Transport properties and the nature of the low-temperature phase of $EuMo_6S_8$

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Quantitative transport measurements on several hot-pressed and melted $EuMo_6S_8$ samples are presented. The low-temperature results can be interpreted in terms of a model of two weakly overlapping bands and show that $EuMo_6S_8$ is a semimetal below the phase transition at 110 K. The anomalous magnetic field dependence of the transport properties in this phase can be explained as a result of exchange splitting of the two overlapping bands.

I. INTRODUCTION

Since the discovery of superconductivity in the magnetic rare-earth-metal molybdenum sulfides[1] seven years ago, $EuMo_6S_8$ is still one of the most intriguing compounds in the context of magnetic superconductors and the subject of current investigations. Especially, the absence of superconductivity in the Eu compound as well as the anomalous behavior of the superconducting transition temperature T_c and the upper critical field H_{c_2} in the Eu-rich region of the pseudoternary $Eu_{1-x}Sn_xMo_6S_8$ (Ref. 2) have attracted a great deal of attention. Recently Baillif *et al.*[3] have observed a structural phase transition in $EuMo_6S_8$ at 110 K, where the system transforms from the rhombohedral high-temperature phase into a slightly distorted triclinic low-temperature phase.

This phase transition is certainly responsible for the rapid increase of the resistivity below 110 K observed first by Maple *et al.*[4] Harrison and coworkers[5] have found by Hall-effect measurements that the effective carrier concentration at low temperature is very small in accordance with the absence of superconductivity in $EuMo_6S_8$. Recently, several groups[5–7] reported the observation of superconductivity in $EuMo_6S_8$ at 11 K under hydrostatic pressure greater than 7 kbar. By measuring the Meissner effect under pressure, McCallum *et al.*,[8] however, have found no evidence for bulk superconductivity in this compound.

Several possible reasons for the absence of superconductivity in $EuMo_6S_8$ have been discussed in the literature. But as yet there is no detailed model that can consistently explain the important physical properties of this compound, such as transport or magnetic properties. In order to perform quantitative transport measurements we have developed a hot-pressing technique for preparation of dense bulk samples. In this paper, we present new data on the electrical resistivity, magnetoresistance, and Hall effect in the temperature region $1.5 < T < 300$ K and in magnetic fields up to 6.5 T. It will be shown that all our experimental results can be qualitatively interpreted in terms of a two-band model with a low density of states at the Fermi level.

II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

Samples of composition $Eu_xMo_6S_8$ with slightly different Eu concentrations $(1.0 \leq x \leq 1.2)$ were prepared by heating mixtures of EuS, Mo, and S up to 1200 °C for 24 h in evacuated and sealed quartz tubes. The reaction products were then crushed, pressed into pellets, and annealed at about 1200 °C for 48 h under Ar atmosphere. After this pretreatment, the nearly single-phased samples were hot pressed at about 1400 °C under uniaxial pressures of 1.7–3 kbar for several hours with the use of a graphite matrix or melted in a special high-pressure furnace[3] (autoclave) at 1800 °C under 2 kbar. Using these preparation techniques we obtained very homogeneous and compact samples, which are much more appropriate to transport measurements than the usual sintered ones. The density of the samples differed from the theoretical value by less than 2%; x-ray investigations did not reveal any impurity phases in our best samples, and micrographic studies showed that in those samples the concentration of such impurity phases was well below 1%.

The possible impurity phases (EuS, Mo_2S_3, Mo) enter as small inclusions at the grain boundaries. The grain size of the hot-pressed samples was of the order of 1 μm, that of the melted sample $\sim$1 mm. This difference in the grain size influences only slightly the room-temperature resistivity, as can be seen from Table I, where the exact characterization of all investigated samples is presented.

