Change in physical properties of superconducting molybdenum sulfides after irradiation and subsequent annealing

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The changes in critical temperature T_c, upper critical field $H_{c2}(T)$, and electrical resistivity $\rho(T)$ of $Pb_{1-x}U_xMo_6S_8$ ($x \leqslant 0.5$) after thermal neutron irradiation ($\Phi \leqslant 7\times10^{18}$ cm^{-2}) and subsequent annealing at temperatures between 300 and 900 °C have been investigated. It is found that with increasing uranium content the effect of irradiation on the critical parameters and $\rho(T)$ increases sharply and a correlation is observed between T_c and the ratio $\alpha = \rho(300\text{ K})/\rho(15\text{ K})$. The increase of electrical resistivity induced by irradiation and subsequent annealing at intermediate temperatures ($T_a < 600$ °C) up to $\rho(15\text{ K}) \geqslant 10^{-2}\Omega$ cm results in a change in sign of the derivative $\partial\rho/\partial T$ which is negative over practically the whole range from 15 to 300 K. After annealing at T_a = 700–900 °C the quantities T_c, H_{c2}, and $\rho(T)$ return to approximately their previous values; in samples with $x = 0.3$ or 0.5 even a small increase of T_c and α is observed. The relation between possible alterations of the electronic structures of the compounds investigated and their characteristics in the superconducting and normal states is discussed.

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INTRODUCTION

There has been a large amount of work, both experimental and theoretical, on the effect of impurities, irradiation and other factors which significantly affect the properties of superconducting alloys and compounds.

Superconducting molybdenum chalcogenides AMo_6X_8 (A = Pb, Sn, Cu . . .; X = S, Se) with rhombodhedral structure have recently attracted much attention in this connection.[1–3] It has, for example, been shown[4,5] that a small amount of iron impurity produces a sharp suppression of the superconductivity of these systems. On the other hand, alloying of ternary molybdenum sulfides (TMS) with rare earths raises the critical parameters in a number of cases.[6,7] Molybdenum sulfides in which rare earths are introduced as the third component, i.e., A = La, Yb, or Dy, are also superconducting.[8,9] TMS's with actinides, unlike molybdenum sulfides with rare earths, do not show superconductivity.[6,10] We showed in previous work[10] that alloying the compound $PbMo_6S_8$ with actinides (U and Th) leads to a lowering of its critical parameters. It follows from these results[10] that the lowering of T_c in the system $Pb_{1-x}U_xMo_6S_8$ is most probably related to a reduction in the density of electron states at the Fermi surface $N(E_F)$. Since irradiation of such specimens can lead to additional change in their physical properties, it was of interest to elucidate how the presence of actinides would influence the nature of the change in critical parameters and in some other characteristics of molybdenum sulfides. Results are given here of studies of the effect of irradiation and subsequent annealing of T_c, on the upper critical field $H_{c2}(T)$, and on the electrical resistivity $\rho(T)$ of polycrystalline specimens of $SnMo_6S_8$ and $Pb_{1-x}U_xMo_6S_8$ ($0 \leqslant x \leqslant 0.5$).

THE EXPERIMENTS

Superconducting molybdenum sulfides of the required composition were prepared by direct synthesis from the basic components or from their sulfides, in a way similar to that described earlier.[11] After synthesis, the powders of the compounds were thoroughly ground in an agate mortar and cylindrical specimens of diameter 5–5.5 mm and length 10–20 mm were pressed out of them under a pressure of 15–20 kbar. The specimens were given a 24 h homogenizing anneal at 950–1000 °C in quartz ampoules filled with pure helium (P = 0.2 bar). The starting materials in this work for molybdenum sulfides with actinides were the same specimens[1)] as used earlier.[10] Since about ten specimens of each composition were required for the irradiation experiments, the original specimens were cut into several smaller ones with dimensions $1\times1\times5$ mm. An x-ray method was used to monitor the lattice parameters and phase composition of the specimens.

The $\rho(T)$ dependences between 2 and 300 K were measured by a standard 4-contact potentiometric method using a constant current with a value usually between 10^{-5} and 10^{-3} A, depending on the resistivity of the specimen. A Cu/Cu + Fe thermocouple was used for temperature measurement.

For greater accuracy in determining T_c a calibrated carbon resistance thermometer was used to plot transition curves of the specimens from the superconducting to normal state. The values of T_c were determined from the middle of the transition curve and the width of the transition ΔT_c was taken as the temperature interval corresponding to a change of resistance from 0.1 to 0.9 ρ_n, where ρ_n is the resistivity of the specimen in the normal state near T_c.

The upper critical field $H_{c2}(T)$ in the low temperature region was measured in a pulsed magnetic field, as in earlier work.[4,12] The specimen was then oriented perpendicular to the magnetic field and a current at a frequency 5–8 kHz and of amplitude 10^{-4}–10^{-3} A was passed through it.

The transition of the specimen from the superconducting to the normal state under the action of a 0.01 s duration

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pulsed magnetic field produced an unbalance signal which was amplified and fed to an oscilloscope with memory. To construct the transition curves $\rho(H)$ ($T = \text{const}$), the unbalance signal values used corresponded to the amplitude of the pulsed magnetic field where the derivative $\partial H/\partial t$ was a minimum. With a sufficiently reliable thermal contact between specimen and refrigerant, errors resulting from heating effects, which can be especially noticeable for a rapid rise of magnetic field, can be almost completely eliminated by using such a procedure.

Before irradiation the specimens were placed in high-purity aluminum foil or sealed in high-purity quartz ampoules filled with helium. To reduce the heating, the container with the specimens was cooled with liquid nitrogen when irradiating with γ- rays and with water when irradiating with thermal neutrons.

