Magnetic-Field–Induced Phase Transition in the Quasi-One-Dimensional Material $Ta_{0.8}Fe_{0.2}S_3$

S. Dai, X. Z. Zhou, A. H. Morrish, and Q. A. Pankhurst
Department of Physics, University of Manitoba, Winnipeg, Canada R3T 2N2

and

Z. Shan
Institute of Physics, Academica Sinica, Beijing, China
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^{57}Fe Mössbauer spectra of $Ta_{0.8}Fe_{0.2}S_3$ recorded as a function of applied magnetic field at 4.2 K show that a reversible phase transitions occurs at $H_c \simeq 15$ kOe. Magnetization measurements confirm this observation. The experimental results are consistent with some form of antiferromagnetic ordering for $H > H_c$, inferring that charge-density waves and spin-density waves may coexist in this material.

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The influence of external magnetic fields on charge-density-wave (CDW) conductors at low temperatures is an important area of physical research today. Recently Coleman *et al.*,[1] Parilla, Hundley, and Zettl,[2] and Everson *et al.*[3] reported an anomalous magnetoresistance in monoclinic $NbSe_3$. It appears that the applied magnetic field modifies the electronic spectrum near the Fermi level so that the ratio of condensed (CDW) to normal electrons increases. In 1986 Butz *et al.*[4] studied the two-dimensional material $2H$-TaS_2 by means of time-differential perturbed angular correlation; they found evidence for the coexistence of a charge-density wave and a spin-density wave (SDW) when a field of 3.5 kOe was applied at a temperature of 1.5 K. In 1987, Osada *et al.*[5] interpreted the observation of a nonlinearity in the transverse conductivity of the organic conductor tetramethyltetraselenafulvalinium chlorate, $(TMTSF)_2ClO_4$, in terms of a magnetic-field–induced spin-density-wave phase transition.

Recently we published an account of a Mössbauer study of the quasi-one-dimensional materials $Ta_{1-x}Fe_xS_3$ and their associated charge-density-wave phenomena.[6] In $Ta_{0.95}Fe_{0.05}S_3$, two Peierls transitions associated with the onset of electron condensation were observed at $T_1 \simeq 215$ and $T_2 \simeq 153$ K. These temperatures are slightly lower than those observed in TaS_3, showing that the presence of iron inhibits but does not prevent the CDW formation. For higher concentrations of iron T_1 and T_2 decrease, with T_2 falling below 77 K for $x > 0.30$.

In the present work $Ta_{1-x}Fe_xS_3$ samples with $x \leq 0.20$ were subjected to the influence of applied magnetic fields at temperatures in the liquid-helium regime. Reversible field-induced phase transitions were observed: In this Letter we report on the evidence that leads to this conclusion, and discuss the inference that both CDW's and SDW's may coexist in the high-field phase.

$Ta_{1-x}Fe_xS_3$ samples were synthesized with use of high-temperature and high-pressure technology: pure powders of Ta, Fe, and S were heated for 30 min under a pressure of 3 GPa at $T \simeq 970$ K.[6] X-ray diffractograms showed that the crystal structure is monoclinic; it is the same as that of monoclinic TaS_3 and similar to that of $NbSe_3$. Each Ta ion lies at the center of a trigonal prism of six S ions. Adjacent prisms share triangular faces and are stacked along the monoclinic b axis, forming lengthy chains. There are three inequivalent prisms, hereafter referred to as I, II, and III, which may be distinguished by their shortest S−S bond length (in the basal plane perpendicular to the b axis), viz. 0.2068, 0.2105, and 0.2835 nm, respectively.[7] A low temperature NMR study of the similar compound, $NbSe_3$, showed that both chains I and II exhibit the CDW state, whereas chain III is an insulator.[8] Mössbauer measurements indicate that the same is true in $Ta_{1-x}Fe_xS_3$.[6]

The specific magnetization curves of $Ta_{1-x}Fe_xS_3$ samples with $x = 0$, 0.05, 0.10, and 0.20, were measured at $T = 1.5$ K with a conventional magnetometer (Fig. 1). At low fields, e.g., $H \lesssim 10$ kOe for $Ta_{0.8}Fe_{0.2}S_3$, σ increased roughly linearly as a function of H, implying that the sample was in a paramagnetic state. However,

