Experimental evidence for bulk superconductive behavior of $EuMo_6S_8$ under pressure

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The pressure dependences of the structural and superconducting transition temperatures (T_s and T_c, respectively) of a melted high-quality sample of $EuMo_6S_8$ have been measured under nearly hydrostatic pressure up to ~15 kbar. Applied pressure (P) depresses T_s rapidly from T_s 109 K at zero pressure to $T_s=0$ just below 13 kbar where the slope dT_s/dP is nearly vertical. A very sharp superconducting transition is observed above 13 kbar; at 13.2 kbar, $T_c=12.2$ K and has a width $\Delta T_c=0.03$K. Above 13 kbar, T_c decreases nearly linearly with pressure at a rate $dT_c/dP=-0.18$ K/kbar, which is comparable to that observed for other superconducting Chevrel-phase compounds. The upper critical magnetic field H_{c2} as a function of temperature was measured up to 8 T and displays features that are indicative of the exchange-field compensation effect.

INTRODUCTION

At ambient pressure, the series of rare-earth (R) molybdenum sulfide compounds RMo_6S_8 are all superconducting with the exception of those formed with $R=$Ce and Eu.[1,2] It has been suggested that the absence of superconductivity in the Ce and Eu compounds may be due to anomalously strong exchange scattering associated with the Kondo effect and/or valence fluctuations since the temperature dependences of the electrical resistivity of both compounds display features that are reminiscent of Kondo lattice or valence fluctuation phenomena.[2,3] While this explanation is probably appropriate for $CeMo_6S_8$, its applicability to $EuMo_6S_8$ seems questionable in view of certain experimental results that were reported after this initial suggestion was advanced. Baillif *et al.*[4,5] discovered a structural phase transition in $EuMo_6S_8$ at 109 K from the room-temperature rhombohedral structure to a low-temperature triclinic structure in which the compound exhibits nonmetallic behavior. Such an insulating ground state in $EuMo_6S_8$ would be incompatible with superconductivity. At about the same time, two groups independently reported the appearance of superconductivity in $EuMo_6S_8$ with an onset near 11 K at pressures higher than ~7 kbar.[6,7]

Whereas the discovery of superconductivity under pressure in $EuMo_6S_8$ stimulated a great deal of interest in this compound, the bulk character of the superconductivity of $EuMo_6S_8$ has been seriously questioned[8–11] due to the absence of a Meissner effect, failure of some samples to exhibit superconductivity under pressure, and incomplete resistive transition curves with a finite resistance below T_c that is pressure dependent. In order to account for these observations, it has been proposed that the superconductivity that appears above ~7 kbar is associated with impurities that are located at grain boundaries, rather than being an intrinsic property of $EuMo_6S_8$.[9,11] On the other hand, it has been argued that the systematic evolution of the pressure dependence of T_c as x is varied from 0 to 1.2 in pseudoternary systems $M_{1.2-x}Eu_xMo_6S_8$ where $M=$Sn,[12] La,[13] and Yb (Ref. 14) is evidence for bulk superconductivity of $Eu_{1.2}Mo_6S_8$ (and $EuMo_6S_8$) under pressure.

The absence of superconductivity in $EuMo_6S_8$ at zero pressure has also been attributed to the competing effect of a charge-density-wave transition that opens up a gap over part of the Fermi surface.[15] Suppression of the charge-density-wave transition with pressure could account for the appearance of superconductivity above ~7 kbar.

Only two studies have addressed the question of the relationship between the structural transition and superconductivity.[16,17] Both studies were carried out on the $Sn_{y-x}Eu_xMo_6S_8$ system with $y=1.0$ or 1.2, on sintered samples under pressures up to ~14 kbar[16] and on high-quality dense samples at ambient pressure.[17] The measurements on the sintered $Sn_{y-x}Eu_xMo_6S_8$ samples under pressure[16] revealed that the structural transition temperature T_s is depressed with pressure, while the measurements on the series $Sn_{1-x}Eu_xMo_6S_8$ at ambient pressure[17] indicated that there is a competition between the structural and superconducting transitions. Although these experiments suggest that the disappearance of T_s is correlated with the appearance of T_c, a quantitative relationship could not be established because of sample inhomogeneities.