RESULTS

The change in T_c of $PbMo_6S_8$ and $SnMo_6S_8$ specimens irradiated with γ rays ($E \sim 25$ MeV) was less than 0.05 K for integrated fluxes $\Phi = 5\times10^{15}$, 2×10^{16} and 5×10^{16} cm^{-2}. Specimens of molybdenum sulfide with lead, alloyed with uranium irradiated with γ rays also showed practically no effect on T_c and $\rho(T)$ up to the maximum values of $\Phi = 5\times10^{16}$ cm^{-2}. For example, after irradiation of a $Pb_{0.7}U_{0.3}Mo_6S_8$ specimen ($\Phi = 5\times10^{16}$ cm^{-2}), its T_c was reduced by 0.07 K and the resistivity ratio $\alpha = \rho(300\text{ K})/\rho(15\text{ K})$ changed by 2%, which is only slightly greater than the uncertainty in the measurements.

A considerably greater effect of irradiation was obtained in experiments with thermal neutrons. It can be seen from Fig. 1 that with increasing uranium content in specimens of the system $Pb_{1-x}U_xMo_6S_8$, the effect of irradiation on the change in T_c and in transition width ΔT increases sharply. In specimens of $Pb_{0.5}U_{0.5}Mo_6S_8$ the transition

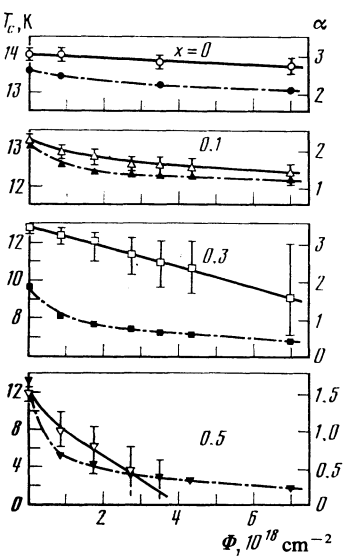

FIG. 1. Changes of critical temperature T_c, of the width of the superconducting transition (vertical intervals), and of the resistivity ratio $\alpha = \rho(300\text{ K})/\rho(15\text{ K})$ (dark symbols) for specimens of the system $Pb_{1-x}U_xMo_6S_8$ with various uranium contents, $x = 0$; 0.1; 0.3 and 0.5, after irradiation with thermal neutrons.

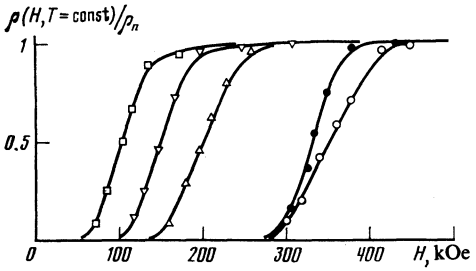

FIG. 2. Transition curves $\rho(H,\ T = \text{const})/\rho_n$ for the original $Pb_{0.7}U_{0.3}Mo_6S_8$ specimen (●) and after thermal neutron irradiation ($\Phi = 0.85\times10^{18}$ cm^{-2}, light symbols), measured in pulsed magnetic fields for various values of the temperature: ●,○) 4.2; △) 8; ▽) 9 and □) 10 K.

curves for $\Phi > 2.5\times10^{18}$ cm^{-2} are so smeared out that they remain in the resistive state down to 1.6 K.

Transition curves $\rho(H, T = \text{const})/\rho_n$ are shown in Fig. 2, measured in pulsed magnetic fields at three fixed temperatures for one of the irradiated specimens ($\Phi = 0.85\times10^{18}$ cm^{-2}) with uranium content $x = 0.3$. The transition curves $\rho(H, T = 4.2\text{ K})/\rho_n$ for an unirradiated specimen of the same composition are also shown here (dark symbols). It can be seen that after irradiation the upper critical field H_{c2} (4.2 K) for $x = 0.3$, determined from the middle of the transition curves, increased by about 5–7%. For specimens with high uranium content ($x = 0.5$) the upper critical field at 4.2 K after irradiation with a dose of 0.85×10^{18} cm^{-2} is almost halved as a result of a sharp fall in T_c. We note, however, that in both cases the derivative $\partial H_{c2}/\partial T$ (averaged over the linear part of the $H_{c2}(T)$ relation in the temperature interval from 0.5 T_c to T_c) increases by 10 to 15%.

It can be seen by comparing Figs. 1 and 3 that on thermal neutron irradiation, the reduction in T_c for the Chevrel phase, just as for A-15 compounds,[13–15] is accompanied by an increase in $\rho(300\text{ K})$ and a reduction in the resistance ratio α. The derivative $\partial\rho/\partial T$ retains its positive sign for $PbMo_6S_8$ and $Pb_{0.9}U_{0.1}Mo_6S_8$ specimens up to the maximum values of $\Phi = 7\times10^{18}$ cm^{-2}, while for specimens with larger uranium content (0.3 and 0.5) $\partial\rho/\partial T$ changes sign for $\Phi > 10^{18}$ cm^{-2} and becomes negative over practically the whole temperature range from 15 to 300 K.

The temperature dependence $\rho(T)$ for the initial $Pb_{0.7}U_{0.3}Mo_6S_8$ specimen (curve *1*) and for specimens of the

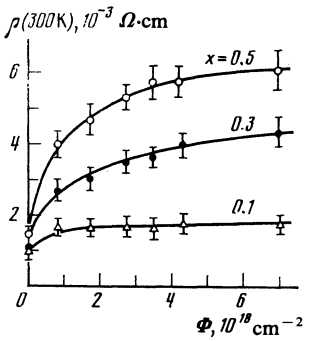

FIG. 3. Dependence of resistivity of $Pb_{1-x}U_xMo_6S_8$ specimens ($x = 0.1$, 0.3 and 0.5) on the fluence (integrated flux) Φ.

