Effect of pressure on the properties of molybdenum sulfides in the superconducting and normal states

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The effect of pressure on the critical superconducting transition temperature T_c and on the critical magnetic field H_0 of the chalcogenides of molybdenum, Mo_5SnS_6 and $Mo_5SnGa_{0.5}S_6$, is investigated. The measurements were carried out in the pressure ranges 0–5 and 170–100 kbar. It is shown that T_c decreases with pressure, and dT_c/dp significantly exceeds the corresponding value for the ordinary metallic superconductors.

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As is well known,[1-4] the sulfides of molybdenum transform into the superconducting state at rather high temperatures and in this case have high critical fields. The quantity dH_{c2}/dT lies in the range from 30 to 60 kOe/°K for a number of sulfides of molybdenum.[4,5] Recently, anomalous magnetic properties have been discovered in the molybdenum sulfides.[6]

It has been suggested that the distance between the molybdenum atoms in the lattice of the compounds plays a very important role in the appearance of superconductivity of such systems.[7] It was proposed that an increase in this distance, brought about by the introduction of atoms of a third metal, for example, aluminum or gallium, has a favorable effect on the superconducting characteristics. On the other hand, such an assumption does not agree fully with the experiment data.[2]

It can also be assumed that T_c depends on the angles of the rhombohedral lattice, which change upon the introduction of a fourth component. In this connection, it is of interest to carry out an investigation of the effect of pressure on T_c of molybdenum sulfides.

For measurements in the low-pressure region, we used a constant pressure bomb prepared of beryllium bronze. A similar one was used in [8]. Bridgman anvils were used in the high pressure region. The samples were prepared by direct reaction of the components at T = 700°C and were placed in quartz ampules filled with helium. Cylindrical tablets were prepared from the resultant compound by a method similar to that described in [4]. The samples were cut from such tablets. Their dimensions were 1 × 2 × 5 mm. The magnetic field was produced by a superconducting solenoid.

The transition to the superconducting state was registered both from measurement of the resistance of the sample and also from the change in the inductance of the measuring coil in which the sample was located. In the recording of the superconducting transition, measurements of the resistance (or inductance) were usually made as a function of the temperature for constant magnetic field and pressure. In this case, the bomb which generated the pressure served as the thermal block. The temperature was measured with the help of a Cu-Cu + (0.01%) Fe thermocouple.

Figure 1 gives the superconducting transition curves for one of the $Mo_5SnGa_{0.5}S_6$ samples, plotted for various pressures at H = 0, while Fig. 2 shows the dependence of T_c on the pressure. As is seen from the figures, T_c for the samples studied falls off with increase in pressure. $dT_c/dp|_{p=0} \approx -1.9 \times 10^{-4}$ °K/bar, i.e., it is much larger than for pure superconducting materials. In the high pressure region, the derivative dT_c/dp falls off and is equal to -8.0×10^{-5} °K/bar near p = 100 kbar.

The resistivity ρ_n of the samples near the transition decreased upon compression. H_{c2} also fell off upon compression. The change of dH_{c2}/dT with pressure is shown in Fig. 3.[1)] If we estimate the value of the electronic specific heat from the values of dH_{c2}/dT and ρ_n,[2)] i.e., the Sommerfeld constant γ and its change with pressure, then it turns out that γ for $Mo_5SnGa_{0.5}S_6$ decreases with pressure by several percent at p ~ 4.5 kbar; here the value of dT_c/dp can be reconciled with the change in γ under compression.

