Effect of pressure on the properties of the system $Fe_xSnMo_6S_8$

N. E. Alekseevskiĭ, V. N. Narozhnyĭ, and E. P. Khlybov

Instutute of Physics Problems, USSR Academy of Sciences

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The dependence of the critical superconducting-transition temperature on the iron concentration x and on the pressure P was measured for the system $Fe_xSnMo_6S_8$. The $T_c(x)$ dependence is similar to that of Abrikosov and Gor'kov, and the critical concentration is $x_{cr} = 0.061$ (0.41 at.%). At $x = 0.04$ the absolute value of $\partial T_c/\partial P$ increases by more than three times compared with $x = 0$ and reaches -3.2×10^{-4} K/bar. The $T_c(P)$ dependence at $x = 0.04$ is nonlinear. This behavior can be attributed to enhancement, under pressure, of the exchange interaction of the conduction electrons with the magnetic moments of the impurity. The magnetic susceptibility changes little at a pressure ~ 5 kbar.

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1. INTRODUCTION

It is known that in most superconductors magnetic impurities lower the critical temperature T_c of the superconducting transition (see, e.g., the review[1]). The cause of the superconductivity suppression is the breaking of the Cooper pairs by the exchange interaction of the conduction electrons with the magnetic moments of the impurity atoms.[2]

An interesting possibility of studying the interaction of superconductivity with magnetism has been afforded of late by investigations of ternary molybdenum chalcogenides (TMC), whose composition AMo_6Ch_8, where Ch = S or Se and A can be an entire series of elements of the periodic system.[3,4] TMC exhibit a number of interesting physical features, including anomalously high critical magnetic fields, the presence of soft lattice modes, a metal–semiconductor transition, and others.[3,4]

TCM are divided into two groups, depending on the ion radius of the A atom and on its displacement from the inversion-symmetry center (the center of the rhombohedral unit cell)[3–5] The first group (A = In, Fe, Co, Ni, Cu, Zn) includes compounds with rhombohedral angle $\alpha_R > 90°$, in which the element A is significantly displaced from the inversion center and can occupy positions close to $(0,0,\frac{1}{2})$. The second group includes compounds with $\alpha_R < 90°$, with the large-radius element A (Pb, Sn RE—rare earth) localized near the inversion center (0,0,0). It is precisely compounds of the second group that contain superconductors with record high critical magnetic fields.

The TMC intensively studied at present are those with rare earth. Most $REMo_6Ch_8$ compounds have rather high $T_c \approx 8$ K, even though 7% of the atoms in the compound have a localized magnetic moment.[6] This is attributed to the strong localization of the *f*-electron wave functions, as well as to the large distances of the RE atoms from the Mo atoms whose electrons are assumed to be mainly responsible for the superconductivity in these systems.[3] For a number of compounds of the $REMo_6Ch_8$ type, coexistence of superconductivity and magnetic ordering was observed in the system of the magnetic moments of the RE atoms.[7]

The influence of the magnetic impurities of the iron group on the TMC superconductivity was investigated in less detail. A rather strong supression of the superconductivity of a number of TMC by an iron impurity was observed in Ref. 8 ($\partial T_c/\partial x = -26$ K at.% for $Fe_xSnMo_6S_8$),[1)] and it was noted that the rate of superconductivity suppression, as well as the effective magnetic moment μ_{eff}, is larger the larger the coefficient γ of the electronic heat capacity. The coefficients γ increases strongly in turn with increasing iron concentration.[10] Introduction of a small amount of iron impurity not only lowers T_c, but leads to a strong enhancement of the dependence of T_c on the pressure P: according to Ref. 11, the derivative $|\partial T_c/\partial P|_{P=0}$ increases for $Fe_xSnMo_6S_8$ by approximately three times at $x = 0.04$ compared with $x = 0$. Finally, at sufficiently high iron concentration, the temperature dependence of the resistivity acquires a minimum in the low-temperature region.[12]

It must be noted that introduction of iron in TMC of the second group, say into $SnMo_6S_8$, can be regarded[13] as formation of a mixed-type phase, i.e., a phase in which both positions of the type (0,0,0) and $(0,0,\frac{1}{2})$ are occupied at least in part. When RE atoms, e.g., Eu, are introduced in $SnMo_6S_8$, no mixed-type phases are produced, since both Sn and Eu occupy positions close to (0,0,0). A weak influence of Eu on T_c was noted[14] for the $Eu_xSn_{1-x}Mo_6Ch_8$ systems at $x < 0.5$.