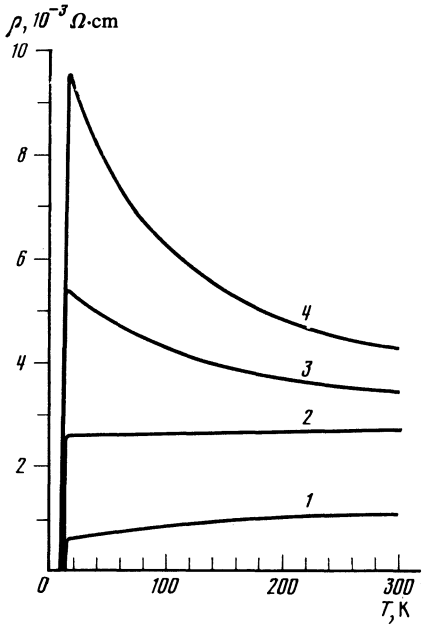

FIG. 4. Temperature dependences of resistivity of the original $Pb_{0.7}U_{0.3}Mo_6S_8$ specimen (curve 1) and of specimens of the same composition, irradiated with thermal neutrons for three values of Φ: curve 2) 0.85×10^{18}, 3) 2.6×10^{18}, and 4) 7×10^{18} cm^{-2}.

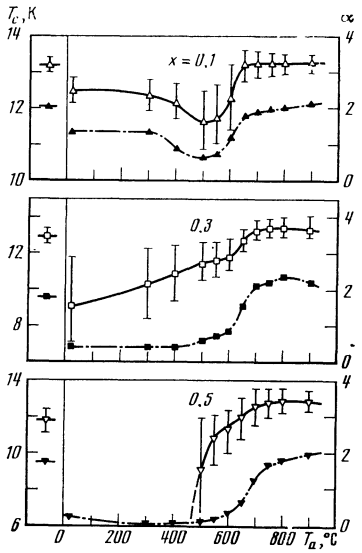

FIG. 5. Change in critical temperature T_c, width of the superconducting transition, resistance ratio α for $Pb_{1-x}U_xMo_6S_8$ specimens after two-hour anneals at fixed values of the temperature T_a. The symbols mean the same as in Fig. 1. The values of the same quantities for the original (unirradiated) specimens are shown on the left for comparison.

same composition, irradiated with thermal neutrons for three values $\Phi = 0.85\times10^{18}$, 2.6×10^{18} and 7×10^{18} cm^{-2} (curves *2, 3* and *4* respectively) are shown in Fig. 4.

The large increase in resistivity before the transition to the superconducting state is not usual for superconductors and is observed in relatively rare cases.[2)]

The specimens were annealed after irradition. To this end they were sealed in small-volume quartz ampoules filled with pure helium ($P = 0.2$ bar at 300 K), and inserted into a furnace. At each temperature the annealing time was usually 2 h. The dependences of the change in T_c, ΔT_c, the resistivity ratio α and ρ (15 K) on annealing temperature are shown in Figs. 5 and 6 for specimens of $Pb_{1-x}U_xMo_6S_8$ with $x = 0.1$, 0.3 and 0.5 irradiated with the maximum value of $\Phi = 7\times10^{18}$ cm^{-2}.

For comparison, values of the same quantities for the original unirradiated specimens are shown at the left of the figures. The existence in the $T_c(T_a)$ plot for the compound with $x = 0.1$ of a minimum that correlates with the minimum of the resistance ratio α is noteworthy. It can be seen by comparing Figs. 5 and 6 that the reduction in T_c and α in the temperature range 400 °C $< T <$ 500 °C is accompanied by a sharp increase in resistivity of the specimens. The temperature dependences of the reduced resistivity ρ/ρ (300 K) of specimens with $x = 0.1$ irradiated at $\Phi = 7\times10^{18}$ cm^{-2} (curve 3) and subsequently annealed for two hours at various values of the temperature T_a from 400 to 900 °C (curves 4–10) are shown in Fig. 7. The ρ/ρ (300 K) plots of the original specimen (curve 1) and after irradiation at lower values of $\Phi = 0.85\times10^{18}$ cm^{-2} (curve 2) are also shown in this figure. The corresponding plots of ρ/ρ (300 K) for specimens with higher uranium content $x = 0.3$ and 0.5 are shown in Figs. 8 and 9. The increase in resistivity of specimens with $x = 0.1$ after annealing at 400 °C $< T <$ 550 °C is, as can be seen by comparing Figs. 6 and 7, accompanied by a change in sign of the derivative $\partial\rho/\partial T$. Analysis of the results shows that the nature of the change in $\rho(T)$ for a specimen with $x = 0.1$ anealed at 400 °C is similar to that observed for specimens with larger uranium content, $x = 0.3$ and 0.5 after irradiation at $\Phi > 10^{18}$ cm^{-2}. For $Pb_{0.9}U_{0.1}Mo_6S_8$ specimens annealed at $T = 500$ °C, $\rho(T)$ varies practically linearly with T. It can be seen from Fig. 7 that as the annealing temperature is raised from 500 to 600 °C the derivative $\partial\rho/\partial T$ changes most strongly in the low temperature region 15 K $< T <$ 80 K.

After annealing at $T_a \geqslant 650$ °C the difference in the values of T_c, α, and the $\rho(T)$ dependence for the irradiated and

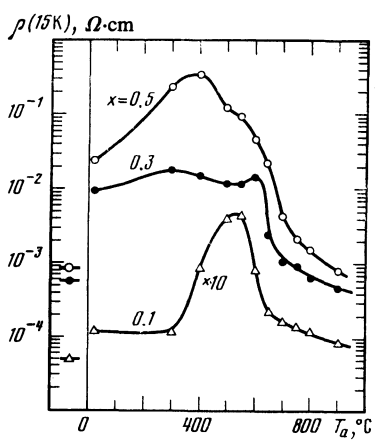

FIG. 6. Dependence of resistivity ($T = 15$ K) of $Pb_{1-x}U_xMo_6S_8$ specimens ($x = 0.1$; 0.3 and 0.5) on annealing temperature T_a (annealing time 2 h). To avoid confusion values of ρ(15 K) (T_a) for specimens with $x = 0.1$ are moved down by one decade. Values for the unirradiated specimens are shown at the left.