For the resistance and magnetoresistance measurements, the samples were cut with the use of a low-speed diamond saw, in the shape of small bars of $\sim$7 mm length and 0.3×0.3 mm^2 cross section. For the Hall measurements, the samples were cut into thin plates of 5 mm length, 3 mm width, and 0.3 mm thickness. The electrical resistance and the magnetoresistance were measured by means of a standard four-terminal ac technique (120 Hz). The Hall measurements were performed using an ac technique (220 Hz) with a steady magnetic field. The Hall signal was balanced out in zero field by means of a three-contact method. The Hall voltage V_H was determined by taking the mean value of the results obtained in two opposite field directions.

III. EXPERIMENTAL RESULTS

In Fig. 1, the normalized electrical resistivity of four samples with slightly different Eu concentrations and small changes in the sample preparation (see Table I) is shown. The temperature dependence of the resistance of sample no. 3 coincides exactly with that of sample no. 2 (note the similarity of the sample preparation) but is not explicitly shown in the figure. The resistivity of all samples investigated is temperature independent at high temperatures $T>150$ K. This behavior is different from the high-temperature behavior of typical Chevrel-phase compounds like $PbMo_6S_8$ or $SnMo_6S_8$, which show a nearly linear decrease of the resistivity as T decreases. At about 110 K there occurs an anomaly of the resistivity, which is presented in the insert of the figure in more detail. The anomaly is particularly marked in the melted sample no. 5. This resistance anomaly is clearly correlated to the structural phase transition, which was found to appear in all samples independent of the details of the sample preparation. The occurrence of the phase transition was detected by low-temperature x-ray diffraction. Below the phase transition, the resistivity increases like a quasisemiconductor, but there is no exponential temperature dependence, and at low temperature the resistivity appears to vary linearly with T.

The longitudinal magnetoresistance of four samples at about 2 K is reported in Fig. 2. All samples exhibit a strong, negative magnetoresistance, which can be saturated when $\mu_B H > k_B T$. The saturation value was not the same in all samples. The maximum magnetoresistance we have observed was as large as 92% at 2 K in sample no. 5, which also has the largest resistance ratio. That means the resistance at low temperature can be depressed nearly down to the room-temperature value by applying a magnetic field. The magnetoresistance of sample no. 1 turned out to follow the square of the magnetization, whereas in the other samples (nos. 2–5) a more or less clear deviation from the M^2 law was observed. No hysteresis was found within the experimental errors.

In Fig. 3, the Hall resistivity $\rho_H = wV_H/I$ (w is the thickness of the sample and I the current through the sample) is shown as a function of the

TABLE I. Nominal composition and characterization of the samples studied. The different symbols for the samples will be consistently used in the figures of the paper.

Number	Symbol	Nominal composition	Preparation technique	ρ(300 K) (mΩ cm)	$\rho(2\text{ K})/\rho(300\text{ K})$
1	○	$Eu_1Mo_6S_8$	hot pressing 1400 °C, 1.7 kbar	1.3	15
2	●	$Eu_1Mo_6S_8$	hot pressing 1170 °C, 2.9 kbar	1.0	17
3	▽	$Eu_1Mo_6S_8$	hot pressing 1400 °C, 3 kbar	1.5	17
4	▲	$Eu_{1.2}Mo_6S_8$	hot pressing 1420 °C, 1.7 kbar	1.1	9.7
5	■	$Eu_{1.1}Mo_6S_8$	melting 1800 °C, 2 kbar	1.0	23.8

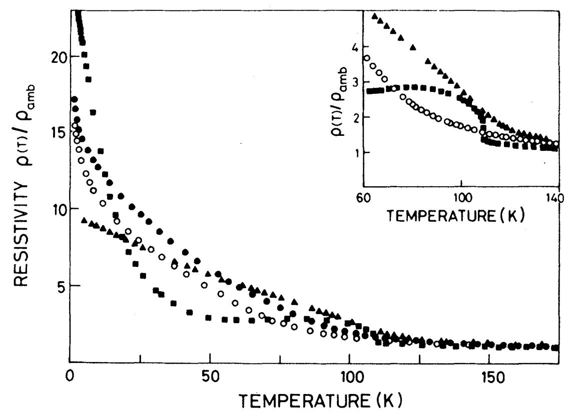

FIG. 1. Normalized resistivity of four $Eu_xMo_6S_8$ samples (nos. 1,2,4,5; see Table I) vs temperature. The insert of the figure shows the resistivities near the phase transition in more detail.

