Superconducting and magnetic properties of ternary chalcogenides of molybdenum

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It is shown that superconducting ternary chalcogenides of molybdenum have high critical magnetic fields which are apparently due to the high density of the electron states. Addition of a fourth component produces besides a small increase of T_c, a strong increase in the magnetic susceptibility in the normal state and a nonlinear dependence of the magnetic moment on the field.

It was recently demonstrated that certain ternary compounds of molybdenum chalcogenides are superconductors with relatively high superconducting-transition temperatures.[1,2] The highest values of T_c are possessed by compounds in which the third component is copper, tin, or lead.

It was of interest to measure the critical magnetic field of such systems and to investigate their magnetic properties, and in particular to measure the magnetic susceptibility in the normal state.

The superconducting ternary chalcogenides of molybdenum were prepared by direct synthesis from the original components in a quartz ampul in a helium atmosphere. Immediately after the synthesis, the width of the superconducting transition was several degrees. The samples were then pressed into pellets and

Composition	T_c, °K	$(dH_c\ dT)_R$ kOe/°K	$(dH_c/\ dT)_L$ kOe/°K	$\chi_{T \to T_c}$ $H \to 0$ CGS/g · 10^6
Mo_3CuS_4	10.8	20	15	0.05
Mo_5SnS_6	11,3	37	30	2,0
Mo_6PbS_7	12.5	41.5	37	1.9
$Mo_5SnAl_{0.5}S_6$	13.6	–	27	32
$Mo_5SnGa_{0.5}S_6$	13,3	–	28,5	97

annealed at 1000 °C for a day. After annealing, the width of the transition decreased to 0.1–0.3 °K. The sample compositions and the transition temperatures are listed in the table.

The plots of the superconducting transition in magnetic fields were obtained either by measuring the dc resistance or by an inductive method, by determining the change ΔL of the self-induction of the coil in which the investigated sample was placed. The measurement of ΔL was performed with the aid of an ac bridge at a frequency ~8 kHz. Magnetic fields up to 150 kOe were produced by a solenoid of the Bitter type.[1]

For all the investigated samples, in magnetic fields up to 150 kOe, the $H_c(T)$ plot was a straight line (see Fig. 1). The values $(dH_c/dT)_R$ determined by measuring the resistance exceeded somewhat the values $(dH_c/dT)_L$ obtained by the inductive method.[2] The width of the superconducting transition was practically independent of the magnetic field.

The magnetic susceptibility χ above T_c was measured with a string magnetometer in a cryostat for intermediate temperatures. The construction and operating principle of the magnetometer are described in detail in[3].

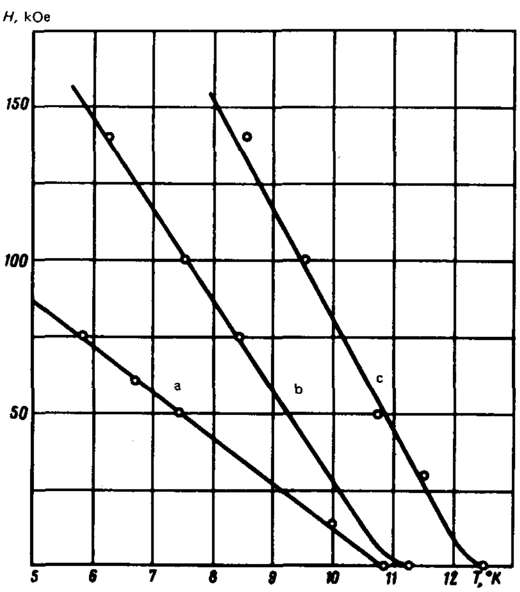

FIG. 1. Plots of $H_c(T)$ for ternary chalcogenides of Mo_3CuS_4 (a), Mo_5SnS_6 (b), and Mo_6PbS_7 (c), measured by the inductive method.

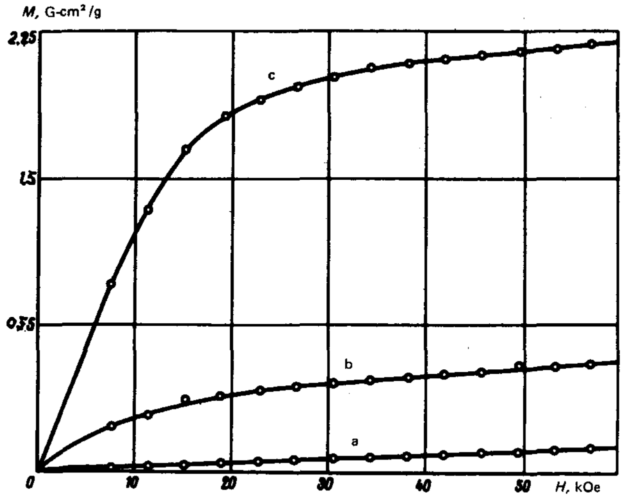

FIG. 2. Field dependence of the magnetic moment at 15 °K for Mo_5SnS_6 (a), $Mo_5SnAl_{0.5}S_6$ (b), and $Mo_5SnGa_{0.5}S_6$ (c).

