Observation of the Transition from Semiconductor to High-T_c Superconductor in $(Sn_xEu_{1-x})_yMo_6S_8$ under High Pressure

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Pressure-induced high-temperature superconductivity is observed in semiconducting $(Sn_xEu_{1-x})_yMo_6S_8$, where $0 \leq x \leq 0.1$ and $y = 1.0$ and 1.2, having a carrier concentration $\simeq 10^{19}/cm^3$ at 4.2 K as determined from Hall-effect measurements. Above a threshold pressure $\simeq 7$ kbar, superconductivity appears with $dT_c/dP \simeq 2$ K/kbar. The maximum superconducting temperature ($T_c \sim 10$ K), reached at ~ 12 kbar, represents the highest pressure-induced T_c in any semiconductor. For $P \geq 13$ kbar, the temperature-dependent resistance appears metallic.

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The Chevrel-phase compounds $Eu_yMo_6S_8$ (where $1 \leq y \leq 1.2$) and pseudoternaries $(Sn_xEu_{1-x})_yMo_6S_8$ exhibit interesting anomalous behavior,[1-3] quite different from the behavior predicted by the Abrikosov-Gor'kov theory[4] of well-localized magnetic moments in a superconducting matrix. $Eu_yMo_6S_8$ is not superconducting down to 17 mK,[5] whereas $(Sn_xEu_{1-x})_{1.2}Mo_6S_8$ has a high superconducting transition temperature ($T_c \sim 11$ K) for $x \geq 0.5$ but T_c falls rapidly to zero as x is decreased to about 0.1.[1,3] Maple and co-workers[2] observed a resistance anomaly in $Eu_{1.2}Mo_6S_8$ occurring at ~ 100 K below which the resistance increased sharply such that $R(4\text{ K})/R(300\text{ K}) \simeq 7$. We[3] also have established that a similar behavior is present in Eu-rich ($x \leq 0.2$) compounds in the system $(Sn_xEu_{1-x})_{1.2}Mo_6S_8$ and in $Eu_{1.0}Mo_6S_8$. Maple[2] proposed that the resistance anomaly arises from an interconfigurational fluctuation-induced Kondo-like effect. However, Mössbauer isomer-shift measurements on $Sn_{0.75}Eu_{0.25}M_6S_8$ (Ref. 6) and $Sn_{0.5}Eu_{0.5}Mo_6S_8$ (Ref. 7) compounds clearly show a well-defined Eu^{2+} resonance that does not shift with temperature down to 4 K. Similar conclusions were drawn from magnetization measurements on $(Sn_xEu_{1-x})_yMo_6S_8$.[3] Such results provide substantial evidence against valence fluctuations in these systems. We have found[3,5] from measurements of the magnetic and transport properties on $(Sn_xEu_{1-x})_{1.2}Mo_6S_8$ ($0 \leq x \leq 0.4$) that it is not possible to rationalize both properties of Eu-rich compounds in terms of existing theories of the Kondo effect. Instead it appears that the resistance anomaly in $Eu_{1.2}Mo_6S_8$ and Eu-rich pseudoternaries results from a decreasing density of conduction electrons, due presumably to a small gap at the Fermi energy E_F. Furthermore, we observed[3] a rather large negative magnetoresistance in those compounds exhibiting a resistance anomaly. This behavior is reminiscent of the transport properties found in a large number of magnetic semiconductors, in particular the Eu-based chalcogenides.[8]