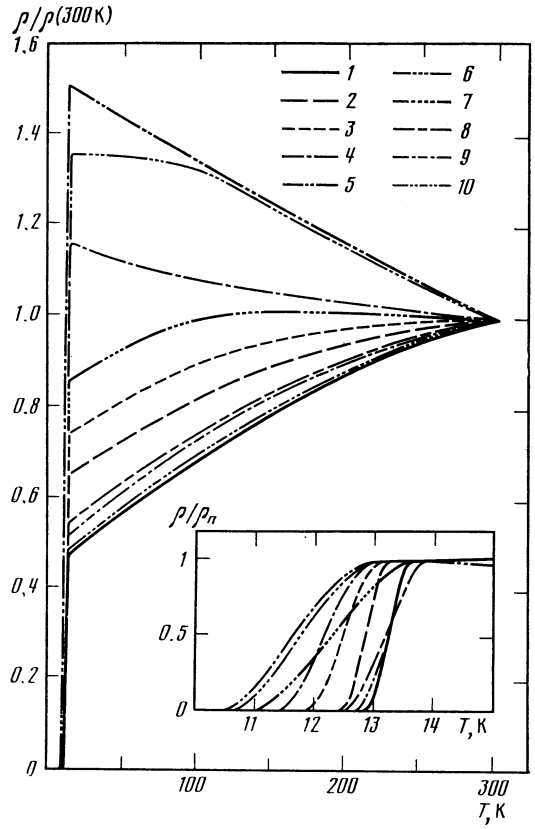

FIG. 7. Superconducting transition curves and temperature dependences of the reduced resistivity of the original $Pb_{0.9}U_{0.1}Mo_6S_8$ specimen (curve 1) and irradiated at $\Phi = 0.85\times10^{18}$ and 7×10^{18} cm^{-2} (curves 2 and 3). Curves 4, 5, 6, 7, 8, 9 and 10 correspond respectively to irradiation at $\Phi = 7\times10^{18}$ cm^{-2} and two-hour annealing at $T = 400$, 500, 550, 600, 650, 700 and 800 °C of specimens of the same composition.

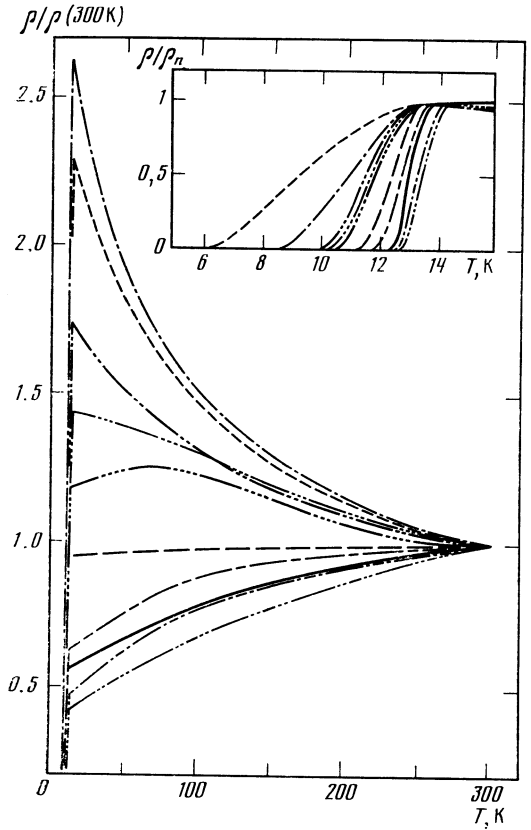

FIG. 8. Transition curves and temperature dependences of reduced resistivity of $Pb_{0.7}U_{0.3}Mo_6S_8$ specimens. The notation corresponds to the same Φ and T_a as in Fig. 7.

original specimens becomes small, and for T_a = 800–900 °C almost completely disappears. In this connection we note that the $\rho(T)$ dependence for alloyed unirradiated specimens with $x \leqslant 0.5$ is fairly close in shape to the $\rho(T)$ dependence for ternary molybdenum sulfides with lead ($x = 0$), the characteristic feature of which is the existence of regions linear in temperature in the range from 15.5 to 50–80 K[3)] with a subsequent monotonic reduction in $\partial\rho/\partial T$ on the high temperature side.

The resistivity of the system with $x = 0.3$ ($\Phi = 7\times10^{18}$ cm^{-2}) after annealing at T_a = 300–600 °C varies much less (see Fig. 6). As for specimens with $x = 0.1$, annealing at T_a = 300 and 400 °C decreases the ratio α (see Fig. 8). However, the form of the $\rho(T)$ plot remains practically the same. Annealing at 500–550 °C leads, as for specimens with $x = 0.1$, to a severe change in $\partial\rho/\partial T$ at temperatures $T < 80$ K, whereas at $T > 80$ K $\partial\rho/\partial T$ almost does not vary for specimens with $x = 0.3$. After annealing such a specimen after irradiation at T_a = 600 °C, a maximum appears in the region of 70 K in the $\rho(T)$ plot (curve 7 in Fig. 8).

It is possible that the maximum in $\rho(T)$ is connected with scattering of conduction electrons by intense low frequency Einstein-like modes (optic phonons), with characteristic frequencies for $PbMo_6S_8$ close to 5×10^{-3} eV or ~60 K.[18,19] Something similar is observed, for example, in the Pd-H system where the contribution to $\rho(T)$ from optic modes has a maximum at $T \approx 100$ K.[20]

As can be seen from Figs. 5 and 8, annealing of irradiated specimens with $x = 0.3$ at higher temperatures $T_a \geqslant 700$ °C leads to their T_c and α becoming higher than for the initial unirradiated specimen, and moreover higher than T_c and α of lightly alloyed specimens with $x = 0.1$.

Irradiation and subsequent annealing has a specially strong influence on the temperature dependences of the resistivity of specimens with large uranium content, $x = 0.5$ (see Fig. 9). The $\rho(T)$ dependence changes sharply and the ratio $\rho(4.2\text{ K})/\rho(300\text{ K})$ increases from 5.6 to 140 on irradiating such a specimen with $\Phi = 7\times10^{18}$ cm^{-2} and annealing at 300 °C. A subsequent two-hour anneal at 400 °C practically does not change the form of $\rho(T)$ except for the low-temperature region $T < 10$ K, which can evidently be regarded as evidence of the first signs of superconductivity. As the annealing temperature is raised, the effect of superconductivity on $\rho(T)$ at temperatures $T < 14$ K increases (curve 5 in Fig. 9) and after annealing at $T \geqslant 550$ °C the specimens become superconductors (see Figs. 5 and 9).[4)] Subsequent annealing at 800–900 °C raises T_c compared with the initial specimen by more than a degree, while ρ (15 K) and the ratio α increase to practically the original values.