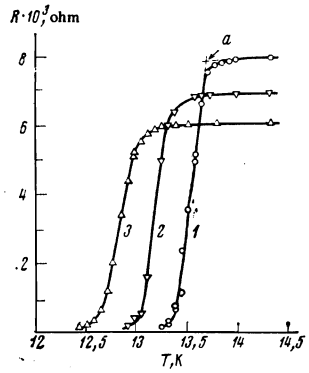

FIG. 1

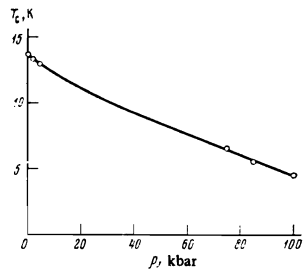

FIG. 2

FIG. 1. Superconducting transition curves of $Mo_5SnGa_{0.5}S_6$ for different pressures and H = 0. The temperature at the point a is taken as T_c. Curve 1–p = 0, curve 2–p = 1.8 kbar, curve 3–p = 4.4 kbar.
FIG. 2. Dependence of T_c of the pressure for $Mo_5SnGa_{0.5}S_6$.

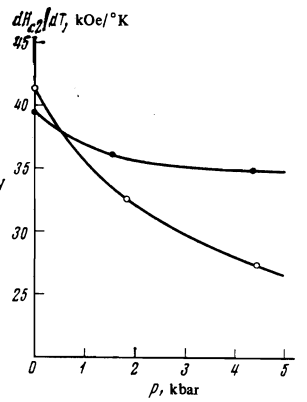

FIG. 3. Dependence of the quantity dH_{c2}/dT on pressure: ●–for Mo_5SnS_6, ○–for $Mo_5SnGa_{0.5}S_6$.

The data given above indicate that under hydrostatic compression the sample undergoes a decrease in its critical temperature, and the derivative of T_c with respect to pressure greatly exceeds the known values for superconducting metallic systems and has in the high pressure region a value close to the dT_c/dp of reduced titanate.[9] This might be regarded as a confirmation that the interatomic distances play the decisive role for T_c.[3)] However, if such a viewpoint were valid,[7] then the value ot T_c for $Mo_6Pb_{1.2}Se_8$ would increase with pressure.

As noted in [7], the interatomic distance d_{Mo-Mo} for Mo_3Se_4 is equal to 3.26 Å, which evidently corresponds to its optimal value. Therefore, an increase in the interatomic distance for alloys of the three components should lead to a decrease in T_c. Actually, T_c for $Mo_6Pb_{1.2}Se_8$ amounted to 3.6 °K, as against 6.25°K for Mo_3Se_8; here d_{Mo-Mo} = 3.49 Å. Decrease in the interatomic distance for $Mo_6Pb_{1.2}Se_8$ upon compression should lead to an increase in T_c, i.e., the derivative dT_c/dp should be positive.

The experiments that we have carried out do not confirm this. The derivative dT_c/dp for $Mo_6Pb_{1.2}Se_8$ turned out to be negative, as also for Mo_3Se_4, and amounted to $\approx -1.6 \times 10^{-4}$ °K/bar. Therefore, we can assume that although the interatomic distances are important for the critical temperature of molybdenum chalcogenides, they can not uniquely determine its value.

It is not excluded that in the determination of the factors which affect T_c one must take into account the angles of the rhomohedral lattice. It can also be assumed that the hydrostatic compression lowers T_c because of the increase in the magnetic interactions in the system. Taking into account the nonlinear dependence of the magnetic moment M(H), which is observed for $MO_5SnGa_{0.5}S_6$, [4,6], we see that such an assumption would be very probable. However, as was noted by us earlier,[4] different phases can be responsible for the superconducting and magnetic properties of the system. Thus, for example, we recently observed a nonlinear dependence of M(H) for Mo_5GaS_6.

Further study of the magnetic properties of chalcogenides and the effect of pressure on their properties will in all probability definitely establish the real causes of the magnetic and superconducting properties of the chalcogenides.

[1)]The values of dH_{c2}/dT for the sample of Mo_5SnS_6 are shown in the same figure; dT_c/dp for this sample was equal to -1.7×10^{-4} °K/bar.

[2)]For this case it is assumed that the measured value of ρ_n corresponds to ρ_{res} of the studied sample.

[3)]By interatomic distance here we mean the distance d_{Mo-Mo} between the molybdenum atoms of the neighboring octahedra.

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