These features of TMC with magnetic impurities make them quite interesting research objects. In this paper we report the results of an investigation of the parameters of the system $Fe_xSnMo_6S_8$ as functions of the iron concentration and of the hydrostatic pressure. Particular attention was paid in the paper to the question of existence of a critical concentration x_{cr} of iron for this system.

2. EXPERIMENT

The investigation of the influence of an iron impurity on the properties of TCM has its own peculiarity. The large value of the derivative $|\partial T_c/\partial x|$ of the $Fe_xSnMo_6S_8$ system causes superconductivity to exist only at $x < 0.4$ at.% Fe. The difficulty of introducing accurately into the sample so small an amount or iron, and of monitoring its content, is

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TABLE I. Iron content and lattice parameters of the system $Fe_x SnMo_6S_8$.

Sample No.	Set	x_{change}	x_{exp}	a_H, Å	c_H, Å	V_H, Å³	a_R, Å	α_R, deg
1	*G*	0	0.0009	–	–	–	–	–
2		0.02	0.017	–	–	–	–	–
3		0.04	0.038	–	–	–	–	–
1	*K*2	0	0.0039	9.182	11.366	829.9	6.516	89.59
2		0.02	0.023	–	–	–	–	–
3		0.04	0.044	9.189	11.358	830.5	6.518	89.65
4		0.06	0.064	9.193	11.368	832.0	6.521	89.63
5		0.10	0.11	9.200	11.350	831.9	6.521	89.72
6		0.20	0.215	9.215	11.338	833.9	6.526	89.82
7		0.40	0.37	9.231	11.332	836.3	6.533	89.91
8		0.06	0.066	–	–	–	–	–
1	*N*	0	–	9.184	11.354	829.4	6.515	89.64
2		0.4	–	9.233	11.301	834.3	6.527	90.02
3		0.6	–	9.235	11.318	835.8	6.531	89.98
4		0.8	–	9.234	11.336	837.1	6.535	89.91

obvious. On the other hand formation of a mixed-type phase and the uncertainty of the solubility limit of iron have made it necessary to monitor the parameters of the crystal structure and of the phase composition of the samples.

The samples were prepared by direct fusion from the components in a helium-filled sealed ampoule at $T = 900°C$. We used previously prepared tin and iron sulfides SnS and FeS. After the fusion, the samples obtained were thoroughly ground in an agate mortar, pressed in cylindrical molds to a pressure 15–20 kbar, and subjected to homogenizing annealing at $t = 950$ °C for 24 hours. A set of $Fe_x Sn_{1-x} Mo_6O_8$ (substitutional solution) and several sets of $Fe_x SnMo_6S_8$ (interstitial solution) were prepared. It was not obvious beforehand which of the solutions is preferable. The actual iron content in the sample was monitored with the aid of activation anaylsis.[2)] The result of the analysis is given in the table, which shows a sufficiently good agreement between the concentration in the charge and that obtained in experiment, the difference between the two not exceeding usually 10%.

The crystal-lattice parameters and the phase composition of the sample was determined with a "Geigerflex" diffractometer $(CuK)_\alpha$ radiation, $\lambda = 1.541$ Å). The internal standard was silicon powder. The accuray with which the hexagonal-cell parameters were determined ~0.003 Å.

At $x \leqslant 0.2$ the samples consist of a Chevrel phase and a small amount of MoS_2, which does not exceed 10%. No traces of free iron or of its compounds were revealed by x-ray anaylsis. At $x \geqslant 0.3$ the x-ray patterns begin to show a very slight amount of β-Sn and SnS. The lines of the $FeMo_6S_8$ compound appear at $x > 0.4$.

