High-T_c superconducting phase in the $Fe_{1-x}S$ system

G. A. Petrakovskiĭ, G. V. Loseva, N. I. Kiselev, S. G. Ovchinnikov, N. B. Ivanova, and V. K. Chernov

Institute of Physics, Siberian Branch of the Academy of Sciences of the USSR, 660036, Krasnoyarsk

(Submitted 3 July 1991)
Pis'ma Zh. Eksp. Teor. Fiz. **54**, No. 4, 224–227 (25 August 1991)

A decrease in the resistivity of $Fe_{1-x}S$ has been observed at a temperature of 110 K. Decreases in the magnetic moment and susceptibility have been observed at 128 K. These decreases indicate the appearance of a superconducting phase with $T_c = 128$ K.

The cations in binary sulfides of 3*d* metals, MeS, with a NiAs (*B* 8) vacancy structure form one-dimensional chains along the *C* hexagonal axis. The crystal remains three-dimensional, but the symmetry of some of the *d* bands (in particular, d_{z^2}) is such that a quasi-one-dimensional *d* band forms against the background of the three-dimensional bands.[1] Spin density waves and charge density waves are characteristic of such systems, resulting from an instability of the metallic system with the quasi-one-dimensional bands.[2,3] A metallic instability occurs in MeS (Me = V, Cr, Fe, Ni), for example, upon a metal–insulator transition.[4] An important consequence of the theory is the coexistence of superconducting and insulating pairings. Since the electron density of states is relatively high at the edges of the insulating gap which arises upon the formation of a spin density wave or a charge density wave, a superconducting pairing can lead to fairly high superconducting transition temperatures T_c (Ref. 5)

An increase in the sulfur content in $Me_{1-x}S$ systems increases the concentration and degree of order of the cation vacancies. These changes are accompanied by the formation of superstructures of various symmetries with various multiples of the lattice constant of the (main) NiAs (1*c*) lattice, with a disordered arrangement of cation vacancies, by an increase in the role of covalent Me–S bonds, by a "metallization" of the sulfides, and (sometimes) by an intensification of magnetic properties. The electrical and magnetic properties of the $Fe_{1-x}S(0<x<0.125)$ system have been studied quite thoroughly above room temperature,[6,8] but only slightly at low temperatures.

In this letter we are reporting measurements of the electrical and magnetic properties of intermediate phases of the $Fe_{1-x}S$ system, with $0.07<x<0.125$, over the temperature range 4.2–300 K. Our goal was to learn about the low-temperature conversions that occur in magnetically ordered binary sulfides with the NiAs vacancy structure.

Polycrystalline samples of intermediate phases of the $Fe_{1-x}S$ system, with $x = 0.074$, 0.083, 0.091, 0.111, and 0.125, were synthesized in vacuum quartz cells from the pure elements. According to x-ray structural analysis, the test samples had the structures of intermediate pyrrhotites of the series FeS–Fe_7S_8 (Ref. 6) at 300 K.

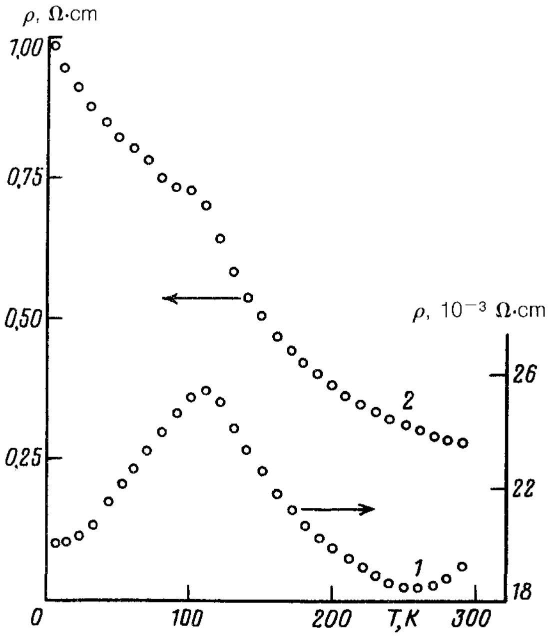

FIG. 1. Temperature dependence of the resistivity of $Fe_{1-x}S$ samples 1 ($x = 0.125$) and 2 ($x = 0.111$).

