Effect of iron impurity on the superconducting transition temperature and magnetic properties of some ternary molybdenum sulfides

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A strong suppression of superconductivity by an iron impurity and large effective magnetic moments per impurity atom in the ternary molybdenum sulfides such as $PbMo_6S_8$, which can cause a strong indirect exchange, indicate that the investigated compounds may be ferromagnetically unstable.

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The ternary molybdenum chalcogenides (TMC) of the formula $MMo_6X_8(X = S,Se)$, where, as is well known, M can be a number of different elements (see, for example, Refs. 1–5), are some of the more interesting and currently intensively studied classes of superconducting components. The effect of ferromagnetic impurities of 3*d*-elements on the suprconducting properties of TMC has been studied very little. There is some evidence that the Fe and Mn impurities strongly suppress superconductivity of $SnMo_6S_8$.[4,6,7]

In this paper we investigate the effect of iron impurity in the region of low concentrations on the superconducting transition temperature T_c and magnetic susceptibility of the ternary sulfides MMo_6S_8 in the normal state, where M = Pb, Sn, Cu, and Ag. The choice of compounds was determined by the fact that when the difference between the critical temperatures T_c is small, the values of $\partial H_{c2}/\partial T$ for the compounds with Pb and Sn are appreciably higher than those for the compounds with Cu and Ag (see Table I). The samples of the $Fe_x MMo_6S_8$ compounds were prepared by a direct synthesis from powders of the starting components and then annealed in the same way as earlier (see, for example, Refs. 4 and 7). The maximum concentration of iron x in the basic formula for all compounds was $\leqslant 0.05$. The superconducting transition temperature was determined inductively by using ac current. The magnetic susceptibility was measured in the magnetic field of the superconducting solenoid by a string magnetometer whose operating principle was described elsewhere.[8]

The dependence of superconducting transition temperature on the concentration of the iron impurity measured by us is shown in Fig. 1 for all four systems. The results are given in the T_c/T_{c0} coordinates, where T_{c0} is the superconducting transition temperature of the pure sample. In the investigated region of concentrations it can be seen that T_c for all compounds decreases linearly with increasing concentration of the impurity: the values of $\partial T_c/\partial c$ and $(1/T_c)(\partial T_c/\partial c)$ per at.% of the impurity are given in Table I.

The measurements of the magnetic susceptibility χ of the samples without mag-

TABLE I.

Composition	T_c, K	$\frac{\partial H_{c2}}{\partial T}$ $\frac{\text{kG}}{\text{K}}$	$\frac{\partial T_c}{\partial c}$ $\frac{\text{K}}{\text{at.\%}}$	$\frac{1}{T_c}\frac{\partial T_c}{\partial c}$ (1/at.%)	χ (300 K) 10^{-6}CGS/g	γ $\frac{\text{mJ}}{\text{K}^2\text{.mole}}$	$\gamma_{\Delta c}$, $\frac{\text{mJ}}{\text{K}^2\text{.mol}}$	μ_{eff}/μ_B
$PbMo_6S_8$	13.5	50	28	2.1	0.37	–	101	5
$SnMo_6S_8$	11.4	37	26	2.3	0.46	106	85	4.2
$Cu_{1,8}Mo_6S_8$	10,9	15.5	7.8	0.72	0.26	63	46	3
$AgMo_6S_8$	8.5	7	4,6	0.54	0.09	32	27	2.5

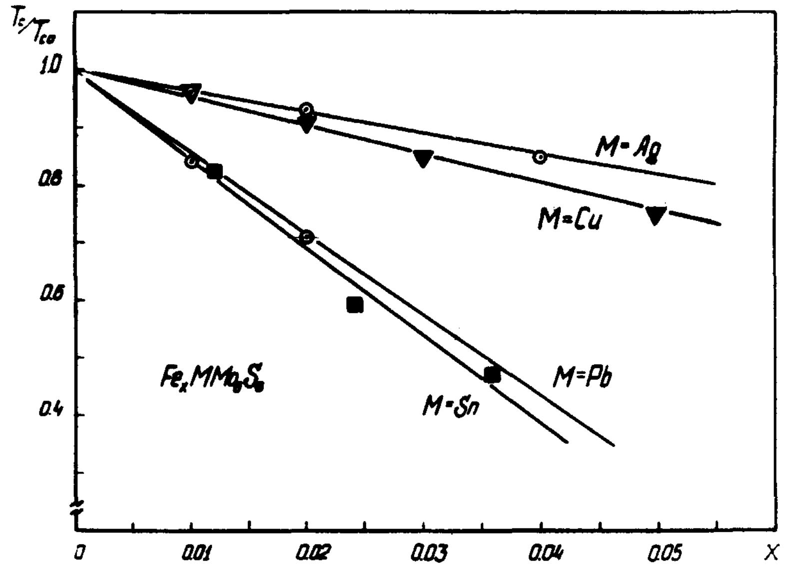

FIG. 1. Dependence of the superconducting transition temperature T_c/T_{c0} on the iron concentration.