The most "stable" parameter, i.e., least dependent on the preparation conditions for TCM (Chevrel phases), is a_H (Ref. 15). Figure 1 shows the dependence of this parameter on the iron concentration for the two types of solution. In the substitutional solution $Fe_x Sn_{1-x} Mo_6S_8$ the iron is dissolved only in a relatively low concentration, $x \approx 0.04$. In the interstitial solution $Fe_x SnMo_6S_8$, on the contrary, the iron density in the lattice can reach $x = 0.3$ to 0.4. It follows from the x-ray data that up to a concentration $x = 0.3$ the parameter a_H increases practically linearly with increasing concentration. At higher concentrations saturation is observed on the $a_H(x)$ plot, and at $x > 0.4$ the lines of the compound $FeMo_6S_8$ appear on the x-ray patterns.

The kinetic temperature of the samples at normal incidence was measured by both an inductive and a resistive method. For samples with sufficiently high iron concentration ($x = 0.06$ and 0.10) the measurements were made at infralow temperatures ($T \geqslant 0.1$ K) obtained by adiabatic demagnetization of yttrium aluminum garnet[16] or of potassium chrome alum.

The pressure was produced in a fixed-pressure cylinder-made of beryllium bronze. Its inside and out side diameters were 8 and 26 mm. Before the final finishing of the channel, the cylinder was subjected to self-frettting. The pressure-transmitting medium was a 50% mixture of transformer oil and kerosene. The bomb made it possible to obtain a pressure up to 12 kbar at $T = 4.2$ K. The pressure was monitored by the shift of the superconducting transitions of tin and lead, and also with a manganin sensor. T_c in the vessel as measured with a $Cu–CuFe_{0.01\%}$ thermocouple places in the high-presure region. For greater reliability, the critical temperatures of three samples with different iron contents were measured in a single experiment.

To determine the effect of the pressure on the magnetic susceptibility of the investigated samples we used the string-magnetometer setup described in Ref. 17. The samples for the susceptibility measurements were cylinders 10 mm long and ~3.5 mm in diameter. The susceptibility of the samples measured by us ($x \leqslant 0.1$) was smaller by approximately an

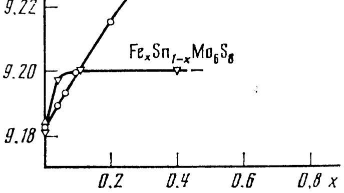

FIG. 1. Hexagonal cell parameter a_H vs concentration for two types of Fe solutions in $SnMo_6S_8$.

order of magnitude that for the samples investigated in Ref. 17. To increase the sensitivity of the magnetometer we used therefore a thinner tungsten string of 37 μm diameter. To improve the magnetometer operating stability, special efforts were made to keep it vertical. This was accomplished with adjustable platform on which the superconducting solenoid was placed, and monitored against a level gage mounted on the magnetometer head.

To reduce the experimental data the temperature was subdivided into interval of 0.5 K, and for each interval we calculated the average force and then the susceptibility. The errors in the determination of the susceptibilities of our samples in each interval was $(0.2\text{–}0.4)\times 10^{-6}$ cm^3/g. Control measurements of the sample susceptibility without the pressure cylinder were in good agreement with the susceptibilities measured in the unpressurized vessel.

3. RESULTS

Figure 2 shows the dependence of the superconducting-transition temperature of the $Fe_xSnMo_6S_8$ system on the iron concentration. Samples from the same batch are marked by the same symbol. The arrow marks the sample with $x = 0.1$ for which no superconductivity symptoms were observed at $T \geqslant 0.1$ K. The dashed curve shows the $T_c(x)$ dependence of the theory of Abrikosov and Gor'kov,[2] plotted using the experimentally determined initial slope $\partial T_c/\partial x$.

The upper curve is a plot of $T_c(x)$ for $Cu_xSnMo_6S_8$. Comparing the lots of $T_c(x_{Fe})$ and $T_c(x_{Cu})$ we readily see that in the case of Cu the lowering of T_c is much less than in the case of Fe, even though the Cu atoms occupy apparently the same positions in the lattice as the Fe atoms (near $(0,0,\frac{1}{2})$).[18] It can therefore be concluded that the effect of the iron impurity on T_c of the $SnMo_6S_8$ compound is basically magnetic in character.

When examining the obtained dependence of T_c on the iron concentration, we must note first of all that at a concentration higher than 0.04 a deviation from linearity is observed, and the curvature of the $T_c(x)$ plot is negative.

