

# High-pressure superconducting phase of the complex molybdenum sulfides $\text{SnMo}_6\text{S}_8$ , $\text{PbMo}_6\text{S}_8$ , and $\text{HgMo}_6\text{S}_8$

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High pressures and temperatures change the crystal lattice of the ternary molybdenum sulfides  $\text{SnMo}_6\text{S}_8$  and  $\text{PbMo}_6\text{S}_8$ , which have the Chevrel-phase structure, but leave these compounds superconducting. The high-pressure phases have a monoclinic structure and space group  $P2_1/m$ . The critical magnetic fields for the high-pressure phases are several times lower than those for the original Chevrel phases.

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Complex superconducting sulfides of molybdenum with the Chevrel-phase structure<sup>2,3</sup> were subjected to high pressures (30–80 kbar) and high temperatures (300–1100 °C) in Ref. 1. Over these pressure and temperature ranges the compounds retain the Chevrel-phase structure, simply acquiring new lattice parameters and, correspondingly, new superconducting parameters. It was shown in Ref. 1 that the critical temperature is a linear function of the volume of the hexagonal cell for the Chevrel phases studied.

In the present letter we are reporting additional data for systems containing lead and tin, treated at temperatures exceeding 1200–1300 °C and at pressures in the range 30–80 kbar. The treatment changes the crystal structure; the new phases remain superconducting.

The compound which is produced by treating the Chevrel phase of the composition  $\text{SnMo}_6\text{S}_8$  at  $T = 1200\text{--}1400$  °C and  $P = 30\text{--}70$  kbar has a superconducting transition temperature between 4.5 and 14.4 K, depending on the particular treatment conditions. For the better samples, the transition width is no greater than 0.3–0.4 K. Similar results were obtained in the synthesis of the compound  $\text{SnMo}_6\text{S}_8$  from a mixture of the corresponding elements in a high-pressure chamber. The superconducting transition temperature for the compound  $\text{PbMo}_6\text{S}_8$  increases by about 1 K, reaching 15.5 K, and the transition width is 0.2 K. Better results were obtained in the synthesis of the compounds from a mixture of the corresponding elements. Umarji *et al.*<sup>4</sup> have reported synthesizing the compound  $\text{HgMo}_6\text{S}_8$  with a Chevrel-phase structure which does not go superconducting above 4.2 K.

We produced a superconducting compound containing mercury through synthesis from the elements. This synthesis was carried out at  $P = 70\text{--}80$  kbar and  $T = 1500\text{--}1700$  °C. The temperature of the superconducting transition lay between 4 and 7 K. The resulting compound had a structure different from a Chevrel phase.

The transition temperatures of all the samples were measured by both resistive and inductive methods. Judging from the amplitude of the transitions measured on a

mutual-induction bridge, the superconducting phase usually occupies at least 80% of the volume of the sample. Grinding the sample into a powder left the transition amplitude approximately the same; i.e., the superconductivity is not of a surface nature.

The values of the critical magnetic fields represent an important distinction between these compounds and Chevrel phases. The critical magnetic fields of the corresponding Chevrel phases are record high values, exceeding 500 kOe (Ref. 5). The compounds which we produced at high temperatures and pressures have much lower critical magnetic fields. For the compounds  $\text{SnMo}_6\text{S}_8$  and  $\text{PbMo}_6\text{S}_8$ , for example, with critical temperatures of 14.4 and 15.5 K, respectively, the critical fields  $H_{c2}$  at 2 K are 65 and 70 kOe, and we find the derivatives  $(dH_{c2}/dT)_{T=T_c} = 6.5$  and  $-7.5$  kOe/K. For a  $\text{HgMo}_6\text{S}_8$  sample, with  $T_c = 6.3$  K, we find  $(H_{c2})_{T=2\text{K}}$  kOe and  $(dH_{c2}/dT)_{T=T_c} = -9.1$  kOe/K.

Analysis of x-ray powder diffraction patterns shows that the compounds produced at high temperatures and pressures of the systems containing lead, tin, and mercury have crystal structures similar to that of the compound  $\text{Mo}_2\text{S}_3$ , which has a monoclinic structure (group  $P2_1/m$ ; Refs. 6 and 7), but the intensity distribution among the diffraction peaks is different from that of  $\text{Mo}_2\text{S}_3$ . Most of the diffraction patterns of these compounds exhibit superstructural lines which show that the corresponding  $\text{Mo}_2\text{S}_3$  cell is apparently only a pseudocell. For  $\text{SnMo}_6\text{S}_8$ , its parameters are  $a = 6.095$  Å,  $b = 3.208$  Å,  $c = 8.637$  Å,  $\beta = 102.41^\circ$ . For  $\text{PbMo}_6\text{S}_8$ , the parameters are  $a = 6.108$  Å,  $b = 3.208$  Å,  $c = 8.645$  Å,  $\beta = 102.25^\circ$ , while those for  $\text{HgMo}_6\text{S}_8$  are  $a = 6.099$  Å,  $b = 3.208$  Å,  $c = 8.642$  Å,  $\beta = 102.25^\circ$ . Comparing these data with results available for the compound  $\text{Mo}_2\text{S}_3$ , for which  $a = 6.092$  Å,  $b = 3.208$  Å,  $c = 8.633$  Å,  $\beta = 102.4^\circ$ , we see that the parameters of the new phases obtained during the treatment in the pressure chamber are similar to those of  $\text{Mo}_2\text{S}_3$ . In certain cases the x-ray diffraction patterns of these phases have lines which correspond to molybdenum disulfide and the lines of the free metal—lead or tin (in the case of mercury, lines of mercury sulfide). Lines corresponding to a Chevrel phase are completely missing.

As expected, baking the compounds containing lead and tin led to the appearance of lines corresponding to Chevrel phases on the x-ray diffraction patterns. The critical magnetic fields increased sharply, assuming the characteristic values for samples with the Chevrel phase structure. It may thus be suggested that the new compounds produced by treatment at high pressures and temperatures are high-pressure phases representing a modification of the Chevrel-phase structure.

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