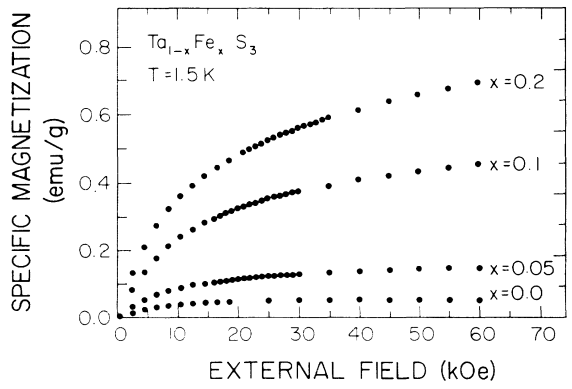

FIG. 1. The specific magnetization σ of $Ta_{1-x}Fe_xS_3$ as a function of applied field H at $T = 1.5$ K.

for larger fields the rate of change of $\sigma(H)$ decreased, as would be consistent with the presence of some form of antiferromagnetic or ferrimagnetic order. To further investigate this behavior, ^{57}Fe Mössbauer spectra of a polycrystalline sample of $Ta_{0.8}Fe_{0.2}S_3$ were recorded at $T=4.2$ K in applied fields of up to $H=25$ kOe (Fig. 2). In all cases the γ-ray beam was directed parallel to the applied magnetic field. Qualitatively it is clear that at $H\simeq 15$ kOe the spectral characteristics change: for $H<15$ kOe the spectra comprise a broad pair of lines; for $H>15$ kOe a third, central absorption line appears.

Computer analysis of the spectra was performed with a full powder average of the subspectra obtained by diagonalization of the Hamiltonian representation of the combined electric and magnetic hyperfine interactions. A number of restrictions were imposed on the fitting process. On the basis of the earlier observations,[6] the relative probability of an iron atom occupying a type I, II, or III tantalum site was taken to be 3:3:4. Further, it was assumed that CDW's were present on chains I and II only, and that there was an equal probability that any given Fe^{3+} ion in those chains would lie in a region of electronic excess (the peak of the CDW's, or P branch) or electronic deficit (the valley of the CDW's, or V branch). In this way, five subpatterns were fitted to each Mössbauer spectrum, corresponding to the sites denoted I_P, I_V, II_P, II_V, and III, respectively.

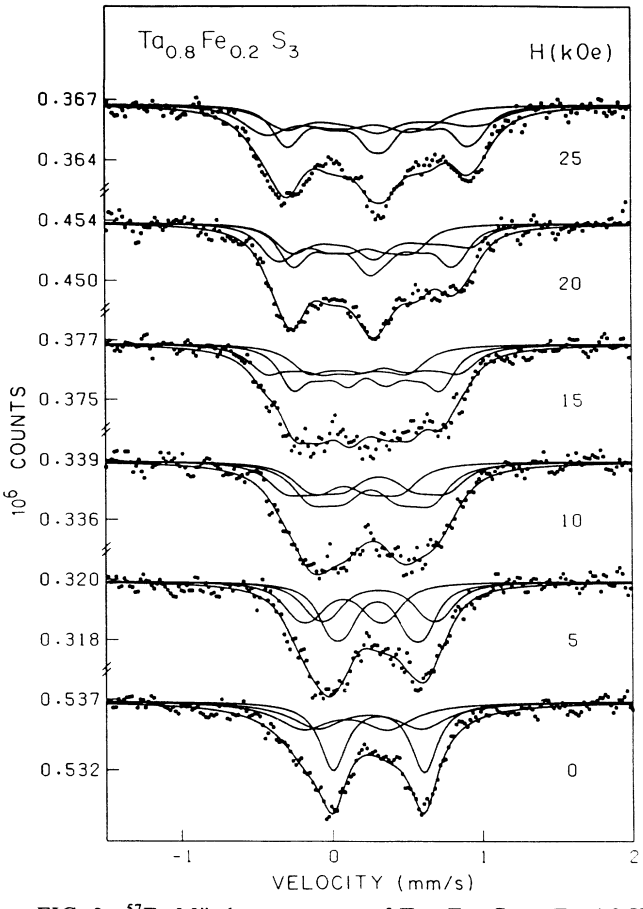

FIG. 2. ^{57}Fe Mössbauer spectra of $Ta_{0.8}Fe_{0.2}S_3$ at $T=4.2$ K for applied magnetic fields $0\leq H\leq 25$ kOe. Full curves are computer-fitted theoretical spectra, as discussed in the text. Subpatterns correspond to (i) sites I_P and II_P, (ii) sites I_V and II_V, and (iii) site III.