Jarlborg and Freeman[9] have performed self-consistent linear-muffin-tin-orbital band-structure calculations on a number of Chevrel-phase compounds, including $Eu_{1.0}Mo_6S_8$. These calculations show that $Eu_{1.0}Mo_6S_8$ is a metal and exhibits a high density of states (DOS), $N(E_F)$, at the Fermi energy, which is known to be favorable for a high superconducting transition temperature. This high DOS, coming primarily from the Mo d-band electrons, is comparable to $N(E_F)$ found for the high-T_c $A15$ compounds. Just above E_F, a gap in the DOS appears which they ascribe to a bonding-antibonding "gap" of the metal d electrons. In agreement with experimental evidence,[3,6,7] they also find that the interaction between conduction electrons and the magnetic Eu^{2+} (spin-$\frac{7}{2}$) ions is small. Therefore, it appears that, if $Eu_yMo_6S_8$ were a metal, then this compound should be superconducting with a high T_c. The same conclusion might be drawn from the systematics of the

temperature-dependent resistance for the $(Sn_x Eu_{1-x})_y Mo_6S_8$ system as a function of x.[3]

We have studied the effect of pressure on the transport properties of sintered samples of $(Sn_x Eu_{1-x})_y Mo_6S_8$ for $0 \leq x \leq 0.1$ and $y = 1.0$ and 1.2. $Eu_{1.0}Mo_6S_8$ was chosen in particular so that a direct comparison could be made with the theory of Jarlborg and Freeman.[9] The samples were prepared with use of standard powder metallurgy techniques. X-ray and scanning-electron-microprobe analyses revealed the presence of a small amount ($\leq 5\%$) of second phase (probably MoS_2) and inclusions of EuS, with the second phase content being greatest in the ternaries $Eu_yMo_6S_8$. Chemical analysis showed the composition to be very close to the nominal concentrations of constituent elements. In addition, we have looked for possible lattice transformations using x-ray diffractometry and differential thermal analysis (DTA) down to 4 K and find no detectable phase transformations in these samples.

Simultaneous measurements of resistance and susceptibility changes of the samples were carried out in a self-clamped pressure bomb[10] as a function of temperature from 250 to 1.5 K and of pressure up to 21 kbar. The resistance was measured with use of a standard four-terminal ac technique, while the susceptibility signal was obtained from a secondary coil wrapped directly around the sample. A lead manometer situated in close proximity to the samples was used to determine the pressure. The accuracy of the pressure measurements was ±0.5 kbar and that of the temperature was better than 2%.

Representative results on the temperature-dependent resistance of our samples for various fixed pressures are shown in Fig. 1. For $P \sim 0$ kbar, we see a resistance anomaly beginning at ~100 K. As the pressure is increased, the magnitude of the resistance anomaly, e.g., $R(10\text{ K})/R(200\text{ K})$, is depressed and the temperature at which the anomaly first appears decreases slightly, indicating a narrowing of the gap. Furthermore, the absolute value of the resistance decreases substantially. At about 6–7 kbar, we see the onset of superconductivity, even though the resistance anomaly, i.e., semiconductorlike behavior, is still present. This behavior resembles that found in $Sn_{0.24}Eu_{0.96}Mo_6S_8$ at $P = 0$ kbar.[3] Susceptibility measurements indicate that the superconductivity is a bulk effect, although the inductively measured T_c onset is typically ~1 K below the resistive T_c onset. At still higher pressures, the resistance looks metallic, i.e.,

