Anomalous temperature dependence of the electrical resistance of ternary molybdenum sulfides with an iron impurity

Yu. F. El'tsev, V. M. Zakosarenko, V. R. Karasik, and V. I. Tsebro
P. N. Lebedev Physics Institute, USSR Academy of Sciences

(Submitted 25 April 1980)
Pis'ma Zh. Eksp. Teor. Fiz. **31**, No. 12, 741–745 (20 June 1980)

It is shown that an introduction of an iron impurity into ternary molybdenum chalcogenides such as $PbMo_6S_8$, in addition to strongly suppressing the superconductivity observed earlier, produces large minima in the temperature dependence of the electrical resistance. This effect correlates with the effective magnetic moment of the impurity and with the density of the electronic states.

PACS numbers: 72.80.Ga, 71.55.Ht

It was shown in Ref. 1 that a strong suppression of superconductivity by an iron impurity in ternary molybdenum chalcogenides (TMC), formula $M\,Mo_6S_8$ ($M =$ Pb, Sn, Cu, Ag), is accompanied by large, effective magnetic moments μ_{eff} per impurity atom, which are determined from the temperature dependence of the magnetic susceptibility in the normal state. The larger the γ coefficient for the given system after the electronic contribution to the specific heat, i.e., the density of the electronic states $N(0)$ at the Fermi level, the larger are the observed values of μ_{eff}. In the investigated series of compounds μ_{eff} varies from 2.5 μ_B when Fe is dissolved in $AgMo_6S_8$ to $\sim 5\ \mu_B$ in

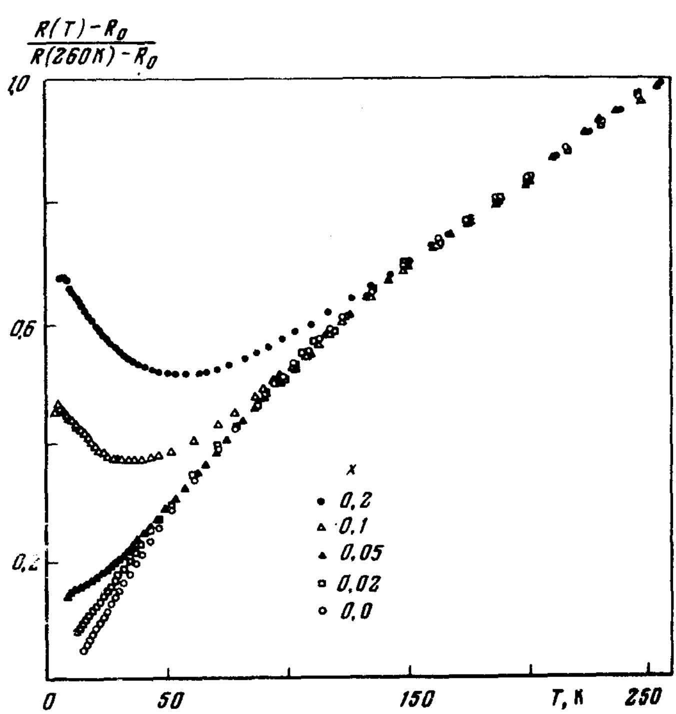

FIG. 1. Normalized temperature dependences of the electrical resistance of $Fe_xPbMo_6S_8$ samples with different iron concentrations (0, $x = 0$; □, $x = .02$; ▲, $x = 0.05$; △, $x = 0.1$; ●, $x = 0.2$).

$PbMo_6S_8$. The latter value greatly exceeds the value of μ_{eff} for metallic iron or, for example, Mo-Fe solutions, and is only a factor of 2 lower than μ_{eff} for Pd-Fe solutions.

The large values of μ_{eff} and their dependence on $N(0)$ show that the interaction of conduction electrons with the electrons of the unfilled 3*d* shells of the iron, i.e., with the magnetic moment of the impurity, play a key role. We thought it would be of interest to study the effect of Fe impurity on the temperature dependence of the resistance $R(T)$, where this interaction would manifest itself. With that end in view, we measured the $R(T)$ dependences of TMC samples of the aforementioned compositions with an iron concentration C ranging from 0 to 1.3 at.% ($0 \leqslant x \leqslant 0.2$ in the formula $Fe_xMMo_6S_8$).

The $Fe_xMMo_6S_8$ samples were prepared by direct synthesis from powders of the original components and then annealed for homogenization. The annealing was preceded by the compression of the synthesizing material into 5-mm-diam, 5 to 7-mm-high cylindrical discs at a pressure of 30 kbar. The $1 \times 1 \times 5$-mm samples of rectangular cross section were then cut out from the discs. The electrical resistance of the samples was measured with a direct current in the temperature range of 2 to 300 K by using a standard four-contact method.

