΔH_0 being the residual width of about 0.4 G at $T \simeq T_c$. Such a critical behavior is distinctive for the ESR lines in TTF-CA as compared with a thermally activated motional narrowing in polyacetylene.[10] A possible mechanism of the line narrowing in TTF-CA is supposed to be due to a critically enhanced motion of the paramagnetic spins near T_c.

The total spin susceptibility associated with the NI transition can be obtained from the integrated intensities of the ESR spectra. The results (closed circles) are plotted in Fig. 4 against T^{-1}. The dc conductivity measured along the stack axis is also shown for comparison. The susceptibility is negligibly small above T_c and shows a sharp discontinuous rise at T_c. Simultaneously, the dc conductivity shows a jump, indicating a creation of mobile charge carriers at the onset of the ionic phase. In the ionic region below T_c, the total spin susceptibility follows a Curie law, indicating a constant spin density for $T < T_c$. This is in contrast to the case of ionic CT crystals such as *p*-phenylenediamine-CA where the spin density shows an exponential temperature dependence due to a thermal excitation of the spin excitons.[9] Under the assumption that $S = \frac{1}{2}$, the spin density is estimated to be about 1×10^{-4} spins per molecule below T_c. Such a low spin density in the ionic phase of TTF-CA is in contradiction to the predicted diamagnetic-to-paramagnetic change at the NI phase transition.[11]

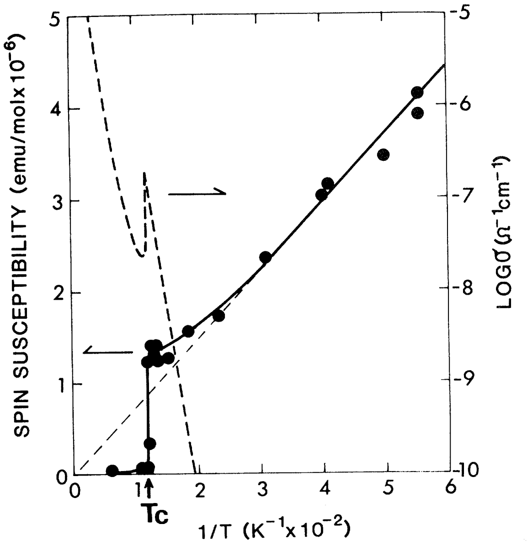

FIG. 4. The total spin susceptibility and dc electric conductivity (dashed curve) of TTF-CA single crystal plotted against T^{-1}. Dashed straight line represents the paramagnetic Curie law.

The characteristic features of the ESR spectra as described above were observed in pure and strain-free single crystals of TTF-CA. In powder samples, only broad ESR signals with a half-width as large as 15 G were observed instead of the narrow lines. Similar broad signals were occasionally found as a background of the narrow lines in single crystals, when the crystals had been exposed to air for a considerable period. These broad signals are observable up to room temperature. Their intensities and linewidths do not show a critical change at all at T_c. When pure single crystals were intentionally doped with a small amount of substitutional weak-acceptor molecules such as trichloro-*p*-benzoquinone, the narrow ESR signals were considerably broadened, and their linewidths were found to be almost temperature independent below T_c. This implies that the critical motion of the paramagnetic spins is quenched by doping with these impurities. These observations exclude the possibility that the narrow ESR lines in pure TTF-CA crystals might be due to some unidentified extrinsic defects or impurities, in accord with the aforementioned interpretation that they are of an intrinsic origin.

Thus, the experimental results presented above evidently indicate that intrinsic and delocalized paramagnetic defects are created and annihilated in a reversible way, when temperature is changed across T_c. Accordingly, the lattice dynamical properties at the phase transition must be closely correlated with the defect-formation mechanism. From infrared and Raman measurements,[4] it has been suggested that the lattice is distorted below T_c by dimerization into D-A pairs. Direct evidence for the lattice dimerization has been subsequently provided by recent x-ray measurements[12] on the same single-crystal samples of TTF-CA as used in the present study. Since the dimerization of alternating donor and acceptor molecules on the stack axis is expected to produce a considerable number of phase-mismatch defects (domain walls) in the ionic lattice, it will be most reasonable to identify them with the paramagnetic defects induced below T_c. A simplified model of such defects is schematically represented by

$$\ldots(\mathrm{D}^{+\rho}\mathrm{A}^{-\rho})(\mathrm{D}^{+\rho}\mathrm{A}^{-\rho})\mathrm{D}^{+\delta}(\mathrm{A}^{-\rho}\mathrm{D}^{+\rho})(\mathrm{A}^{-\rho}\mathrm{D}^{+\rho})\ldots$$

or

$$\ldots(A^{-\rho}\mathrm{D}^{+\rho})(\mathrm{A}^{-\rho}\mathrm{D}^{+\rho})\mathrm{A}^{-\delta}(\mathrm{D}^{+\rho}\mathrm{A}^{-\rho})(\mathrm{D}^{+\rho}A^{-\rho})\ldots,$$

with ρ the degree of charge transfer of the dimers (DA) or (AD). The isolated D (TTF) and A (CA) molecules at the phase-mismatch points (domain walls) bear the effective charges $\pm\delta$ and unpaired spins predominantly located on the molecules. If the lattice distortion around the dimers is not so large, the domain walls will be able to move along the stack axis as soliton- (and antisoliton-)like defect states. The appearance of two kinds of spins, located on TTF and CA sites, respectively, with the density of the order of 10^{-4} molecule^{-1}, and their thermal behavior near T_c, are quite consistent with this picture, and may be regarded as experimental evidence for soliton formation in TTF-CA at the NI phase transition. An increased electric conductivity at T_c might also be due to the induced effective charges carried by the same defects. Another possibility is that the increased conductivity is associated with the charged spin-0 solitons which have been recently predicted to exist in dimerized mixed-stack CT crystals together with chargeless spin-carrying solitons.[13] Yet, this theory is based upon a simple bond-dimerization model analogous to that for polyacetylene, and may not be adequate to deal with the more complicated situation in TTF-CA, where proper account has to be taken for both long-range electrostatic and short-range electron- (and spin-) lattice interactions. The paramagnetic solitons as reported in this Letter will serve as a valuable microscopic probe to investigate more profound aspects of the NI phase transition in the mixed-stack CT complex crystals in the future.

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