If the investigated system has a nonlinear concentration dependence with negative curvature, of the type obtained in Ref. 2, i.e., it has a critical concentration, the $T_c(P)$ plots for iron-containing samples should apparently also be nonlinear at $T_c(P)/T_c(0) < 0.5$. The result of our experiments confirm this assumption.

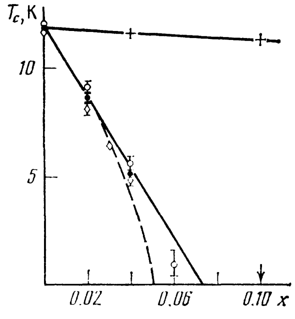

FIG. 2. Critical temperature of $Fe_xSnMo_6S_8$ vs the concentration x. Upper curve—T_c vs x for the system $Cu_xSnMo_6S_8$.

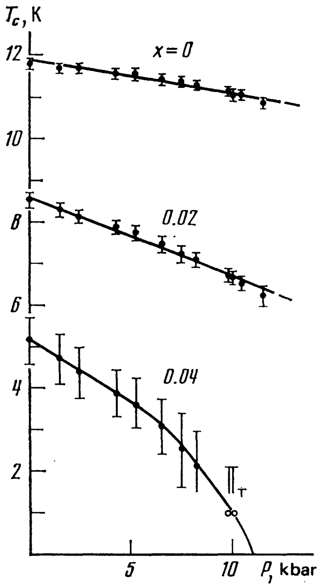

FIG. 3. Dependence of the critical temperature on the pressure for three samples of the $Fe_xSnMo_6S_8$ system.

Figure 3 shows a plot of T_c vs pressure for samples with $x = 0$, 0.02 and 0.04. The vertical lines correspond to the transition width, defined as the distance from 10 to 90% of the total amplitude of the signal registered in the course of the transition. As noted by us earlier,[11] when a large amount of iron ($x \approx 0.3$ at.%) is introduced, the derivative $|\partial T_c/\partial P|_{x=0}$ increases rapidly and reaches a value 3.2×10^{-4} K/bar, much higher than the usual 10^{-5} K/bar of superconductors. At $P > 5$ kbar the plot of $T_c(P)$ for $x = 0.04$ deviates markedly from linearity. (The midpoints of the transitions at $P \approx 10$ kbar were obtained by extrapolating the pressure dependence of the transition widths at lower pressures, and are marked by the light circles. At $P = 11.5$ kbar the sample with $x = 0.04$ showed no signs of superconductivity at $T \geqslant 1.5$ K.) If the $T_c(P)$ plot is extrapolated to $T_c = 0$, it can be seen from Fig. 4 that the critical pressure is $P_{cr} = 11$ kbar. In other words, at $P = 11$ kbar the critical concentration x is equal to 0.04 (see Fig. 4). If the critical concentration at $P = 1$ bar is estimated from these data, it amounts to approximately $x_{cr} = 0.061$ (0.41 at.%). This val-

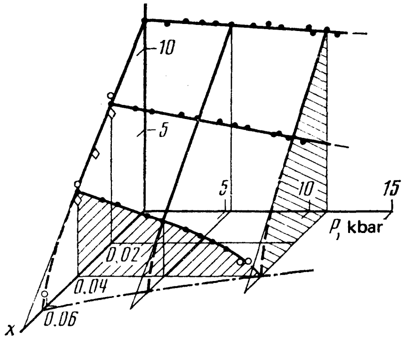

FIG. 4. Critical temperature vs concentration and pressure. Dash-dot line—pressure dependence of the critical concentration x_{cr}.