By comparing Figs. 1 and 3, it can be seen that the increase in resistivity of $Pb_{0.7}U_{0.3}Mo_6S_8$ and $Pb_{0.5}U_{0.5}Mo_6S_8$ specimens through irradiation to values ρ (300 K) $\geqslant 3\times10^{-3}$

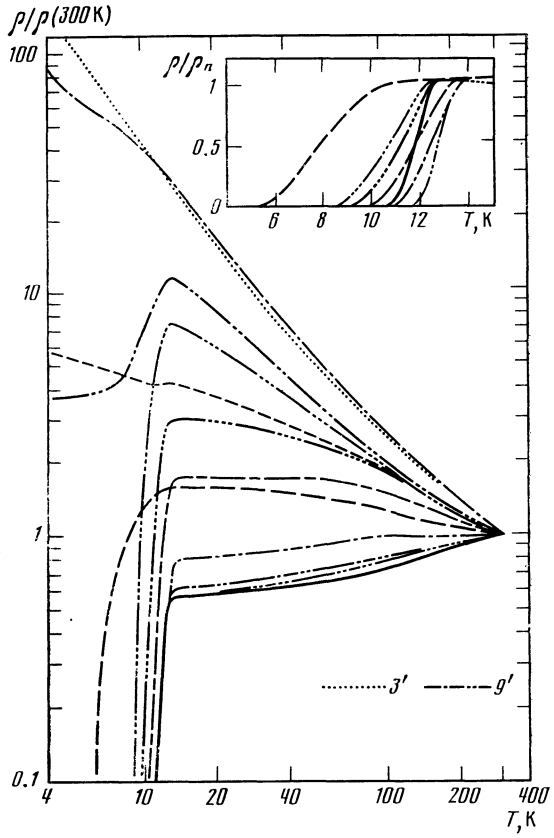

FIG. 9. Transition curves and, in a logarithmic scale, the dependences of reduced resistivity for $Pb_{0.5}U_{0.5}Mo_6S_8$ specimens. The type of curve corresponds to the same irradiation parameters and heat treatment as in Fig. 7. In addition, the dependences of $\rho(T)/\rho(300\,K)$ for specimens of the same composition are shown for $\Phi = 7\times10^{18}$ cm^{-2} and T_a = 300 and 750 °C (corresponding curves are 3' and 9').

Ω·cm leads to α becoming less than unity and $\partial\rho/\partial T$ becoming negative. In lightly alloyed specimens ($x = 0.1$) the value of ρ (300 K) remains less than 2×10^{-3} Ω·cm after irradiation up to the maximum value $\Phi = 7\times10^{18}$ cm^{-2} while $\partial\rho/\partial T$ retains its positive sign. A sharp growth in resistivity and a change in sign of the derivative $\partial\rho/\partial T$ is only observed in irradiated specimens with $x = 0.1$ after they have been annealed at 400–500 °C (see Fig. 6). A feature in this case is that $\partial\rho/\partial T|_{T=300\,K}$ becomes negative for values of ρ(300 K) $> 3\times10^{-3}$ Ω·cm. Annealing at $T_a > 600$ °C of specimens with various uranium contents ($0.1 \leqslant x \leqslant 0.5$) irradiated with $\Phi = 7\times10^{18}$ cm^{-2} leads to a sharp reduction in resistivity, while the sign of $\partial\rho/\partial T$ for values of ρ(300 K) $< 7\times10^{-3}$ Ω·cm changes to positive.

It can be concluded from the results that, independently of the composition of the specimens studied, the change in sign of $\partial\rho/\partial T$ in the high-temperature region occurs for approximately one and the same value of $\rho(300\text{ K}) \approx \rho(15\text{ K}) \approx (5\mp2)\times10^{-3}$ Ω·cm. It should be pointed out that among compounds with the Chevrel phase structure, a similar situation is observed, for example, on replacing sulfur by selenium in the system $Cu_{1.8}Mo_6S_{8-y}Se_y$.[21] In specimens of this system, for values of $\rho(300\text{ K}) < 10^{-2}$ Ω·cm the ratio $\rho(300\text{ K})/\rho_n > 1$, while for $\rho(300\text{ K}) > 10^{-2}$ Ω·cm the behavior of $\rho(T)$ becomes "nonmetallic" ($\rho(300\text{ K})/\rho_n < 1$). At about the same values $\rho(300\text{ K}) = 5\times10^{-3}$ Ω·cm a transition from a metallic to a nonmetallic form of conductivity is also observed on changing the composition of some other chalcogenides, such as $Ce_{2(1+x)}Se_{3(1-x)}$ (Ref. 22) and $BaPb_{1-x}Bi_xO$.[23]

DISCUSSION OF THE RESULTS

Our experiments have shown that irradiation of molybdenum sulfides alloyed with uranium by γ rays ($\Phi \leqslant 5\times10^{16}$ cm^{-2}) leads to practically no change in their T_c and resistance ratio α. An appreciable change in T_c and α is observed on irradiating specimens of $Pb_{1-x}U_xMo_6S_8$ with thermal neutrons ($E < 0.1$ eV) for $\Phi \geqslant 0.8\times10^{18}$ cm^{-2}. As Φ is increased, the resistivity of such specimens increases and the $\rho(\Phi)$ plot at $T = 300$ K has a tendency to saturation (see Fig. 3), while T_c and α decrease monotonically. These properties change especially sharply for specimens with large uranium content ($0.3 \leqslant x \leqslant 0.5$), for which α at $\Phi > 10^{18}$ cm^{-2} becomes less than unity while $\partial\rho/\partial T$ changes sign. Irradiation of specimens with the maximum uranium content ($x = 0.5$) leads to T_c already becoming less than 1.6 K for $\Phi > 3\times10^{18}$ cm^{-2}.

