Appearance and disappearance of superconductivity in Eu-Mo-S under high pressure

M. K. Wu, P. H. Hor, R. L. Meng,* T. H. Lin, V. Diatschenko, X. Y. Shao,† X. C. Jin,‡ and C. W. Chu
Physics Department and Energy Laboratory, University of Houston, Houston, Texas 77004
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Nonbulk superconductivity with a pressure-dependent signal size has been detected but only between 2 and 43 kbar in $Eu_{1.2}Mo_6S_8$ quasihydrostatically. The results not only shed light on the occurrence of superconductivity in this compound but also provide insight to the nature of the superconductivity observed.

The Chevrel ternary compounds $Eu_xMo_6S_8$ (Eu-Mo-S) with $x \sim 1$ have been observed to become superconducting under hydrostatic pressure up to 19 kbar by various groups.[1–4] However, negative results[5,6] were also reported recently. Therefore, we have investigated the resistance of Eu-Mo-S both in the hydrostatic and quasihydrostatic environments. Nonbulk superconductivity has been induced abruptly by a pressure above certain critical values for both environments. The size of the superconducting signal as well as the superconducting transition temperature were found to increase and then decrease with pressure. The results not only shed light on the occurrence of superconductivity in Eu-Mo-S, but also provide insights to the nature of the pressure-induced superconductivity in this compound.

The $Eu_{1.2}Mo_6S_8$ (Eu-Mo-S) investigated in the present study was prepared according to the standard recipe published.[7] Powder x-ray diffraction patterns displayed only the expected Chevrel phase to within the resolution of the Phillips x-ray diffractometer used. No x-ray diffraction intensity analysis was made. Within the estimated resolution of the energy dispersion analysis of x-ray of 15%, the compositions of the compound agreed well with the nominal ones. Since the pressure-induced superconducting properties reported are not sensitive to the exact contents of the constituents,[2,8] no special effort has been attempted to account for the deviation of the composition from the stoichiometric one, namely, $EuMo_6S_8$. Several bar-shape samples were cut from the compacted sintered cylinder of Eu-Mo-S for the hydrostatic pressure measurements up to 20 kbar. Following these measurements, parts of the samples were powdered for the quasihydrostatic pressure measurements up to ~ 51 kbar. The high pressure was generated by a modified clamp technique, using a piston-cylinder arrangement for hydrostatic environment and a Bridgman anvil set (same as that used in Ref. 5) for the quasihydrostatic environment. The resistance R was determined by a standard four-lead ac method at 25 Hz. No short to ground of the kind reported in Ref. 5 was detected throughout our study. The experimental details have appeared elsewhere.[9]

The R of Eu-Mo-S exhibits a large negative temperature slope $\partial R/\partial T$ below ~ 120 K at ambient pressure. The pressure effect on the R-T behavior under the hydrostatic condition previously reported[1,2] has been reproduced. The R-T relationships under the quasihydrostatic condition were displayed in Fig. 1 for some of the pressure examined. The sudden R drop at low temperature under pressure has been identified with an onset of a superconducting transition, since a downward shift in temperature of the R drop by an increase of the measuring electrical current or magnetic field was observed. Nonbulk superconductivity above 1.2 K was induced by pressures only between 2 and 43 kbar as shown in Fig. 2.

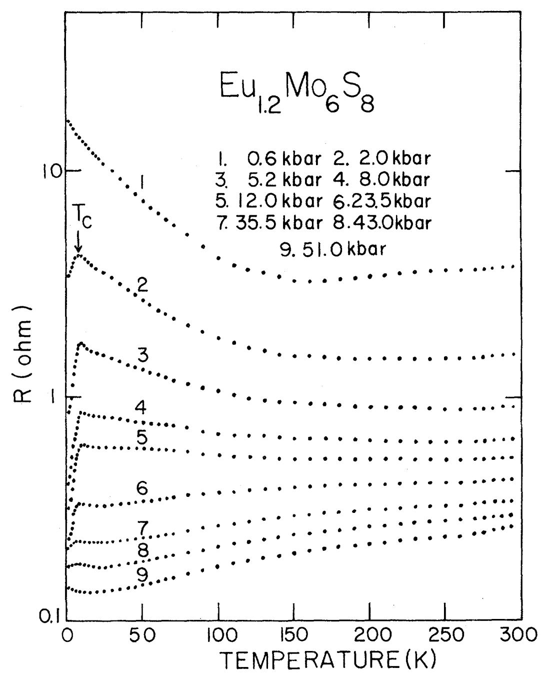

FIG. 1. Temperature dependence of resistance of $Eu_{1.2}Mo_6S_8$ at different quasihydrostatic pressures.

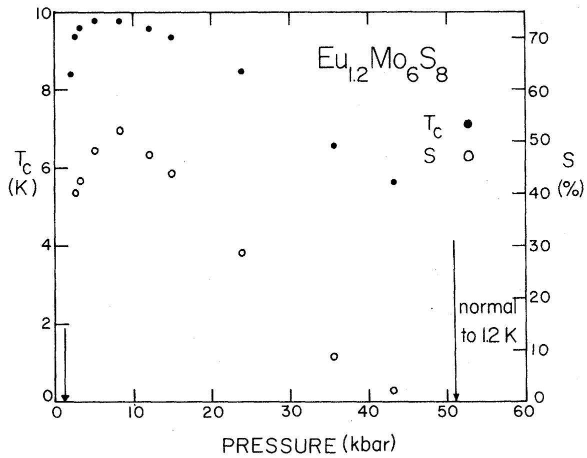

FIG. 2. Pressure dependences of the onset superconducting transition temperature T_c and the resistive superconducting signal size S.