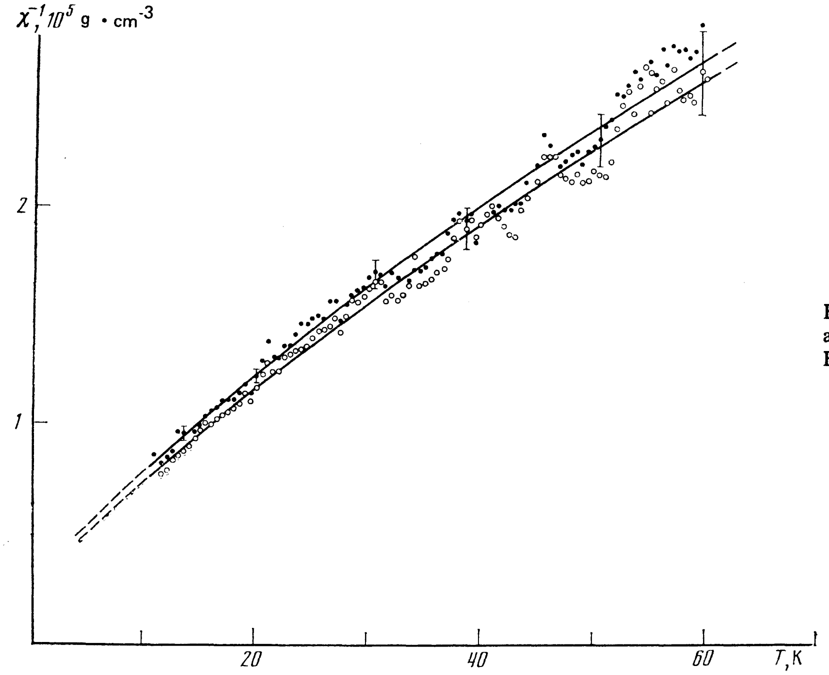

FIG. 5. Reciprocal magnetic susceptibility vs temperature at $P = 1$ bar (○) and $P = 5.3$ kbar (●) for an $Fe_{0.1}MnMo_6S_8$. sample.

ue agrees well with the experimental $T_c(x)$ dependence (see Fig. 2).

We measured also the influence of the pressure on the magnetic susceptibility of several samples with different iron contents. Figure 5 shows the temperature dependence of the reciprocal magnetic susceptibility for the sample $Fe_{0.1}SnMo_6S_8$ at $P = 5.3$ kbar and $P = 1$ bar. Each experimental point corresponds to an average of about 10 points in a 0.5 K temperature interval. Curves were drawn by least squares through the experimental points, in accord with the formula

$$\chi = C/(T-\Theta) + \chi_0,$$

where C is the Curie constant, Θ the Curie temperature, and χ_0 a temperature-independent term.

Under pressure, the magnetic susceptibility decreased in all our experiments, but by not more than 5%. The susceptibility results were reproducible within 5%. Thus, the decrease of the susceptibility under pressure was at the borderline of the accuracy of our experiments.

The effective magnetic moment μ_{eff} at the iron atoms, determined from the Curie constant C by the formula

$$C = N\mu_{\text{eff}}^2/3k_B, \tag{1}$$

where N is the number of magnetic moments per unit mass and k_B is Boltzmann's constant, is approximately $4\mu_B$ (μ_B is the Bohr magneton) and is practically independent of the concentration at $x \leqslant 0.1$. The Curie temperature for samples with $x \leqslant 0.1$ was negative and amounted approximately to -5 K.

4. DISCUSSION OF RESULTS

The question of the influence of magnetic impurities on T_c of superconductors was, as is well known, theoretically considered by Abrikosov and Gor'kov[1]; the impurities were assumed there to be non-interacting, and the scattering of the electron by the impurity magnetic moment was calculated in the Born approximation. The expression obtained for T_c in this approximation is of the form

$$\ln\frac{T_c}{T_{c0}} = \psi\left(\frac{1}{2}\right) - \psi\left(\frac{1}{2} + \frac{xS(S+1)J^2N_B(0)}{4k_BT_c}\right); \tag{2}$$

where x is the impurity concentration, S is the spin of the impurity atom, J is the exchange integral of the s–d or s–f exchange interation, γ is the coefficient of the electronic heat capacity, λ is the electron-phonon coupling constant, $\psi(z)$ is a digamma function of argument z, and

$$N_B(0) = 3\gamma/2\pi^2k_B^2(1+\lambda). \tag{3}$$

At low impurity concentrations,

$$\Delta T_c \equiv T_c - T_{c0} = -(x/8k_B)\pi^2S(S+1)J^2N_B(0), \tag{4}$$

i.e.,

$$T_c/T_{c0} = 1 - 0.691x/x_{cr}, \tag{5}$$

$$x_{cr} = \frac{0.56k_BN_B(0)T_{c0}}{S(S+1)\vartheta^2}; \quad \vartheta = JN_B(0).$$