Figures 1 and 2 show the temperature dependences of the resistance of the $Fe_x PbMo_6S_8$ and $Fe_xSnMo_6S_8$ samples for different concentrations of the magnetic

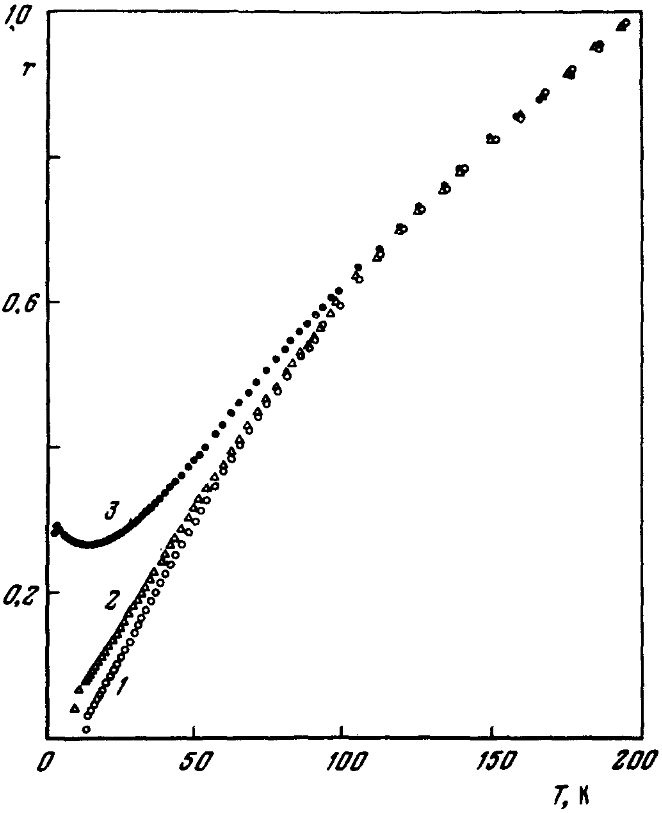

FIG. 2. Normalized temperature dependences of the electrical resistance of $Fe_xSnMo_6S_8$ samples with different iron concentrations (0, $x = 0$; □, $x = 0.02$; ●, $x = 0.05$).

impurity. The temperature-dependent part of the resistance, normalized to the phonon resistance at high temperatures, is plotted along the Y axis (R_0 is the residual resistance). We can see a linear increase of the resistance with the temperature just above T_c for the pure samples, in spite of the fact that the samples have a very small resistance ratio $R\,(300K)/R_0 \lesssim 3$. This peculiarity of the temperature dependence of the resistance of pure $PbMo_6S_8$ and $SnMo_6S_8$ samples, which was reported in Refs. 2 and 3, is apparently associated with the low-frequency maximum in the phonon spectrum of these compounds, which was detected in the inelastic neutron scattering experiments.[4,5]

As seen from the data in Figs. 1 and 2, as a result of introducing iron an impurity contribution appears in the resistance whose magnitude increases with decreasing temperature and increasing impurity concentration, so that at $C \geqslant 0.3$ at.% ($x \geqslant 0.05$) a distinct minimum appears in the $R\,(T)$ dependence. With further increase of the concentration C the depth of the minimum increases and its location is shifted in the direction of high temperatures. The magnetic contribution to the resistance ρ_M depends linearly on $\ln T$ in the temperature range of 15 to 50 K and the normalized

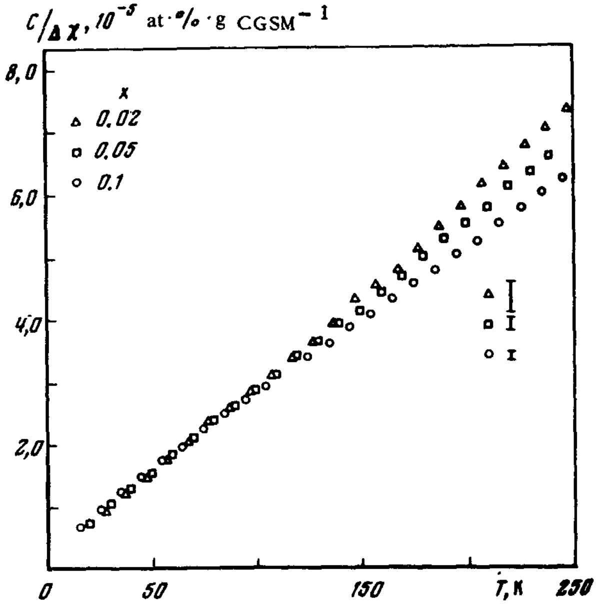

FIG. 3. Reduced temperature dependences of the reverse magnetic susceptibility of the $Fe_xPbMo_6S_8$ samples with different iron concentrations (△, $x = 0.02$; □, $x = 0.05$; $x = 0.1$).

dependences $\rho_M(T)/C$ can be fitted into the universal dependence within the error limits of determining ρ_M and the concentration.