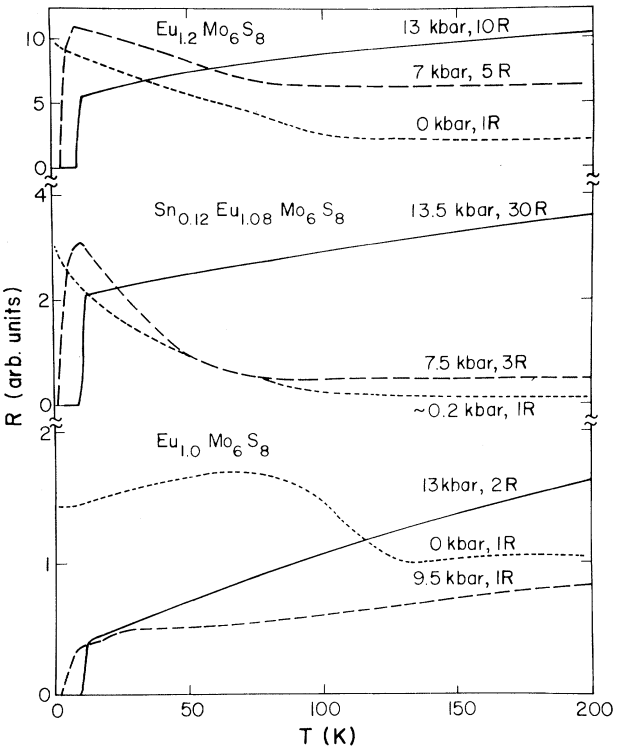

FIG. 1. Resistance R as a function of temperature T for three different sample compositions at various fixed pressures P. Note scale changes, designated as NR for some integer N, at different pressures. We estimate the accuracy of P to be ± 0.5 kbar.

$dR/dT > 0$, and T_c is high. The effect of pressure on $R(T)$ and on superconductivity is analogous to the ambient-pressure results observed in $(Sn_x Eu_{1-x})_{1.2}Mo_6S_8$ as a function of Eu concentration.[3]

The effect of pressure on T_c for the various samples is summarized in Fig. 2. For comparison we also show the pressure dependence of T_c for $Sn_{1.2}Mo_6S_8$ obtained by Shelton.[11] We see for all samples, that once a threshold pressure is exceeded, T_c rises steeply with pressure, saturates, and then decreases slowly with additional pressure. It is interesting that all three Eu-based compounds show nearly identical behavior, with T_c's roughly independent of Eu concentration; however, the data of Fig. 1 for $T > 100$ K suggest that the gap in the Sn-doped sample is narrower than that in $Eu_{1.2}Mo_6S_8$. The high-pressure dT_c/dP and T_c are also similar to that found for $Sn_{1.2}Mo_6S_8$.[11] The initial increase in T_c with P is very strong with $dT_c/dP \sim 2$ K/kbar. Possibly this portion of the curve is sensitive to inhomogeneities, so that dT_c/dP might be even larger with single crystal or very homogeneous samples. For clari-

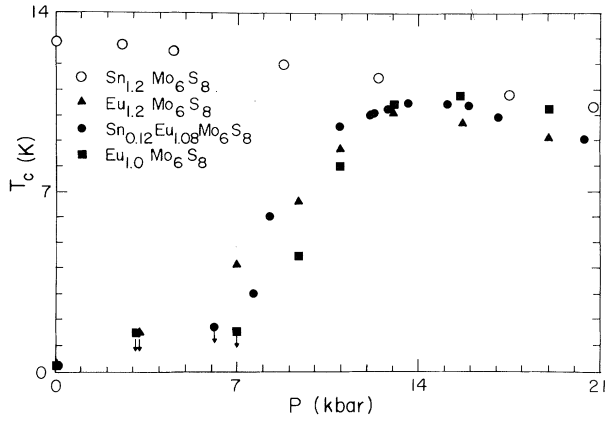

FIG. 2. Resistively measured superconducting midpoint transition temperatures T_c as a function of pressure P. The data for $Sn_{1.2}Mo_6S_8$ is taken from Ref. 11.

ty, we do not show transition widths ΔT_c in the data of Fig. 2, but note that the resistive transitions at low pressure, $6 \leq P \leq 10$ kbar, are generally broad, being typically 2–3 K. At higher pressures, ΔT_c sharpens considerably with $\Delta T_c \sim 0.5$–1.0 K.