Sample 1 ($x = 0.125$) clearly exhibited the Fe_7S_8 monoclinic structure ($4c$ superstructure). It follows from the x-ray pattern of sample 2 ($x = 0.111$) that its composition is close to Fe_8S_9; the single crystal has a 5C superstructure.[6] The x-ray patterns of samples 3 ($x = 0.091$) and 4 ($x = 0.083$) are approximately the same and very difficult to distinguish from each other. In accordance with Ref. 9, a set of phases similar in structure, chemical nature, and composition is proposed for intermediate compositions $Fe_{1-x}S$ (samples 3 and 4 fall in this region). These phases belong to the homologous series Fe_nS_{n+1}. Their crystal structures are based on the NiA ($1c$) structure. The x-ray and DTA analyses of sample 5 ($x = 0.074$) show that the composition of the sample is approximately FeS with a 2C superstructure at 300 K.

Figure 1 shows the temperature dependence of the resistivity of samples 1 and 2. The curves of $\rho(T)$ found for the other samples have the typical semiconducting shape. The $\rho(T)$ curves in Fig. 1 were recorded slowly (at 6–10 min per point) during cooling from 300 to 4.2 K. When the measurements were repeated, the $\rho(T)$ curves did not change. It can be seen from Fig. 1 that the resistivity takes on values of $(18.5\text{–}20.0)\times 10^{-3}$ $\Omega\cdot$cm over the temperature range studied. Near $T = 110$ K, ρ increases to 26.0×10^{-3} $\Omega\cdot$cm; it then falls off at $T < 110$ K.

For sample 2 ($x = 0.111$), there is a knee on the $\rho(T)$ curve at ~ 110 K, with some increase in ρ at 110 K.

Figure 2 shows the temperature dependence of the real component of the initial magnetic susceptibility of the $Fe_{1-x}S$ system. From room temperature down to $T = 128$ K, the behavior of the susceptibility of samples 1–3 is basically paramagnetic, although there are several structural features on the $\chi'(T)$ curve. As the temperature

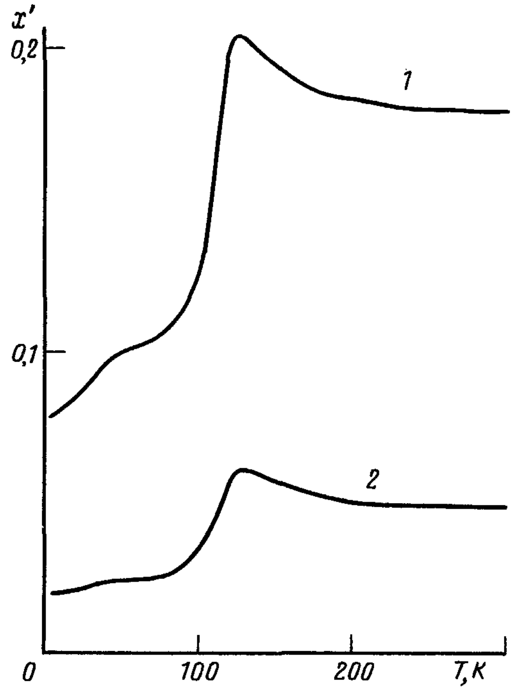

FIG. 2. Temperature dependence of the magnetic susceptibility of $Fe_{1-x}S$ samples 1 and 2.

is lowered below 170 K, the susceptibility increases for samples 1–3 and then decreases sharply at 128 K. The magnitude of the diamagnetic signal falls off from sample 1 to sample 3. For samples 4 and 5, χ' remains essentially constant at a low value $\chi' < 10^{-2}$ in this temperature range. The point at which the diamagnetic effect ap-