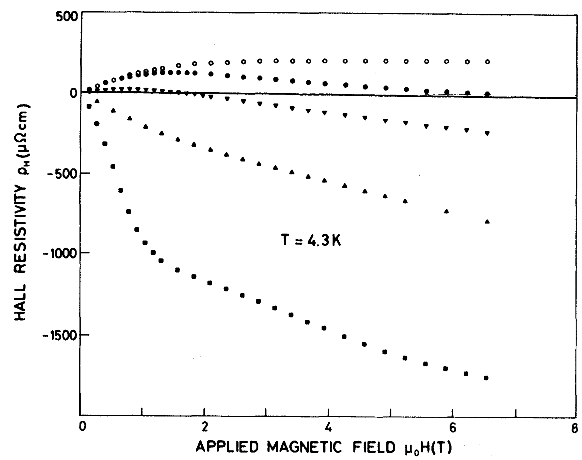

FIG. 3. Hall resistivity of five $Eu_xMo_6S_8$ samples (nos. 1–5; see Table I) vs magnetic field at about 4.3 K.

applied magnetic field for the five samples at 4.3 K. We found an anomalous Hall effect, which was radically different in the various samples. The strong variations in the Hall effect indicate that the number and type of carriers sensitively depend on small quantities of defects. Taking the initial slope of the Hall resistivity we can determine the effective number of carriers, which varies at 4 K from $\sim 5\times 10^{17}$ electrons/cm^3 in sample no. 5 to several 10^{19} holes/cm^3 in sample no. 1. The average mobility $\bar{\mu}=R_H/\rho$ at low temperature is of the order of several hundred cm^2/V sec. Note that the field dependence as well as the magnitude of the anomalous Hall effect here observed is quite different from the extraordinary Hall effect, which is normally observed in magnetic metals.[9] We expect that this latter effect, which is due to skew scattering effects, contributes only very little to the anomalous Hall effect in our samples. In Fig. 4, we report the Hall resistivity of sample no. 5 at different temperatures in order to elucidate in more detail what kind of anomaly is present in the Hall effect of $EuMo_6S_8$. At temperatures lower than the maximum magnetic field available ($k_BT < \mu_BH_{max}$) one can roughly distinguish two field regimes with different values of the Hall coefficient R_H. The Hall resistivity completely changes its behavior at the value of the magnetic field, where the magnetoresistance starts to saturate. In still higher fields a further change of the Hall resistivity appears, which may lead to a saturation. Measurements in fields up to 15 T are planned to clarify this question.

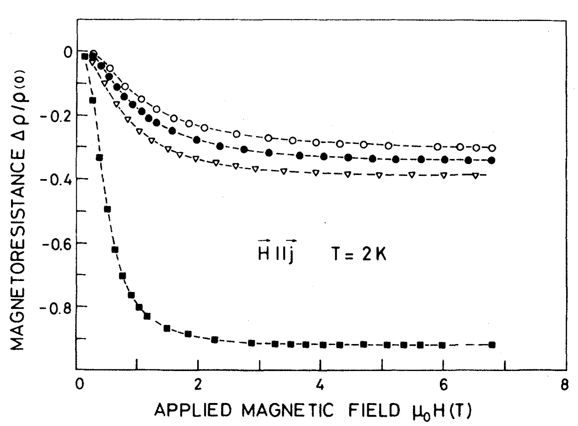

FIG. 2. Longitudinal magnetoresistance of four $Eu_xMo_6S_8$ samples (nos. 1,2,3,5; see Table I) vs the applied magnetic field at about 2 K.