In a number of experiments (see, e.g., Ref. 9), larger values of T_c than given by (2) were observed; in particular, T_c curves with positive curvature were obtained. A theoretical dependence of this type was obtained as a particular case by Muller-Hartmann and Zittartz,[20] who took the Kondo effect into account in electron scattering by a magnetic impurity. An interesting result of the theory of Ref. 20 was the prediction of the existence of superconductors with non-single-valued $T_c(x)$ dependence.[21] A characteristic feature of Refs. 20 and 21 is the absence of a critical concentration, i.e., T_c approaches zero asymptotically with increasing impurity concentration. Muller-Hartmann, Schuh, and Zittartz[22] have shown that allowance for the energy dependence of the scattering parameter can lead to the presence of a critical concentration on the $T_c(x)$ curve. Subsequently Shuh and Muller-Hartmann developed a self-consistent theory for superconductors with infinite magnetic-impurity density,[23] with numerical results that agree well with Ref. 22. At low concentrations Ref. 22 gives

$$\Delta T_c = -\frac{x}{8k_B N_B(0)} \frac{\pi^2 S(S+1)}{\ln^2(T_{c0}/T_K^*) + \pi^2 S(S+1)}, \tag{6}$$

where $T_K = T_K/12.9$, T_K is the Kondo temperature.

Our experimental data on the $T_c(x)$ dependence for the $Fe_x SnMo_6S_8$ system seem to point to the pesence of a critical iron concentration in this system. The experimentally observed $T_c(x)$ dependence does not differ very strongly from Eq. (2).[3)] A similar situation was noted in Ref. 24 for Fe and Cr impurities in PdH, where a deviation from Eq. (2) towards higher T_c at x close to x_{cr} was attributed to a decrease of the scattering parameter at $T_c < T_K$. It was noted in the same paper that the pair-breaking action of the magnetic impurity can weaken if antiferromagnetic spatial and temporal correlations occur in the system of impurity spins prior to establishment to the spin-glass state.

For the system investigated by us, the role of the correlations in the system of the magnetic moments of the impurity can be substantial, since the observed Curie temperature is quite high, approximately -5 at $0.02 \leqslant x \leqslant 0.10$.

When considering the deviation from relation (2) in TMC, account must be taken also of the following possibilities: at sufficiently large impurity density some of the iron atoms may occupy positions farther from the Mo atoms and close to (0,0,0). This can lead to an effective decrease of the density, i.e., to a deviation of the $T_c(x)$ dependence towards larger T_c.

In the Abrikosov-Gor'kov theory the ratio x_{cr}/x_{extr} is 0.691 [see Eq. (5)]. Here x_{extr} is the concentration obtained by extrapolating the initial slope of $T_c(x)$ to $T_c = 0$ (Fig. 4). The experimental ratio x_{cr}/x_{extr} obtained by us is somewhat larger, 0.83 at $P = 11$ kbar. If the experimental relation is represented in the form

$$T_c/T_{c0} = (1 - x/x_{cr})^n, \tag{7}$$

then

$$x_{cr}/x_{extr} = n.$$

It can be assumed in first-order approximation that n is independent of pressure. The pressure dependence of the critical concentration can then be repesented in the form

$$x_{cr}(P) = 0.83 T_c(0,P) \, |\partial T_c(P)/\partial x|_{x=0}^{-1}. \tag{8}$$

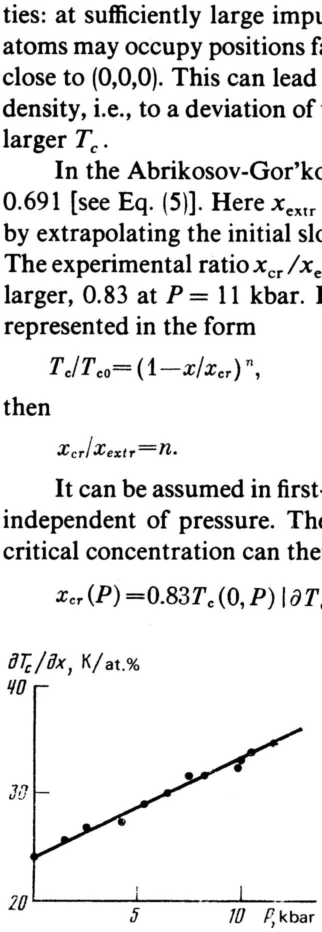

FIG. 6. Dependence of the initial rate $|\partial T_c/\partial x|_{x=0}$ of conductivity suppression of the pressure for $Fe_x SnMo_6S_8$.