A further increase in resistivity is observed for $Pb_{1-x}U_xMo_6S_8$ specimens ($\Phi = 7\times10^{18}$ cm^{-2}) after annealing at intermediate temperatures ($T_a \leqslant 600$ °C). For example, ρ(15 K) for specimens with $x = 0.1$ increases several tens of times (see Fig. 6), the derivative $\partial\rho/\partial T$ changes sign (see Fig. 7), while T_c and α decrease (see Fig. 5). With an increase in annealing temperature to 700–900 °C, ρ(15 K) of the specimens falls while the values of T_c and α become practically the same as before irradiation. Even some increase in T_c, amounting to ~1 K for $x = 0.5$, is then observed for specimens with large uranium content. It is interesting to note that the critical temperature is also raised (from 11.8 to 13.6 K) for the ternary sulfide $PbMo_6S_7$ after fast neutron ($E > 10^5$ eV) irradiation and annealing at $T > 900$ °C.[24]

As is well known, the change in physical properties of specimens on irradiation is mainly associated with damage to the crystal lattice.[25] Since the effect of neutron irradiation on the change of properties of TMS's grows sharply with increasing uranium content, it is reasonable to assume that the interaction in the specimens between the neutron flux and the uranium nuclei, and in particular their fission, is the determining factor in the formation of radiation defects. On irradiating with thermal neutrons ($E < 0.1$ eV), the effective cross section for the fission reaction is especially high for the nucleus of the ^{235}U isotope which comprises $\sim0.7\%$ of natural uranium. Calculations show that for $\Phi = 7\times10^{18}$ cm^{-2} the number of acts of fission of uranium nuclei in $Pb_{0.5}U_{0.5}Mo_6S_8$ specimens is of the order of 5×10^{13} or 10^{-6} of the total number of all the atoms in the specimen. It can be seen by comparing the x-ray pictures of specimens before and after irradiation that the diffraction maxima are greatly reduced in magnitude. (We should point out that in the superconducting compound U_6Fe almost complete disappearance of the maxima, due to the crystal lattice becoming

amorphous, is observed for fission of $\sim 5\times 10^{-6}$ of the total number of uranium atoms.[26]) It can be concluded on the basis of these results that as a consequence of one fission act the radiation damage spans a relatively large volume containing up to 2×10^5 atoms. At the boundaries of the radiation-damage regions most defects will probably be caused by displacements of the most weakly bound of the Pb and U atoms from the crystallographic positions (0, 0, 0).

As was mentioned earlier,[10] the coefficient of the electronic specific heat γ and the electron density of states $N(E_F)$ decrease with increasing uranium content in TMS's with lead. Displacement of Pb and U atoms on irradiation can produce a change in the charge transfer from them to Mo_6 clusters and, as a result, to an additional change in $N(E_F)$. In addition, $N(E_F)$ can change because of spreading out of $N(E)$ by the field of the defects.[27,28]

If we use the expression for $\gamma = 2.2\times 10^{-5}(-\partial H_{c2}/\partial T)\rho_n^{-1}$ from earlier work,[29] assuming that it is applicable for the case considered here, we can attempt to estimate the change in

$$N(E_F)=3\gamma\,[2\pi^2 k_B^2(1+\lambda_{e-p})]^{-1}$$

on irradiation and annealing on the basis of our results. (Here k_B is Boltzmann's constant, λ_{e-p} the constant of the electron–phonon interaction.) It follows from the results given in Table I that γ decreases under the action of irradiation, with the largest change in γ occurring for specimens with large uranium content. Such a strong reduction in γ is evidently connected mainly with a fall in $N(E_F)$, especially if we consider that λ_{e-p} must at the same time also decrease.[5)]

It follows from the estimates obtained that $N(E_F)$ for a specimen with $x = 0.1$, for example, is almost halved as a result of irradiation at the maximum value of $\Phi = 7\times 10^{18}$ cm^{-2}. Since T_c then changes by less than 10%, it may be supposed that the great reduction in $N(E_F)$ must be compensated by a corresponding increase in the square of the electron–phonon interaction-matrix element[6)] $\langle J^2\rangle$ and, possibly, by an increase in the effective volume V_H of the hexagonal cell.[33]

In principle, due to the closeness of the Fermi level to the energy gap in the $N(E)$ dependence[34,35] and the existence of quasicongruent sections of the Fermi surface,[36] the system could be unstable relative to partial dielectrization of the electron spectrum.[37] As follows from band calculations,[34] the position of the Fermi level relative to the energy gap in Chevrel phases is mainly determined by the number of valence electrons, n_{ec}, per Mo_6 cluster. The value of n_{ec} in ternary molybdenum sulfides $A_xMo_6S_8$ can, for example, change because of charge transfer from atoms A to Mo_6 clusters.[38] As has been shown,[39] the critical temperature for TMS's reaches a maximum for the optimal value $n_{ec} = 22$. As n_{ec} increases, the Fermi level shifts[34] in the direction of the energy gap and reaches its center at $n_{ec} = 24$. As n_{ec} approaches 24, which is just what is necessary for the maximum number of covalent bonds (12) in a Mo_6 cluster, the degree of localization of conduction electrons in them increases, while $N(E_F)$ is correspondingly lowered. These changes in electronic structure are accompanied by a reduction in intercluster distances d_{Mo-Mo} (Ref. 38) and by a lowering of T_c.

Since V_H, T_c and $N(E_F)$ decrease[10] with increasing x in the system $Pb_{1-x}U_xMo_6S_8$, it can be proposed on the basis of the model of Yvon and Paoli[38] and of band calculations[34–36] that on replacing lead by uranium the charge transfer to Mo_6 clusters grows and n_{ec} is increased. The fact that $\rho(T)$ for the compound UMo_6S_8 is nonmetallic and that $T_c < 1.6$ K[6,10] favors this proposal. Displacement of Pb and U atoms on irradiation can lead not only to a smearing of $N(E)$ but to an increase in n_{ec}, which in turn produces a shift in E_F to the edge of the conduction band and a reduction[7)] in $N(E_F)$. We can expect that in this case for some critical value $E_F = E_c$ ("the mobility edge") to which corresponds a nonzero $N(E_F)_c$, a so-called Anderson transition to a nonmetallic state[40] will take place in the system disordered by irradiation. Since the difference $E_F - E_c$ is minimal in specimens with large uranium content, according to the previous discussion, they should be least stable with respect to Anderson localization. This is probably one of the reasons for the exceptionally strong influence of irradiation on superconductivity and $\rho(T)$ for specimens with $x = 0.3$–0.5.

