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Study of lattice instabilities in Sn$_x$Eu$_{y-x}$Mo$_6$S$_8$ ($y = 1.0$ and $1.2$)

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An anomaly in the heat capacity of Eu$_{1.3}$Mo$_6$S$_8$ at $\sim 120$ K ($T_0$) has been observed and identified as a structural transformation. The heat capacity, electrical resistance, and Hall coefficient for the Eu-rich pseudoternaries have been measured under pressure to obtain the pressure dependence of $T_0$. The depression of $T_0$ by pressure is used to explain the pressure dependence of the superconducting transition temperature and the anomalous temperature dependence of the critical field.

The unusual transport properties of the ternary compound Eu$_{x}$Mo$_6$S$_8$ are currently of great interest. At ambient pressure the electrical resistance ($R$) and carrier concentration ($n$) (obtained from Hall-effect data) show an abrupt change from metallic-like behavior ($dR/dT \geq 0$ and $dn/dT \sim 0$) for $T \geq 100$ K to “semiconductor-like” behavior ($dR/dT < 0$ and $dn/dT > 0$) for $T \leq 100$ K, with no evidence of superconductivity. The Hall data indicate that the absence of superconductivity results from low values of $n$ ($\sim 10^{18}$ cm$^{-3}$ at 1.5 K) in apparent conflict with band calculations, based on the rhombohedral crystal structure determined at room temperature, which predict that EuMo$_6$S$_8$ should be a metal and is likely to be a high-transition-temperature superconductor because of a high density of states. However, superconductivity has been obtained by application of pressure ($P$) greater than $\sim 7$ kbar, with a peak in superconducting transition temperature ($T_c$) at $\sim 11$ K for $P \sim 14$ kbar.

Comparison of the transport and superconducting properties of Eu$_{1.3}$Mo$_6$S$_8$ with those of other ternaries suggests that the resistance anomaly at $T \sim 100$ K is associated with a lattice transformation. In particular, the abrupt change in $dR/dT$ at $\sim 100$ K is rather like that observed in CuMo$_6$Se$_8$, where it is associated with a transformation from rhombohedral symmetry at high temperature to a triclinic distortion at low temperature. Furthermore, a peak in $T_c(P)$ has been observed in CuMo$_6$Se$_8$, Cu$_{0.71}$Mo$_6$Se$_4$, and ZnMo$_6$S$_8$, all of which have similar lattice instabilities, while no such peak is observed in nontransforming ternaries.

In this Brief Report, we present data on the pressure and temperature dependence of the heat capacity ($C$), resistance, and Hall coefficient of Eu$_{1.3}$Mo$_6$S$_8$ and Eu-rich pseudoternaries Sn$_x$Eu$_{y-x}$Mo$_6$S$_8$. These data confirm the existence of a lattice transformation and yield the pressure dependence of the transformation temperature ($T_0$). Using our high-pressure data, we then explain for the first time the anomalous electrical, magnetic, and superconducting properties of Eu$_{1.3}$Mo$_6$S$_8$ and resolve the apparent conflict between the observed transport properties and the band calculations.

The samples used in this work are the same as those described in Ref. 1. The heat capacity was measured at ambient pressure by the static adiabatic method using a precalibrated platinum thermometer and at pressures up to $\sim 8$ kbar by the steady-state ac method using a Constantan heater driven at 1.5 Hz and a copper-Constantan thermocouple whose output (3 Hz) was detected by a lock-in amplifier. Techniques for generation of high pressures and measurement of resistance and Hall coefficient were as described in Ref. 1.

Figure 1(a) shows the static heat-capacity data between 80 and 150 K measured on several Eu$_{1.3}$Mo$_6$S$_8$ chips held together with GE 7031 varnish. Because of the small available mass ($\sim 3$ g) of sample in comparison with the copper block in our apparatus, the relatively small contribution ($\sim 15\%$) from the sample to the total measured heat capacity resulted in a scatter in the data of $\sim 10\%$. However, it is clear that there is an anomaly in the heat capacity ($C$) at $T_0 \sim 120$ K. The dashed line is drawn simply
to aid the reader. In this temperature range, $C$ is dominated by the lattice and hence this anomaly is likely to be associated with a lattice transformation from the high-temperature rhombohedral structure to the low-temperature triclinic distortion as in CuMo$_2$S$_6$, Cu$_2$Mo$_5$Se$_6$, and ZnMo$_2$S$_6$. Figure 1(b) shows the temperature dependence of $C$ measured on a $\sim 10$-mg sample of Eu$_{1.2}$Mo$_6$S$_8$ by the ac method. An anomaly is visible at $T_0 \sim 77$ K. The magnitude of the anomaly diminished rapidly with increasing pressure, and we were unable to observe the transition in $C(T)$ data above $\sim 8$ kbar.