In Fig. 3, we show the measured Hall coefficient R_H and carrier concentration n [$n \equiv (e|R_H|)^{-1}$] as a function of temperature for four different Eu concentrations in the system $Sn_xEu_{1.2-x}Mo_6S_8$ at ambient pressure. For $x \leq 0.24$, R_H changes sign from positive (holelike) to negative (electronlike) around 70 K. This temperature decreases with increasing x. We have determined that grain boundary and anomalous Hall-effect corrections represent minor errors in these data. We note that for $x \leq 0.24$, n is small, $\sim 10^{19}/cm^3$, at low temperatures and decreases with decreasing T; hence they are semiconductorlike. This is consistent with a small gap (~ 50 K) inferred from fitting $R(T)$ for $Sn_{0.12}Eu_{1.08}Mo_6S_8$ to a Fermi-like function. The $x = 0.24$ composition is superconducting with $T_c \sim 2.5$ K.[3] For $x = 0.48$, $n \sim 10^{22}/cm^3$ at all T, confirming a metalliclike conductivity. The temperature dependence of R_H below 70 K suggests that conduction takes place in two or more bands. We also have measured R_H for $x = 0.12$ at $P \sim 7$ kbar and find that $R_H > 0$ at all T, with $n \sim 6 \times 10^{19}/cm^3$, just above T_c. The use of n, as defined above, sets an upper limit on the electron carrier concentration $n_e < 10^{19}/cm^3$, which is comparable to the small electronlike n ($\sim 3 \times 10^{18}/cm^3$) at 4.2 K and $P \sim 0$ kbar.

There are several possible explanations for our observations:

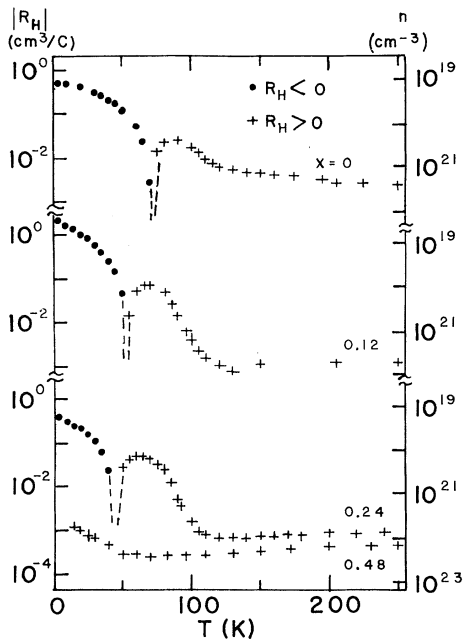

FIG. 3. Hall coefficient R_H and carrier concentration n [obtained from $n \equiv (e|R_H|)^{-1}$] as a function of temperature T for the system $Sn_x Eu_{1.2-x} Mo_6S_8$ at ambient pressure. Circles correspond to electronlike carriers; plusses correspond to holelike carriers. Samples with $x = 0.24$ and 0.48 superconduct at 2.5 and 11.3 K, respectively (Ref. 3).

(1) Superconductivity occurs in the low-n ($\leq 10^{20}/cm^3$) materials GeTe (Ref. 12) and $SrTiO_3$ (Ref. 13) presumably through an attractive electron-electron interaction mediated by intervalley phonon processes; however, the T_c's are low, ≤ 0.5 K. Similar mechanisms, in conjunction with impurity band effects, may be active in our samples for $P \geq 7$ kbar.

(2) A sharply varying DOS near E_F could explain the pressure- and temperature-dependent transport properties which we observe. However, the "universal" behavior of $T_c(P)$ is difficult to understand solely in terms of this model. Likewise such a strong variation in the DOS would suggest the occurrence of lattice instabilities. No DTA anomaly was observed in $Eu_{1.2}Mo_6S_8$ down to 4 K for $P \simeq 0$ and 12 kbar.

(3) An increased carrier concentration by $4f$ delocalization or valence change under pressure is also possible. Additional experiments (e.g., Mössbauer, magnetization and Hall effect) under pressure are in progress to elucidate these possibilities.

(4) Exotic mechanisms, such as proposed by

Abrikosov,[14] while appealing, are still quite speculative.

(5) We note that the transport characteristics which we observe at ambient pressure are similar to those found in SmB_6.[15]

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