In addition, the orientation and asymmetry (but not the magnitude) of the electric quadrupole interactions, which were found to be ill defined in the experimental spectra, were constrained to theoretically reasonable values. The electric-field-gradient tensor was estimated by means of a simple point-charge model: Ignoring the contribution of valence electrons, the electric field gradient at a given site was attributed to the charges on the surrounding ions. Diagonalizing this tensor yields the electric-field-gradient principal components V_{xx}, V_{yy}, and V_{zz}, and, by definition the asymmetry parameter $\eta=(V_{xx}-V_{yy})/V_{zz}$. With use of the room-temperature ionic positions of TaS_3,[7] and with the assumption that the ionic charge distribution is analogous to that in $NbSe_3$,[9] summations performed within a sphere of radius 3.5 nm centered at the reference ion gave the following estimates: $\eta\sim 0.7$ at sites I and II, and ~ 0.3 at site III: V_{zz} negative in sign and oriented in the basal a-c plane at site I, and positive in sign and oriented along the monoclinic b axis at sites II and III. Although it is unrealistic to presume that these parameters might correlate exactly with $Ta_{0.8}Fe_{0.2}S_3$ at 4.2 K, they are preferable to a completely arbitrary assignment.

The spectra were subjected to one further fitting constraint. The isomer shift δ and quadrupole splitting $\Delta=\frac{1}{2}eQ|V_{zz}|$ at the two P-branch sites, I_P and II_P, were assumed to be equal; similarly, δ and Δ at the V-branch sites I_V and II_V were taken to be equal. The resultant least-squares fits are shown in Fig. 2, and the corresponding hyperfine parameters are given in Table I. Since the subspectra at the P-branch and V-branch pairs of sites were found to have very similar profiles, only three subpatterns are displayed for each spectrum in Fig. 2, although five sites were incorporated in the computer analysis.

For the low-field spectra, $H\leq 15$ kOe, good fits were obtained under the assumption that the material was in a paramagnetic state, so that the hyperfine field H_{hf} was zero at all the sites. However, this condition could not be retained for the high-field spectra, $H>15$ kOe. After a large number of possibilities had been tested, it was concluded that the best fits were for a model in which the Fe ions in chains I and II were antiferromagnetically ordered along the monoclinic b axis, while those in chain III remained paramagnetic. Induced hyperfine fields of order 5–10 kOe were fitted (Table I), with H_{hf} being somewhat larger on chain-I sites than on chain II. A significant discontinuity in the P- and V-branch quadrupole splittings was observed, presumably related to a lat-

TABLE I. Mössbauer parameters of $Ta_{0.8}Fe_{0.2}S_3$ at $T=4.2$ K as a function of applied field H (kOe), as discussed in the text: isomer shift relative to α-iron, δ (mm/s), and quadrupole splitting, Δ (mm/s), for the P- and V-branch sites of chains I and II, and for chain III; and the hyperfine field H_{hf} (kOe) on chains I and II.

H	δ_P	Δ_P	δ_V	Δ_V	δ_{III}	Δ_{III}	H_{hf}^{I}	H_{hf}^{II}
0	0.07	0.55	0.23	0.68	0.30	0.56	...	...
5	0.06	0.48	0.30	0.71	0.29	0.48	...	...
10	0.07	0.51	0.30	0.65	0.25	0.53	...	...
15	0.03	0.54	0.34	0.60	0.23	0.55	...	...
20	0.06	0.16	0.29	0.49	0.27	0.51	9.5	5.5
25	0.05	0.20	0.31	0.50	0.31	0.52	10.4	3.8

tice distortion accompanying the phase transition.

Spectra were recorded after the removal of the applied field; they showed no change from those recorded before the field was applied, implying that the phase transition is reversible. In addition, a second series of experiments was conducted with $Ta_{0.95}Fe_{0.05}S_3$ at 4.2 K. The results were qualitatively similar to those in $Ta_{0.8}Fe_{0.2}S_3$, except that the phase transition occurred for a smaller applied field, $H_c \simeq 10$ kOe.

In conclusion, it is clear on the basis of our magnetization and Mössbauer data that a reversible magnetic-field-induced phase transition takes place in $Ta_{1-x}Fe_xS_3$ at low temperatures. For applied fields exceeding a critical value ($H_c \simeq 15$ kOe for $Ta_{0.8}Fe_{0.2}S_3$) a magnetically ordered state develops. The observations are consistent with a model in which the Fe ions on the chains which carry charge-density waves, chains I and II, are antiferromagnetically ordered. The presence of a hyperfine field implicitly infers the presence of spin-density waves. Therefore, it appears that $Ta_{1-x}Fe_xS_3$ is another example of a material in which CDW's and SDW's may coexist.

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