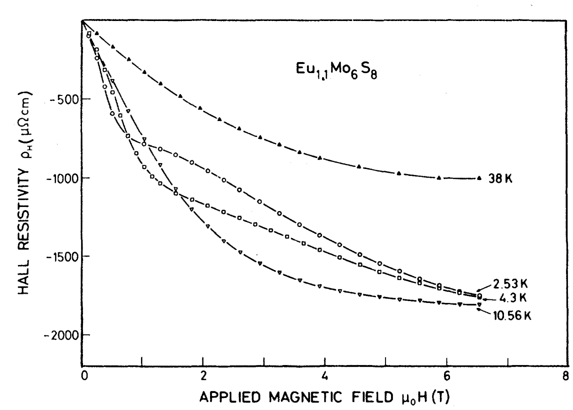

FIG. 4. Hall resistivity of sample no. 5 (see Table I) vs magnetic field at different temperatures.

In the high-temperature phase the net carrier density is smaller by a factor of 10 than the one found by Woolam *et al.*[10] in $PbMo_6S_8$: At 140 K we observed 6×10^{21} electrons/cm^3 in sample no. 5, whereas in the hot-pressed samples holelike conduction is dominant with carrier concentrations of $(3-6)\times10^{21}$ per cm^3. The average mobility $\bar{\mu}$ at high temperature is about 1 cm^2/V sec and thus very close to the room-temperature mobility of the mixed valent SmB_6.[11] These results imply that $EuMo_6S_8$ at high temperature behaves like a poor metal with a temperature-independent resistivity due to strong scattering effects.

The occurrence of the phase transition is reflected in the Hall coefficient R_H (Fig. 5) by an abrupt change of its value (2 orders of magnitude in sample no. 5). That means the effective number of charge carriers diminishes at the phase transition by a factor of 100, but at the same time the mobility increases, so that the resistivity rises only by a factor of 2. The temperature T_s at which the anomaly occurs depends on the exact stoichiometry of the sample, which was also found by measuring the specific heat of the sample.[12]

IV. DISCUSSION

Essentially two different models have been proposed in the literature for explaining the anomalous transport properties of $EuMo_6S_8$. The resistance

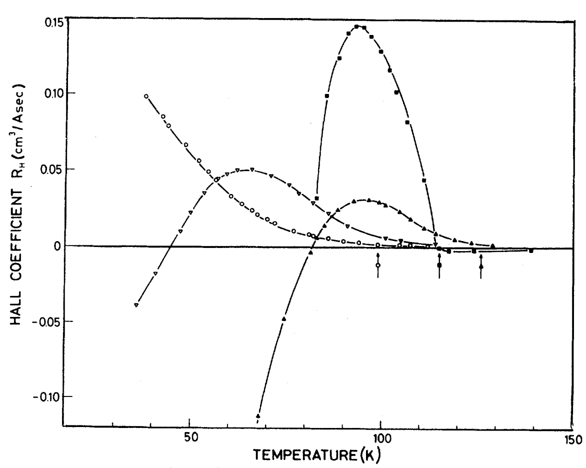

FIG. 5. Hall coefficient $R_H=(d\rho_H/dH)_{H\to0}$ of four $Eu_xMo_6S_8$ samples (nos. 1,3,4,5; see Table I) vs temperature near the phase transition. The arrows in the figure indicate the beginning of the phase transformation, determined by measuring the specific heat of these samples.

rise at low temperature has been discussed by assuming a small semiconducting gap in the density of states at the Fermi level or by assuming strong scattering due to a Kondo effect or intermediate valency. The first idea has been supported by the discovery of the structural phase transition and also by recent band-structure calculations with the actual low-temperature lattice constants as input parameters.[13]

Because of the high quality of our samples, it seems to be certain that the absence of a simple $\exp(1/T)$ law of the resistivity is an intrinsic property of the compound. The continuous increase of the resistivity down to 70 mK without any indication of a saturation[14] indicates that the missing exponential behavior cannot be explained by impurity conduction due to localized states within the gap, so that the existence of a real gap at the Fermi level must be excluded.