Figures 2(a) and 2(b) show the electrical resistance data for Eu$_{1.2}$Mo$_6$S$_8$ and Eu$_{1.8}$Mo$_5$S$_6$ at ambient pressure, found by the intercept of two tangent lines as shown in Fig. 2(a), takes place at $T \sim 115 \pm 10$ K, which coincides with $T_0$ in Fig. 1(a) within our experimental error and is identified as the structural transformation temperature. The pressure dependence of the anomalies in $R$ (determined by the tangent-lines method) and $C$ for the pseudoternaries with different Sn concentrations are presented in Fig. 3(a); from these data we infer that $T_0$ decreases with increasing $P$ and is suppressed to 0 K at $P \sim 12$ kbar. Figure 3(b) displays $T_0$ as a function of Sn concentration $x$ for Sn$_x$Eu$_{1.2}$Mo$_5$S$_6$ at ambient pressure. $T_0$ decreases with increasing $x$, although $T_0$ for $x = 0.12$ deviates somewhat, perhaps due to departure from stoichiometry in this sample (actual composition Sn$_{0.05}$Eu$_{1.125}$Mo$_5$S$_6$). This $x$ dependence indicates that Sn stabilizes the high-temperature rhombohedral phase as does pressure.

Figure 4 shows the carrier concentration as defined by the one-band formula, $n = (e|R_H|)^{-1}$, where $R_H$ is the Hall coefficient, for Eu$_{1.2}$Mo$_6$S$_8$ for $P$ up to 14.2 kbar. For $P \leq 5.4$ kbar, $R_H > 0$ at high temperature and $< 0$ at low temperature; we can see that the temperature at which $R_H = 0$ decreases with increasing $P$. For $P \geq 8.5$ kbar, $R_H > 0$ at all temperatures. Comparison of Fig. 4 with ambient-pressure Hall data for Sn$_x$Eu$_{1.2}$Mo$_5$S$_6$ confirms that the substitution of Eu by Sn has an effect similar to application of pressure. From Fig. 4 we also find that the temperature at which the slope of $R_H$ with respect to $T$ (at a given pressure) changes most rapidly agrees roughly with $T_0$ shown in Fig. 3(a).

Several conclusions can be drawn from our observations:

1. We identify $T_0$ as a structural transformation.
2. The data of Fig. 3(a) show that for $P \geq 12$ kbar the rhombohedral “high-temperature” phase is
FIG. 3. (a) Pressure dependence of structural transformation temperature ($T_0$) for various pseudoternaries Sn$_y$Eu$_{1.2}$Mo$_6$S$_8$ ($y = 1.0$ and 1.2). (R) and (C) refer to data taken from anomalies in resistance and heat capacity, respectively. (b) Variation of $T_0$ with Sn concentration ($x$). (All data from anomalies in resistance.)

retained down to $T \sim 0$ K. The transport data on this phase are characterized by relatively large $n$, positive $dR/dT$, and high-$T_c$ superconductivity and thus are consistent with a metallic band structure and high density of states. The fact that the variation of $T_c$ with pressure in Eu-rich samples above 12 kbar is nearly the same as that of metallic Sn$_{1.2}$Mo$_6$S$_8$, as pointed out in Ref. 1, is further evidence that Eu$_{1.2}$Mo$_6$S$_8$ remains metallic down to low temperatures for $P \geq 12$ kbar. Our results therefore explain the abrupt appearance of high-$T_c$ superconductivity upon application of pressure and support the band calculations of Jarlborg and Freeman, which of course apply only to the “high-temperature” rhombohedral phase.

FIG. 4. Temperature dependence of the carrier concentration, $n = (e|R_H|)^{-1}$ at various pressures. ($R_H$ is the Hall coefficient.)

(3) Our data on the “low-temperature” phase are characterized by rather small $n$, positive $dn/dT$, and negative $dR/dT$, suggesting the opening of a gap at the Fermi surface upon cooling below $T_0$. The fact that $n$ and $R$ level off as $T \to 0$ suggests that the gapping is partial rather than complete. Our finding that $dn/dP$ is positive at low temperature (Fig. 4), suggesting that the gap diminishes with increasing pressure, is qualitatively consistent with the depression of $T_0$ under pressure. Such gapping might be due to charge-density waves. The appearance of gapping at $T < T_0$ suggests that the low-temperature phase may have symmetry lower than that of the high-temperature phase and could therefore be triclinic as in CuMo$_3$S$_4$.

(4) The depression of $T_0$ to 0 K for $P \geq 12$ kbar is consistent with the anomalous temperature and pressure dependence of the critical field observed$^3$ in Eu-rich samples above 12 kbar. Furthermore, the fact that $dn/dP$ is positive explains why the negative conduction-electron spin polarization at the superconducting Mo site originating from the Eu$^{2+}$, as obtained from the critical-field data,$^3$ increases with increasing $P$ since high spin polarization requires large $n$.

High-pressure x-ray work is currently in progress to
determine the pressure dependence of $T_0$ more precisely.

Since the completion of our work we have been informed that Baillif, Dunand, Mueller, and Yvon\textsuperscript{10} have observed the lattice transformation by x-ray diffraction at $T \sim 110$ K and have found the low-temperature phase to have the triclinic crystal structure (distortion).

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