Analysis of the temperature dependence of electrical resistivity can provide additional information on the form of the change in electronic structure of superconducting molybdenum sulfides on irradiation.

TABLE I. System $Pb_{1-x}U_xMo_6S_8$.

x	Φ, 10^{18} cm^{-2}	T_a, °C	T_c, K	ρ(15 K), $\Omega\cdot$cm	$\alpha = \frac{\rho(300\text{ K})}{\rho(15\text{ K})}$	ρ_{max}, $\Omega\cdot$cm	$-\frac{\partial H_{c2}}{\partial T}$, kOe/K	$\frac{H_{c2}}{(4,2}$, kOe/K	γ, $\frac{\text{erg}}{\text{cm}^3\cdot\text{K}^2}$
0	0	960	14.0	$3\cdot10^{-4}$	2.58	–	50±2	460±20	3700
	7	<100	13.8	$4\cdot10^{-4}$	2.13	–	52±2	470±20	3000
	7	900	14.0	$3\cdot10^{-4}$	2.6	–	–	–	–
0.1	0	960	13.2	$4.7\cdot10^{-4}$	2.05	–	46±2	400±20	2200
	7	<100	12.4	$1.25\cdot10^{-3}$	1.35	–	50±2	410±20	880
	7	900	13.25	$8.7\cdot10^{-4}$	2.15	$6\cdot10^{-3}$	45±2	400±20	1150
0.3	0	960	12.8	$6\cdot10^{-4}$	1.8	–	44±2	370±20	1600
	7	<100	9.2	$9.5\cdot10^{-3}$	0.45	$3\cdot10^{-3}$	50±2	310±20	120
	7	900	13.3	$4.7\cdot10^{-4}$	2.2	$7\cdot10^{-3}$	44±2	390±20	2060
0.5	0	960	11.8	$9\cdot10^{-4}$	1.75	–	42±2	330±20	1000
	7	<100	<1.6	$2.5\cdot10^{-2}$	0 25	$3\cdot10^{-3}$	–	–	–
	7	900	12.8	$8\cdot10^{-4}$	1.9	$7\cdot10^{-3}$	42±2	350±20	1100

It is considered[41] that the Anderson transition will occur for a definite value of the "minimum metallic conductivity" $\sigma_{\min} \approx 0.156\, e^2/z\hbar a_E$, where z is the coordination number and a_E is the distance between the localized states. If we take $a_E = a_R = 6.5$ Å for molybdenum sulfides (a_R is the lattice parameter) and $z = 4$, then from the formula above we obtain $\sigma_{\min} \approx 180\,\Omega^{-1}\cdot\text{cm}^{-1}$. The resistivity corresponding to this $(\rho_{\max})_T = 5.6\times 10^{-3}\Omega\cdot$cm is sufficiently close to the value obtained experimentally $\rho_{\max} = \rho(300\ \text{K}) = (3\text{–}7)\times 10^{-3}\Omega\cdot$cm for which sign reversal of $\partial\rho/\partial T|_{T=300\,\text{K}}$ is observed (see Table I) for $Pb_{1-x}U_xMo_6S_8$ specimens with various uranium contents ($0.1 \leqslant x \leqslant 0.5$), i.e., a transition occurs from metallic to nonmetallic resistivity.

Such a transition can, in principle, be due not only to Anderson localization but also to other causes, for example, to appearance of a relatively narrow energy gap or to a change in the nature of the electron–phonon interaction[42] for small mean free paths.

At an Anderson transition when E_F shifts to a region of localized states, the temperature dependence of the conductivity should according to theory[41] have an exponential forms, i.e., at low temperatures $\sigma = \exp(-B/T^{1/4})$ while at high temperatures $\sigma = \sigma_{\min}\exp[-(E_F - E_c)/k_B T]$. However, it follows from an analysis of our results that at low temperatures ($15\ \text{K} < T < 40\ \text{K}$) the temperature dependence of the resistivity of irradiated specimens of $Pb_{0.7}U_{0.3}Mo_6S_8$ can be approximated, within the limits of the experimental accuracy ($\sim 1\%$), by functions of the form $\rho(T) = \rho_A\cdot[1 + C_A(T_A/T)^{1/2}]$.

At higher temperatures ($40\ \text{K} < T < 200\ \text{K}$) the measured $\rho(T)$ can be described by logarithmic dependences of the form $\rho(T) = \rho_0[1 + C_0\log(T_0/T)]$. (In the above expressions, ρ_A, C_A, T_A, ρ_0, C_0 and T_0 are adjustable constants). The temperature dependences of resistivity for $Pb_{0.5}U_{0.5}Mo_6S_8$ specimens irradiated with thermal neutrons for three values $\Phi = 0.85\times 10^{18}$, 2.6×10^{18} and 7×10^{18} cm^{-2} are shown in Fig. 10 with coordinates ρ and log T. It can be seen from Fig. 10 that as Φ increases the temperature range over which the logarithmic law holds moves downwards.

Such a behavior of the resistivity with changing temperature for irradiated molybdenum sulfides recalls approximately the $\rho(T)$ dependences obtained[42] on taking into account interference effects in scattering of conduction electrons by phonons and by lattice defects. The influence of interference effects should grow as the defect concentration in the crystal increases. However, even in systems with limitingly short mean free path, $l \sim a_R$, the influence of these effects on $\rho(T)$ will only be appreciable at low temperatures $T < T_1 \sim \hbar\omega_0/k_B$, where ω_0 is the characteristic frequency of the phonon spectrum. For TMS's $\omega_0 \sim \omega_E \sim 60$ K.