The Kondo-model idea has been supported by the observation of a negative magnetoresistance by Thompson *et al.*,[15] which has been interpreted by a suppression of the spin-flip scattering according to the theory of Beal-Monod and Weiner.[16] But there exist experimental results that contradict that interpretation:

(1) The T_c dependence of the pseudoternary $Sn_{1-x}Eu_xMo_6S_8$ shows that spin-flip scattering is negligible in the Sn-rich region.

(2) In the Eu-rich region preliminary measurements indicate that the magnetoresistance decreases much faster with decreasing Eu concentration than predicted by the Beal-Monod theory.

(3) The missing M^2 law of the magnetoresistance in most of our samples at low temperature is in contrast to the spin-flip model.

(4) It is hard to see how a magnetoresistance of 92% can result from spin-flip scattering suppression. One has to insert an unreasonably small value for the Fermi energy E_F ($\sim$0.0001 eV) into the formula of Beal-Monod, in order to obtain the 92% effect.

We therefore do not interpret the strong negative magnetoresistance by spin scattering.

The Hall-effect measurements suggest another possible mechanism for explaining the transport phenomena in $EuMo_6S_8$. As mentioned before, the Hall resistivity is strongly field dependent, indicating that the carrier concentration may also be field dependent. Because the effect of the external magnetic field H is amplified by the internal exchange interaction J in this compound, band-shift effects can have strong influence on the carrier concentration and thus on the magnetoresistance and the Hall effect, provided that there is a small overlap between two bands at the Fermi level. This possible band structure is also consistent with the observed sensitivity of the Hall effect on small quantities of defects. The simplest possible band model which can describe all of our transport results will be established in the following part.

V. TWO-BAND MODEL

As discussed before, the transport phenomena observed in $EuMo_6S_8$ leads us to believe that the real band structure near the Fermi level can be roughly described by two weakly overlapping parabolic bands (Fig. 6) with a low density of states at the Fermi level. The important parameters involved in this model are the effective masses m_v and m_c of the valence band (VB) and the conduction band (CB), respectively, as well as the overlap between the two bands given by E_c. In the presence of a magnetic field each band is split into two subbands by the action of the applied field H and the internal exchange interaction. The band shift will then be given by

$$E_H = \pm g\mu_B\mu_0 H \pm \bar{J} B_{7/2}(H/T) , \quad (1)$$

where we take $\bar{J} = -10$ meV for the mean exchange interaction in $EuMo_6S_8$.[2,4,17,18] $B_{7/2}$ is the appropriate Brillouin function for the Eu ions.

Since the temperature dependence of the hole and electron mobilities below 100 K is unknown, a detailed calculation of the low-temperature behavior of the resistivity does not make sense. Nevertheless, the resistance rise at low temperature without any tendency to an exponential divergence or a saturation, can be understood in terms of the described model as a temperature effect on the charge-carrier density. The model predicts a diminution of the number of carriers with decreasing temperature, if $m_v/m_e > 1$ and the overlap of the two bands is very small (of the order of several meV). Such a situation implies that the Fermi energy E_F is located very close to the top of the valence band, leading to a low density of states in agreement with the small γ value, extrapolated from specific-heat measurements.[12] The effective masses m_v and m_e are fixed by the amplitude of the Hall resistivity. This means that the two masses, the overlap, and E_F can be determined by the experiment. The only problem in the calculation of the transport properties originates from the unknown mobilities. However, the mobilities enter into standard formulas for the Hall resistivity or the magnetoresistance only with their ratio $K = \mu_h/\mu_e$. Therefore, when considering the field dependence of the different quantities at constant temperature we only need to know one additional parameter K. For our model calculations of the Hall effect and the magnetoresistance, we have arbitrarily set $K = 0.5$.