The $T_c(0,P)$ dependence is shown in Fig. 3 (upper curve). The dependence of $|\partial T_c(P)/\partial x|_{x=0}$ on pressure is shown in Fig. 6. The relation (8) obtained as a result is shown in Fig. 4 by a dash-dot line on the T-P plane. At $P = 1$ bar Eq. (8) yields for x_{cr} an approximate value 0.061 (i.e., 0.41 at.%), in good agreement with the value obtained from the concentration dependence of T_c at $P = 1$ bar (Fig. 2).

Using the estimate (8) for the $x_{cr}(P)$ dependence we can describe our experimental data in the form

$$T_c(x,P) = T_c(0,P)\left(1 - \frac{x}{x_{cr}(P)}\right)^{0,83} = T_{c0}\left(1 - \frac{x}{x_{cr}(P)}\right)^{0,83}\left(1 - \frac{P}{P_{cr}(0)}\right). \tag{9}$$

Our results can be represented in the form of a $T_c(x)$ dependence at various pressures. Figure 6 shows the initial slope $|\partial T_c/\partial x|_{x=0}$ as a function of the applied pressure. It can be seen that the rate of superconductivity suppression by the Fe impurity increases linearly with increasing pressure. The increase of $|\partial T_c/\partial x|_{x=0}$ indicates an increase in the interaction between the conduction electrons and the impurity-atom magnetic moments. According to the Abrikosov-Gor'kov theory (Eq. (4)) an increase of the rate of superconductivity could occur as a result of an increase of the effective moment $\mu_{eff} = g[S(S+1)]^{1/2}$, where g is the Landé factor, of an increase of the state density $N_B(0)$, and finally of an increase of the exchange integral J. If it is assumed that this theory describes satisfactorily our experimental results, we can determine the cause of the increase of $|\partial T_c/\partial x|_{x=0}$ with pressure.

The result of our measurement of the magnetic susceptibility under pressure have shown that the Curie constant changes by not more than 5% when a pressure 5.3 kbar is applied. To account for the increase of $|\partial T_c/\partial x|_{x=0}$, the increase of C should reach ~20%. Thus, the increase of $|\partial T_c/\partial x|_{x=0}$ under pressure can apparently not be attributed to the increase, under pressure, of the effective magnetic moment of the impurity atom. The value of T_c of the sample with $x = 0$ decreases under pressure, and this decrease can be reconciled with the negligible decrease of the electron state density under pressure,[25] whereas an increase of $|\partial T_c/\partial x|_{x=0}$ calls for an increase of $N_B(0)$. Thus, it can be concluded that the increase of the derivative $|\partial T_c/\partial x|_{x=0}$ under pressure is due mainly to the increase of the exchange integral J.

To estimate the exchange integral J and the exchange constant ϑ we used the magnetic moment determined from the measurements of the susceptibility, approximately $4\mu_B$. The state density $N_B(0)$ can be calculated from Eq. (3) and from the data given in Ref. 26; it amounts to 0.49 state/eV·atom·spin. An estimate by Eq. (4) yields accordingly the values $J = 0.31$ eV and $\vartheta = 0.15$. For comparison, we cite the exchange integral in the $CdCr_x$ alloy, equal to 0.6 eV.[27] It must be noted that the value of J in $Eu_x Sn_{1-x} Mo_6Ch_8$ solutions is only 0.01 eV, see Ref. 14.

Assuming that $N_B(0)$ and μ_{eff} change insignificantly under pressure, we can estimate the increase of J and ϑ under pressure: at a pressure 12 kbar the exchange integral J and the exchange constant ϑ increase by approximately 20%.

As noted above, allowance for the Kondo effect in electron scattering by the magnetic moment of an impurity can alter substantially the $T_c(x)$ dependence. For the Kondo effect to exist the exchange integral J must be negative. The negative Curie temperature of the system investigated by us seems to indicate that the coupling is antiferromagnetic.[28] The presence of he Kondo effect at sufficiently high concentration x is probably attested to also by the low temperature minimum on the temperature dependence of the electric resistivity.