netic impurities showed that χ is almost independent of temperature. As the temperature decreased from 300 K to T_c, the magnetic susceptibility, whose values are given in Table I, increased not more than 15% for all the samples. At $\sim T_c$ the magnetic susceptibility of the iron-containing samples increases significantly with increasing concentration of the iron and decreases signficantly with increasing temperature, so that the temperature dependence of the reverse susceptibility $\chi^{-1}(T)$ is almost linear. Figure 2 shows the dependence of $\chi^{-1}(T)$ for $Fe_x PbMo_6S_8$ samples with different con-

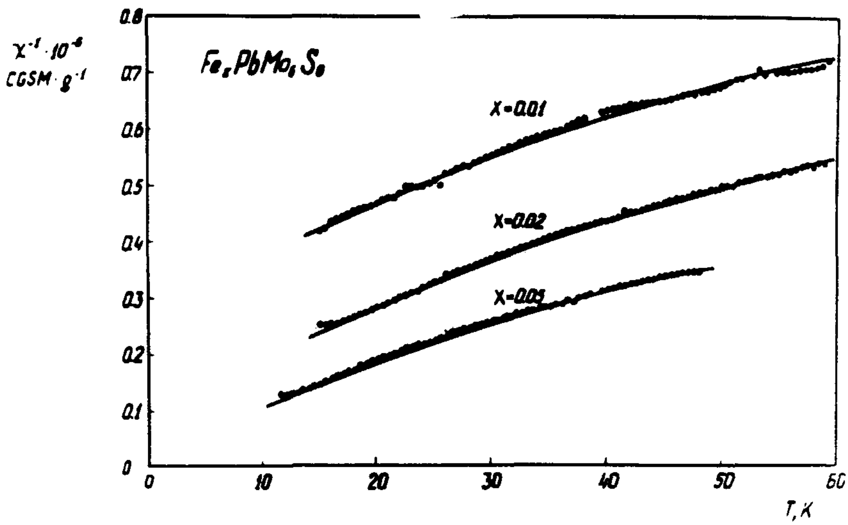

FIG. 2. Temperature dependence of the reverse susceptibility of the $Fe_x PbMo_6S_8$ samples for different concentrations of the iron impurity.

centrations of iron.

The experimental curves $\chi(T)$ for the samples of all the compounds were approximated by an expression of the type

$$\chi(T) = \frac{c}{T-\Theta} + \chi_0 , \qquad (1)$$

where the parameters c, Θ, and χ_0 were determined by the least-squares method. The solid curves in Fig. 2 correspond to the given approximation. The effective magnetic moments per impurity atom, expressed in Bohr magnetons, which were obtained from the Curie constants according to the formula $\mu_{\text{eff}} = (3k_B c/N)^{1/2}$, are given in Table I. The values of the parameter Θ for all compounds were negative and did not exceed 10 K in absolute value and the values of χ_0 were close to those for the susceptibility of the pure samples.

The superconducting transition temperature generally does not decrease significantly in high-temperature superconducting compounds because of the addition of an iron impurity. Thus, for example, the critical temperature T_c of the intermetallic compounds with A15 structure can be reduced $\sim$10% by introducing up to 5 at.% Fe.[9] In our case, an addition of only 0.5 at.% Fe reduced by 20% the transition temperature of $AgMo_6S_8$, $\partial T_c/\partial c$, i.e., the effect is more than an order of magnitude stronger than for superconductors with A15 structure.

It can be seen from Fig. 1 and from the data in Table I that the values of $\partial T_c/\partial c$, which for sulfides with Pb are close to those with Sn, greatly exceed the corresponding values for the compounds with Cu and Ag, for which the values of $\partial H_{c2}/\partial T$ are much smaller than those for the first two compounds. Experimental studies of the specific heat of TMC conducted by us showed that as a result of electron contribution of the specific heat the γ coefficients for $PbMo_6S_8$ and $SnMo_6S_8$ are also much higher than those for $Cu_{1,8}Mo_6S_8$ and $AgMo_6S_8$ (see Table I). The values of γ in Table I were obtained from the analysis of the temperature dependence of the specific heat above T_c (in the same way as in Ref. 7) and from the measurements of the specific heat in the low-temperature region after the destruction of superconductivity by the magnetic field. Moreover, the values of $\gamma_{\Delta c}$, which were obtained in the BCS approximation from the specific heat jump due to the superconducting transition, are given in a separate column. Since the values of $\partial H_{c2}/\partial T$ and γ are determined by the density of states of the electrons at the Fermi surface $N(0)$, we can see that there is a direct correlation between the obtained values of $\partial T_c/\partial c$, μ_{eff}, and $N(0)$.

Although the values of μ_{eff} for $PbMo_6S_8$ and $SnMo_6S_8$ are not as large as those for the solutions of Fe in Pd, they are much larger than those for a pure iron. The large values of μ_{eff} for the Pd-Fe alloys, which are attributable to strong indirect exchange, indicate that the investigated systems may be ferromagnetically unstable. This accounts for the very large values of $\partial T_c/\partial c$. As expected, the magnetic instability is stronger in those systems which have a large density of states $N(0)$ (see, for example, Refs. 10 and 11). Note that, according to the data obtained by us earlier,[7] the γ coefficient increases sharply with increasing concentration of the magnetic impurity, which also confirms in a certain sense the existence of magnetic instability.

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