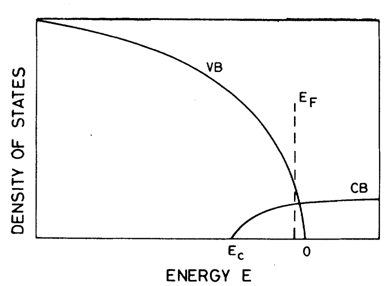

FIG. 6. Proposed band scheme near the Fermi level E_F for $EuMo_6S_8$ in its low-temperature phase.

The longitudinal magnetoresistance and the Hall resistivity were calculated by standard formulas:

$$\frac{\Delta\rho}{\rho(0)} = \frac{Kn_h(T,0)+n_e(T,0)}{Kn_h(T,H)+n_e(T,H)} - 1 , \quad (2)$$

$$\rho_H = \frac{K^2 n_h(T,H) - n_e(T,H)}{e[Kn_h(T,H)+n_{el}(T,H)]^2}\mu_0 H , \quad (3)$$

where n_h and n_e are the density of holes and electrons, respectively.

By adjusting the parameters of the model in the way described above, it follows immediately that the various transport phenomena become highly sensitive to small deficiencies of europium or sulfur, if a rigid-band model is taken as a basis. In Figs. 7 and 8 we present the magnetoresistance and the Hall effect calculated at 4 K with our special choice for the model parameters m_v, m_e, E_c, and K. The three curves in each figure correspond to three different positions of the Fermi level as a consequence of three different Eu concentrations in the phase. It can be seen that less than 0.1% europium deficiencies are sufficient to commute the Hall effect from a negative into a positive behavior and to reduce drastically the amplitude of the magnetoresistance. Furthermore, in agreement with our observations, the highest magnetoresistance ratio is correlated to a negative Hall effect and when the former decreases the Hall resistivity tends to become positive.

The temperature and field dependence of the Hall effect, shown in Fig. 4, can also be understood

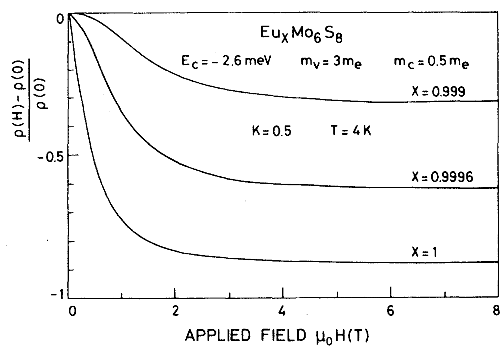

FIG. 7. Calculated magnetoresistance vs magnetic field at 4 K for three different Eu deficiencies.

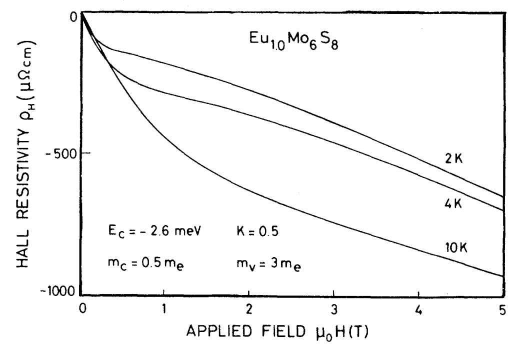

FIG. 9. Calculated Hall resistivity vs magnetic field for a stoichiometric crystal $Eu_{1.0}Mo_6S_8$ at three different temperatures.

semiquantitatively in terms of this simple model. In Fig. 9 we show the Hall resistivity of a stoichiometric crystal ($x=1.0$) for different temperatures, calculated with the same model parameters as before. The anomalous behavior at low temperature and low field results from a rapid increase of the number of electrons and holes, when the bands start to shift. This makes the Hall coefficient less negative and leads to this tendency to an upturn in ρ_H. At higher temperatures, the increase of the number of carriers in the field is less pronounced so that the variation in the Hall resistivity is less dramatic. In our calculation we assume K to be temperature and field independent. The poor reproduction of the crossover of the experimental curves indicate that this is not exactly the case. For example, a change of K from 0.4 at 2 K to 0.5 at 10 K would be enough to explain the observed crossover.