The results listed in the table show that chalcogenides of molybdenum with tin as the third component have very high values of dH_c/dT. This may be due to the large density of states $N(0)$ of the conduction electrons. The rather large values of the magnetic susceptibility χ of these systems in the normal state agree with this assumption.[3]

As seen from the table, T_c, dH_c/dT, and χ increase on going from Cu to Sn and then to Pb.

We have also investigated Mo_5SnS_6 samples with Al and Ga as additives. Introduction of the fourth component leads apparently to a further increase of $N(0)$, for besides higher values of T_c and H_c, we obtained a much larger magnetic susceptibility than in the ternary compounds, and the $M(H)$ dependence became nonlinear at $T > T_c$. Figure 2 shows plots of $M(H)$ for Mo_5SnS_6 without the fourth component and with Al or Ga additives.

An investigation of the $M(H)$ dependences in a wide interval of temperatures has shown that for compounds with a fourth component the nonlinearity of $M(H)$ appears at $T > 30$ °K. At $T = 30$ °K and higher, the $M(H)$ curves were nonlinear for all the compounds.

Inasmuch as the nonlinearity of $M(H)$ could also be the consequence of the presence of ferromagnetic metals, a spectral analysis for Fe, Co, Ni, Mn, and Cr was carried out. With the exception of the iron, the content of which did not exceed 0.1%, no other elements were observed in any of the investigated samples, accurate to 0.001%.[4]

It follows from the presented data that introduction of Al or Ga as a fourth component leads not only to an increase of T_c, but also to a change of the magnetic properties in the normal state—larger values of χ at low H and nonlinear $M(H)$ curves in stronger fields. It is difficult to establish at present the connection between the growth of T_c and the change of the magnetic properties of the system. It would be necessary for this purpose to ascertain first the causes of the pecularities in the magnetic properties. In principle, the nonlinear field dependence of the magnetic moment could be the consequence of the following factors:

a) The presence of ferromagnetic impurities such as Fe. However, as stated above, the Fe content was quite small and an estimate of the possible moment due to the iron yields a value of M much smaller than the experimentally observed values.

b) The formation of ferromagnetic chalcogenides, which coexist with the superconducting phase. Although this is not very probable, such a possibility cannot be fully excluded.

c) The onset of magnetic ordering as a result of indirect exchange via the electron system. In this case, such an order should manifest itself only at low temperatures, and it should hinder the onset of superconductivity. However, if it is assumed that with further lowering of the temperature there can occur in the system superconducting correlations that eliminate the indirect exchange (because the Cooper pair has $s=0$), one can imagine that the system can go from a magnetically-ordered state into the superconducting state.

d) Nor can we exclude the possibility that at $T \sim 30\,^{\circ}\mathrm{K}$ the system experiences a phase transition, as a result of which its magnetic properties are radically altered.

e) Finally, it is also possible that the system investigated by us constitutes at $T < 30^{\circ}$ and $H > 20$ kOe a paramagnet in strong magnetic fields, in which, as is well known, a nonlinear $M(H)$ dependence is observed. We hope that further investigations will reveal the true cause of the singularities of the magnetic properties of the systems investigated by us.

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1)These measurements were performed at the International Laboratory of Strong Magnetic Fields at low temperatures in Wroclaw. Some of the measurements were performed in a superconducting solenoid up to 70 kOe.

2)The $(dH_c/dT)_R$ values measured by us by the electric resistance method agree with the data of[4].

3)This follows also from specific-heat data obtained in[5].

4)In addition, we determined the iron content in the Mo_5SnS_6 sample with Ga impurity by using the Mössbauer effect on Fe^{57}. No iron was observed, accurate to 0.05%.

1. V. T. Matthias, M. Marezio, E. Corenzwit, A. S. Cooper, and H. S. Barz, Science **175**, 1465 (1972).
2. O. Fischer, R. Odermatt, G. Bongi, H. Jones, R. Chervel, and M. Sergent, Phys. Lett. **45A**, 87 (1973).
3. N. E. Alekseevskiĭ, E. P. Krasnoperov, and V. G. Nazin, Dokl. Akad. Nauk SSSR **197**, 814 (1971) [Sov. Phys.-Dokl. **16**, 313 (1971)].
4. R. Odermatt, O. Fischer, H. Jones, and G. Bongi, Solid State Phys. **7**, L13 (1974).
5. R. Viswanathan and A. S. Lawson, Science **177**, 267 (1972).