As is known, the so-called Kondo systems have such properties. The magnetic susceptibility of such systems (see, example, Ref. 6) obeys the Curie-Weiss law $\chi \sim \mu_{\mathrm{eff}}^2/(T-\Theta)$, where Θ is negative value of the order of the Kondo temperature T_K [according to the data,[6] $\Theta \cong (2.5\text{–}10)T_K$]. On the basis of the results of the measurement of $\chi(T)$ in the iron-containing TMC samples,[1] we can show that the impurity-dependent addition $\Delta\chi_M$ of pure samples to the magnetic susceptibility [$\Delta\chi_M(T) = \chi(T) - \chi_0(T)$, where $\chi_0(T)$ is the susceptibility of a pure sample] rigorously obeys the Curie-Weiss law, which is the same for different impurity concentrations, in the temperature range of 4.2 to 100 K. This is illustrated in Fig. 3 which shows the temperature dependences $[\Delta\chi_M(T)/C]^{-1}$ for three concentrations of Fe in the $PbMo_6S_8$ system. We can see that at $T \leqslant 100$ K the values of $(\Delta\chi_M/C)^{-1}$ for all C's are on the same line which crosses the temperature axis at the point $\Theta = -10 \pm 3$ K and has a slope corresponding to the value $\mu_{\mathrm{eff}} = 4.6 \pm 0.2\,\mu_B$. It follows from this that the values of Θ and μ_{eff} are independent of C in the investigated concentration range. A divergence at high temperatures is apparently attributable to the fact that the temperature-independent contribution to χ (for example, due to an increase of $N(0)$[7]), which is noticeable at high temperatures, increases as a result of the introduction of iron.

In contrast to $PbMo_6S_8$ and $SnMo_6S_8$, the Fe impurity does not have a noticeable influence on the $R(T)$ dependence of the $Cu_2Mo_6S_8$ and $AgMo_6S_8$ samples in the investigated concentration range, i.e., a strong influence of the Fe impurity on the

$R(T)$ dependence has been observed only in those systems which have an unusually large $N(0)$.

Thus, we showed in this study that the Fe impurity in TMC with large values of $N(0)$ produces anomalous temperature dependence of the electrical resistance similar to that in the Kondo systems. However, an examination of noninteracting impurity spins in our case is hardly valid, since, first, the Fe concentration at which distinct $R(T)$ minima begin to manifest themselves is sufficiently large (possibly due to a strong phonon contribution to the resistance at low temperatures) and, secondly, the Fe mixture is dissolved in a matrix with a very high density of states $N(0)$, which, it would seem, must lead to an indirect exchange between the impurity spins. It should be noted that at $x \geqslant 0.1$ an increase of the resistance in the $PbMo_6S_8$ samples with decreasing temperature for $T \lesssim 5$–6 K is replaced by a decrease in R, i.e., a low-temperature, local $R(T)$ maximum attributable to spin-glass-type magnetic ordering can be observed.

The authors thank N. E. Alekseevskiĭ and A. I. Rusinov for their interest and useful critical remarks.

[1] N. E. Alekseevskiĭ, G. Wol'f, N. M. Dobrovol'skiĭ, Yu. F. El'tsev, V. M. Zakosarenko, and V. I. Tsebro, Pis'ma Zh. Eksp. Teor. Fiz. **29**, 138 (1979) [JETP Lett. **29**, 123 (1979)].

[2] N. E. Alekseevskiĭ, Proc. Int. Symposium "Physical Properties of Solids in High Magnetic Fields," May 19–20, 1978, Wroclaw, Poland.

[3] J. A. Woollam and S. A. Alterovitz, Solid State Comm. **27**, 571 (1978).

[4] S. D. Bader, G. S. Knapp, S. K. Sinha, P. Schweiss, and B. Renker, Phys. Rev. Lett. **37**, 344 (1976).

[5] S. D. Bader, S. K. Sinha, and R. N. Shelton, 2nd Rochester Conf. on Superconductivity in *d*- and *f*-Band Metals, ed. by D. H. Douglass, N. Y., 1976, p. 209.

[6] M. D. Daybell, in Magnetism, Vol. 5. ed. G. Rado and H. Suhl, Academic Press, N. Y., 1973, p. 121.

[7] N. E. Alekseevskiĭ, G. Wolf, S. Drautz, and V. I. Tsebro, J. Low Temp. Phys. **28**, 381 (1977).