The model calculations were carried out using the Brillouin function for free spins. At low temperature the weak antiferromagnetic interactions between the Eu spins will influence the band-shift effects and make the anomalies appear at somewhat higher fields. Indeed in the experiments (Fig. 4) the anomalies in the field dependence occur at slightly higher fields than in our calculation. Let us finally mention that the temperature dependence of the magnetoresistance is equally well explained by our model calculation.

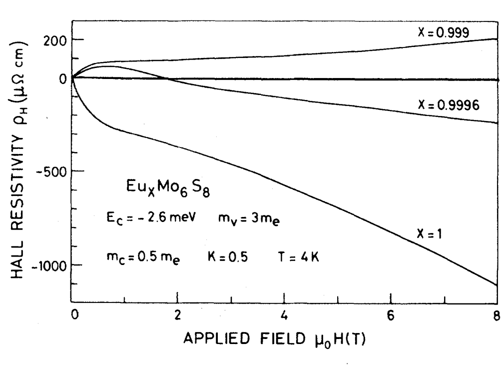

FIG. 8. Calculated Hall resistivity vs magnetic field at 4 K for three different Eu deficiencies.

In conclusion, this simple model reproduces all the main features of the observed and at first sight very anomalous transport properties. We believe that it contains the essential physics for the understanding of these compounds. To make more detailed comparison between experiment and theory one needs first of all information about the temperature dependence of the mobilities. The possibility that more than two bands affect the properties as well as possible correlation effects must also be taken into account.

Recently, Lacoe *et al.*[19] suggested the existence of charge-density waves in this compound. Our model is clearly in agreement with their idea of a partial gapping of the Fermi surface. However, our results show that the mobility of the carriers changes by about a factor of 100 when entering the low-temperature phase. The parameter n, which according to the theory of Bilbro and McMillian[20] describes the fraction of the Fermi surface that is not gapped at low temperature, is therefore smaller than the values assumed in Ref. 19. This will make the calculated T_c vs pressure curve more like a step function. The fact that superconductivity appears gradually with pressure may be due to inhomogeneities. A recent study of the pseudoternary system $Sn_{1-x}Eu_xMo_6S_8$ shows that T_c disappears very abruptly at $x \simeq 0.7$ where the structural phase transition sets in.[21]

VI. CONCLUSION

We have developed a new technique for preparing very compact and homogeneous samples of $EuMo_6S_8$, which can be used for quantitative transport measurements. Especially, the results of our measurements in the presence of a magnetic field, namely the observed giant negative magnetoresistance and the field- and sample-dependent Hall effect, leads us to propose a mechanism for explaining the transport anomalies in $EuMo_6S_8$ that has not been discussed in the literature as yet. Our measurements suggest that the band structure near the Fermi level at low temperatures can be simulated by two slightly overlapping bands with a low density of states at the Fermi level. From this simple band model two important conclusions can be drawn:

(1). The behavior of the magnetoresistance and the Hall effect as a function of the magnetic field is dominated by band splitting effects rather than by spin scattering.

(2). Tiny europium or sulfur deficiencies can crucially affect the density of charge carriers because of the particular position of the Fermi level in $EuMo_6S_8$. This defect sensitivity obviously influences the transport properties of the compound.

It should be pointed out that this unique situation at the Fermi surface will be quickly removed by substituting small quantities of Sn for Eu.

Thus the anomalous magnetoresistance and the anomalous field dependence of the Hall effect is expected to disappear as the Sn concentration increases. Preliminary measurements have confirmed this assumption. Further work on the pseudoternary $Eu_{1-x}Sn_xMo_6S_8$ is in progress to study in detail the influence of the Sn substitution on the transport properties.

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