An important role is played in Ref. 22 by the parameter T_K^*/T_c. The strongest suppression of superconductivity should be observed at $T_K^* \approx T_c$.

The Kondo temperature and the exchange integral can be estimated also from the modified theory.[22] From Eq. (6) for the initial slope we obtain $T_K \approx 7$ or $\vartheta \approx 0.11$, in reasonable agreement with the estimate of ϑ in accord with the theory of Ref. 2.[4]

The foregoing estimates show that the Kondo effect can be significant for the system investigated by us. But it manifests itself probably only at sufficiently high iron concentration. For the concentration at which superconductivity exists our data can apparently be described by the Abrikosov-Gor'kov theory.

As already noted earlier,[8] strong suppression of superconductivity is observed in TMC with large density of states $N_B(0)$. An important role for compounds with large density of states is played by indirect exchange, which can lead to ferromagnetic instability similar to that considered in Ref. 30.

One cannot exclude the possibility that besides the previously considered behavior of superconductors with magnetic impurities at sufficiently high concentrations, two types of behavior may be realized with decreasing temperature. In one of them the system goes over into the spin-glass system, as a result of which the effect of the magnetic impurity on T_c is weakened[24] and the $T_c(x)$ dependence tends only asymptotically to the x axis. In the second case ferromagnetic instability sets in, and then the $T_c(x)$ curve crosses the x axis at a value of x smaller than the x_{cr} of the Abrikosov-Gor'kov theory.

CONCLUSION

The large value of the s-d interaction exchange integral, which leads to a strong suppression of the superconductivity by the iron impurity in TMC a with high density of states, and the considerable growth of the coefficient γ of the electronic heat capacity with increasing impurity concentration, offer evidence of the strong interaction of the conduction electrons with the magnetic moment of the iron impurity in the TMC. When an RE impurity is introduced into a TMC, the exchange integral of the s-f interaction is approximately one-thirtieth of the s-d interaction integral.

Our investigation yielded a sufficiently reliable $T_c(x)$ dependence, and led to the conclusion that a critical concentration exists for iron in the $Fe_xSnMo_6S_8$ system. Mesurement of $T_c(P)$ at various concentrations x confirms additionally the presence of a critical concentration, equal to about 0.061, i.e. 0.41 at.%.

Measurement of the dependence of T_c on the concentration x and on the pressure, as well as measurement of the effect of pressure on the magnetic susceptibility, leads to the conclusion that the exchange integral J increases approximately 20% at $P = 12$ kbar compared with $P = 1$ bar. The threefold increase of the derivative $|\partial T_c/\partial P|_{P=0}$ following introduction of only 0.3 at.% iron and the nonlinear $T_c(P)$ dependence at $x = 0.04$ can be attributed to the increase of the exchange interaction with pressure.

[1] It must be noted that the effect of an Fe impurity on T_c is much weaker in a number of superconducting compounds with A-15 structure. Thus, for example, addition of 5 at.% Fe into Nb_3Sn lowers T_c by less than 10%,[9] probably as a result of the absence of a localized magnetic moment at the iron atoms in these systems.

[2] The authors thank V. N. Samosyuk for the activation analysis.

[3] It must be noted that the $T_c(P)$ with negative curvature obtained by us for the sample with $x = 0.04$ can be approximately described by Eq. (2) if the density is replaced by the pressure:

$$\ln\frac{T_c}{T_{c0}} = \psi\left(\frac{1}{2}\right) - \psi\left(\frac{1}{2} + 0.14\frac{P}{P_{cr}}\frac{T_{c0}}{T_c}\right).$$

[4] We note, however that an estimate in accord with Eq. (6) should be approached with caution, since it was noted in a number of papers[24,29] that the experimentally determined initial slope of $|\partial T_c/\partial x|_{x=0}$ greatly exceeds the maximum allowed in Refs. 20–23, namely $|\partial T_c/\partial x|_{\max} = \frac{1}{8} k_B NB(0)$. For the system investigated in the present paper $|\partial T_x/\partial x|_{\max}$ is approximately 30 K/at.%: at $p = 1$ bar we have $|\partial T_c/\partial x|_{x=0} = 24$ K/at.% and at $P = 12$ kbar we have $|\partial T_c/\partial x|_{x=0} = 35$ K/at.%.

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