While both the hydrostatic (H) and quasihydrostatic (QH) pressures induce nonbulk superconductivity in Eu-Mo-S, and suppress the magnitude of the negative $\partial R/\partial T$ at low temperature and the temperature below which $\partial R/\partial T$ becomes negative, the hydrostaticity of the pressure applied plays an important role in the detailed R-T behavior of the compound. This is evident from our observations: (1) Pressure induces superconductivity above only 2 kbar quasihydrostatically instead of 7 kbar hydrostatically; (2) the onset superconducting transition temperature T_c, defined in Fig. 1, peaks at 6 kbar (QH) instead of 11 kbar (H); (3) the resistive superconducting signal $S \equiv [R(T_c) - R(1.2\text{ K})]/R(T_c)$ decreases with the QH pressure above 7 kbar (Fig. 2) but saturates with the H pressure above 14 kbar to our highest H pressure of 20 kbar, and (4) the negative $\partial R/\partial T$ immediately prior to the superconducting transition persists up to 51 kbar (QH) even after the complete suppression of superconductivity but disappears above 11 kbar (H).

Results from the present study clearly demonstrate that superconductivity occurs only between 2 and 43 kbar (QH) with a mere 3% for S at 43 kbar (QH). This is consistent with the failure[5] to detect a sign of superconductivity in Eu-Mo-S down to 1.2 K under quasihydrostatic pressures of 90 and 130 kbar. Recently four Eu-Mo-S samples with different starting compositions were investigated[6] under hydrostatic pressure. It was found that only two of the four samples exhibited nonbulk superconductivity by ac magnetic susceptibility measurements above 7 kbar and none showed bulk superconductivity by dc magnetization measurements up to 14 kbar. However, in one of the two nonbulk superconducting samples, a small diamagnetic signal was detected below 7 K at ambient pressure through sensitive dc magnetization measurements, suggesting the existence of granular Mo in the samples. An unknown granular Mo-based material was therefore proposed[6] to account for the observed superconductivity[1–6] in Eu-Mo-S. Earlier, it was pointed out[10] that the superconducting properties of granular free Mo were not compatible with those observed in Eu-Mo-S under high pressure and in high magnetic field.

The present study shows that nonbulk superconductivity was induced abruptly by pressure and also destroyed abruptly by pressure (at least for the QH case). Since the rate of T_c suppression at high pressure is 1×10^{-4} kbar^{-1} for both the H and QH cases, an estimated pressure of 100 kbar would be required for the suppression of T_c to below 1.2 K. However, no superconductivity was observed below 1.2 K at 51 kbar QH pressure. In fact, the general R-T dependence at 51 kbar QH pressure shown in Fig. 1 is similar to that reported by Shelton and Moodenbaugh[5] at 130 kbar. The nonmonotonically varying S with QH pressure is particularly intriguing. Since in none of the measurements have we observed the completion of a superconducting transition, i.e., with a zero residual R, such an S-P behavior seems possible when the T_c of a broad superconducting transition shifts up and then down with pressure, especially in the presence of a pressure inhomogeneity of ± 5 kbar across the sample in the Bridgman anvil set. The different peak pressures in the S-P and T_c-P curves in Fig. 2 may then be attributed to an unusual pressure-dependent transition width. However, the continuous decrease of S to almost zero but with a T_c of 6 K at 43 kbar cannot be reconciled with the above explanation.

The results strongly suggest that the observed superconductivity in Eu-Mo-S is of the filamentary type, perhaps, occurring in the grain boundaries of the compound. This is consistent with our recent studies[11] on the pseudoternaries Eu-Mo-(S-Se). Furthermore, it is known that none of the elements or compounds of the constituents in the Chevrel ternary Eu-Mo-S displays the superconducting properties observed under high pressure[1–3, 10, 11] and high magnetic field.[4] The abrupt appearance and disappearance of the superconducting signal without associating with any apparent phase transition are surprising. One may then be tempted to suggest that interfaces[12] in a Chevrel ternary matrix or some subtle characteristics of the Chevrel structure may play a role in the observed superconductivity in Eu-Mo-S, although the exact nature of these possibilities remains unknown. The results further suggest that caution should be exercised in relating the bulk properties of the compound with the observed nonbulk superconductivity under pressure. Our preliminary study on Ba-Mo-S indicates that the above discussed observations under pressure may be quite common in the nonsuperconducting Chevrel ternaries. It should be pointed out that in almost all quasi-one-dimensional superconductors, S is always less than 100%. Currently, we are extending our experiments to lower temperature and higher H pressure.

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*Present address: Physics Institute, Chinese Academy of Sciences, Beijing, China.

†On leave from the Physics Institute, Chinese Academy of Sciences, Beijing, China.

‡On leave from the Physics Department, Nanjing Institute of Chemical Engineering, Nanjing, Jiangsu, China.

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