It is possible that a more detailed analysis of the influence of interference effects on the features of the electron–phonon interaction molybdenum sulfides would lead to better agreement with experiment.

In interpreting the results one cannot entirely exclude from consideration other causes which could also lead to the observed logarithmic $\rho(T)$ dependence for irradiated specimens (see Fig. 10). Logarithmic $\rho(T)$ dependences in the temperature range from 5 to 100 K were observed earlier among

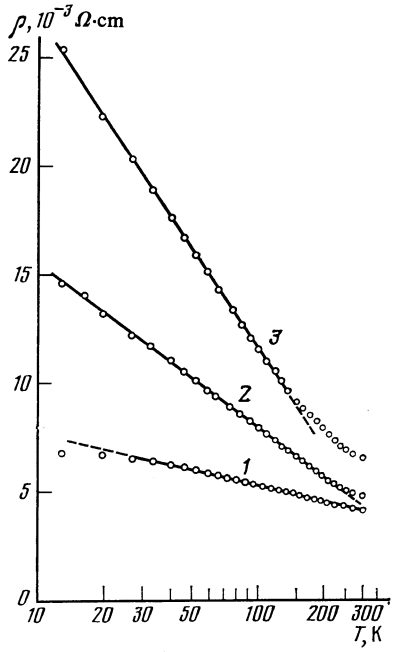

FIG. 10. Temperature dependences of resistivity (coordinates ρ and log T) for $Pb_{0.5}U_{0.5}Mo_6S_8$ specimens irradiated with thermal neutrons for three values of $\Phi = 0.85\times 10^{18}$, 2.6×10^{18}, and 7×10^{18} cm^{-2} (the corresponding curves are 1, 2 and 3).

molybdenum sulfides with the Chevrel phase structure in studies of $Ce_{1.2}Mo_6S_8$ specimens under hydrostatic pressure for $P > 40$ kbar.[43] The authors attribute the logarithmic increase in $\rho(T)$ with decreasing temperature to scattering of electrons by noninteracting localized magnetic moments (Kondo effect), which can arise on cerium atoms as a result of the close proximity of their 4-f levels to the Fermi surface.

In spite of the fact that anomalies in the temperature dependences of magnetic susceptibilities are found[10] in $Pb_{1-x}U_xMo_6S_8$ specimens, the question of a unique relation between the logarithmic dependences and the Kondo effect is still rather problematical for the systems studied. In particular, as has been noted,[44] dependences of the form $\rho(T) \sim \rho_0 \ln(T_0/T)$ are observed at low temperatures for nearly all amorphous alloys, regardless of whether they are diamagnetic, paramagnetic, or ferromagnetic. It seems that such a $\rho(T)$ behavior is a characteristic property of the majority of disordered systems with $\rho(300\ \text{K}) > 1.2\times 10^{-4}\Omega\cdot$cm. A dependence of the form $\rho(T) \sim \rho_0 \ln(T_0/T)$ can also in principle arise after irradiation of a system for which there is a logarithmic singularity in the electron density of states $N(E)$ near the Fermi level.[45]

The interpretation of the results obtained after annealing specimens at intermediate temperatures $T_a < 600$ °C is even more complicated. In this case the rise in resistivity (see Fig. 5) for specimens with small uranium content, $x = 0.1$, is accompanied by a change in sign of $\partial\rho/\partial T$ (see Figs. 6 and 7). It is not impossible that on annealing in the temperature range $T_a = 300$–550 °C, relatively large defects, formed on fission of uranium nuclei, can be dissipated into smaller defects, as a result of which the effective scattering of current carriers by them will be higher.

In a number of cases annealing even at relatively low

temperatures leads to a great change in the form of the $\rho(T)$ dependence. It can be seen from Fig. 9 that the experimental values of $\rho(T)$ obtained at temperatures from 15 to 100 K for $Pb_{0.5}U_{0.5}Mo_6S_8$ specimens ($\Phi = 7\times 10^{18}$ cm^{-2}), annealed at temperatures from 300 to 550 °C, can be approximated by power-law functions of the form $\rho(T)\sim\rho_0(T_0/T)^{\nu}$, where $\nu = 1\mp 0.2$; ρ_0 and T_0 being constants. For some specimens the $\rho(T)$ relation (see Fig. 8) is characterized by a maximum near 60 K, which as noted above, could be related to features of the scattering of conduction electrons by optic phonons.

For a detailed analysis of the $\rho(T)$ dependences for irradiated and annealed $Pb_{1-x}U_xMo_6S_8$ specimens, as well as changes in electronic structure, it is evidently also essential to take account of a change in their phonon spectrum.

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[1)]The specimens were annealed additionally at 950 °C for 24 h.

[2)]We previously observed a growth in resistivity before the superconducting transition when studying $V_{1-x}Al_x$ specimens[16] and also $Mo_6S_6J_2$ and $Mo_6Se_6J_2$ specimens.[12] A very small ($<7\%$) growth in resistivity at low temperatures is also observed after irradiation in a number of superconductors with the A-15 structure.[14,15,17]

[3)]The linear increase in resistivity at low temperatures for ternary molybdenum sulfides is evidently due to scattering of conduction electrons by low frequency optic phonons stemming from oscillations of the third component.

[4)]At any rate their resistivity decreases by not less than five orders of magnitude.

[5)]It follows from Refs. 30 and 31 that on lowering $N(E_F)$, the characteristic frequencies of the phonon spectrum increase (as a result of the weakening of the screening) while λ_{e-p} decreases (see also Ref. 13).

[6)]A similar situation apparently occurs in transition metals and their alloys, for which judging by the results of McMillan[32] the quantity $\lambda_{e-p}\sim N(E_F)\langle J^2\rangle/M\langle\omega^2\rangle$ depends on the denominator, while in the denominator the product $N(E_F)\langle J^2\rangle\sim 7$ eV/Å^2 remains approximately constant.

[7)]It is not excluded that the dielecric pairing[37] which then arises, as well as the causes discussed above, will be accompanied by a sharp reduction in T_c.

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