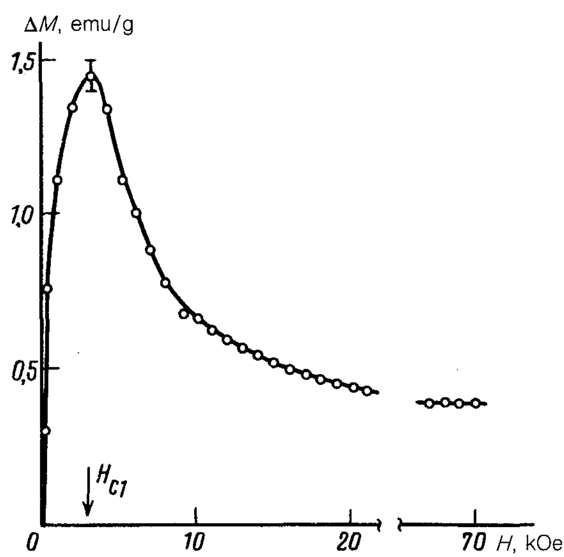

FIG. 3. Field dependence of the diamagnetic moment of sample 1.

pears (128 K) is above the temperature at which the electrical resistivity begins to fall off. Moreover, the diamagnetic effect is exhibited by samples 2 and 3, for which $\rho(T)$ is of a semiconducting nature.

That there is a diamagnetic effect is confirmed by the change in the shape of the hysteresis loop as we go from $T > T_c$ to $T < T_c$. Magnetization curves of sample 1 were measured in fields up to 70 kOe at various temperatures in order to determine the diamagnetic moment. Figure 3 shows the field dependence of the diamagnetic moment, $\Delta M = M(150\text{ K}) - M(4.2\text{ K})$ from these results we find $H_{c1} = 3$ kOe.

In summary, low-temperature measurements of the electrical and magnetic properties of the $Fe_{1-x}S$ system $(0.07 < x \leqslant 0.125)$ for $x = 0.125$, with the NiAs (4*c*) superstructure, reveal a partial diamagnetic effect in the region in which the electrical resistance falls sharply. The absence of a state in which the entire sample has a zero resistance is apparently a consequence of the nonuniformity of the polycrystalline sample. The diamagnetic effect and the decrease in resistivity observed here suggest that a superconducting phase with $T_c = 128$ K is formed.

We wish to thank A. V. Baranov for carrying out the x-ray structural analysis and A. D. Balaev and M. M. Zarpenko for assistance in measurements of the hysteresis loops.

[1] L. M. Mattheis, Phys. Rev. B **10**, 995 (1974).
[2] Yu. A. Bychkov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, Zh. Eksp. Teor. Fiz. **50**, 738 (1966) [Sov. Phys. JETP **23**, 489 (1966)].
[3] L. N. Bulaevskiĭ, Usp. Fiz. Nauk **115**, 263 (1974) [Sov. Phys. Usp. **18**, 131 (1975)].
[4] G. V. Losseva, S. G. Ovchinnikov, and G. A. Petrakovskiĭ, *The Metal–Insulator Transition in the Sulfides of 3d Metals*, Novosibirsk, Nauka, 1983.
[5] Yu. V. Kopaev and R. Kh. Timerov, Zh. Eksp. Teor. Fiz. **63**, 290 (1972) [Sov. Phys. JETP **36**, 153 (1972)].
[6] D. Vogan and J. Craig, *Chemistry of Sulfide Materials* [Russian translation], Mir, Moscow, 1981.
[7] V. L. Volkov, Yu. V. Kopaev, and A. I. Rusinov, Zh. Eksp. Teor. Fiz. **68**, 1899 (1975) [Sov. Phys. JETP **41**, 952 (1975)].
[8] C. B. Van den Berg, Ferroelectrics **4**, 195 (1972).
[9] D. N. Abishev and A. S. Pashinkin, *Magnetic Sulfides of Iron*, Nauka kaz. SSR, Alma-Ata, 1981.

Translated by D. Parsons