Recently, a technique was developed in which very high-quality dense samples of $EuMo_6S_8$ can be produced by melting under a high pressure of argon gas.[18] The high quality of these melted samples is reflected in (1) a large electrical resistance ratio, $R(2\text{ K})/R(300\text{ K})>24$, (2) a sharp jump in the electrical resistivity at T_s, and (3) a pronounced peak in the specific heat at T_s. The absence of any saturation in the electrical resistivity down to 70 mK[19] indicates that the concentration of impurities in these samples that contribute to the conductivity is negligible. Finally, the large peak in the specific heat[5] at T_s reveals the improved homogeneity of the melted samples compared to the sintered samples. In order to investigate the relationship between T_c and T_s quantitatively, we have measured the temperature dependence of the electrical resistivity under nearly hydrostatic pressure up to ~ 15 kbar and in magnetic fields up to 8 T on a $EuMo_6S_8$ specimen taken from the melted ingot that was originally used by Baillif *et al.* in their study of the structural transition.[4,5]

EXPERIMENTAL PROCEDURE

Beryllium-copper piston-cylinder clamps, pressurized at room temperature, were employed to attain pressures up to 18 kbar. The $EuMo_6S_8$ sample and a superconducting Pb manometer were contained within a Teflon capsule filled with a 50:50 mixture of isoamyl alcohol and *n*-pentane which served as the nearly hydrostatic pressure transmitting medium. At low temperatures the pressure was inferred from the superconducting transition temperature of the Pb manometer[20] which was measured by an ac inductive technique at a frequency of 16 Hz. The resistance of the $EuMo_6S_8$ sample was measured by means of a dc or 16-Hz ac four-probe technique. Owing to the very low resistance of the sample at high pressure, a relatively high dc current (20—40 mA) was required to obtain a reasonable signal-to-noise ratio. However, such high dc current values were found to heat the sample somewhat with the result that the values of T_c determined from dc measurements were always a few tenths of a degree Kelvin lower than the values obtained from ac measurements. The heating occurred at the junction between the sample and the current leads which were made with a conducting silver epoxy. The values of T_c and the upper critical field H_{c2} were defined from the midpoint of the resistive transition curve (R vs T). Since the resistive transitions in the high-quality $EuMo_6S_8$ sample were very sharp, this definition of T_c and H_{c2} had no influence on the analysis of the experimental results. A carbon-glass thermometer was used to measure the temperature.

RESULTS AND DISCUSSION

The temperature dependences of the electrical resistivity at several pressures between 4.2 and 10 kbar are displayed in Fig. 1. Increasing pressure has the effect of shifting the jump in resistivity associated with the structural transition to lower temperatures. At 7.7 kbar, there is no sign of superconductivity down to 1.2 K. It is also noteworthy that the semiconductinglike temperature dependence of the resistivity does not appear just below the structural transition, but instead occurs at lower temperatures after the resistivity passes through a minimum. At ambient pressure this minimum occurs at ~ 50 K and coincides with an anomaly in the thermoelectric power.[15] The temperature of the resistivity minimum decreases rapidly with increasing pressure and disappears at ~ 9 kbar. Above 8.8 kbar, the large increase in the resistivity at low temperatures is almost completely suppressed, and the behavior of the resistivity below the structural transition has a metalliclike character. These new data indicate that the behavior of the resistivity at low temperatures cannot be a direct consequence of the structural transition; therefore, a previous and plausible suggestion that the structural transition opens a gap at the Fermi level and leads to a semiconductorlike behavior of the resistivity is not consistent with the experimentally determined temperature dependence of the resistivity above 8.8 kbar.

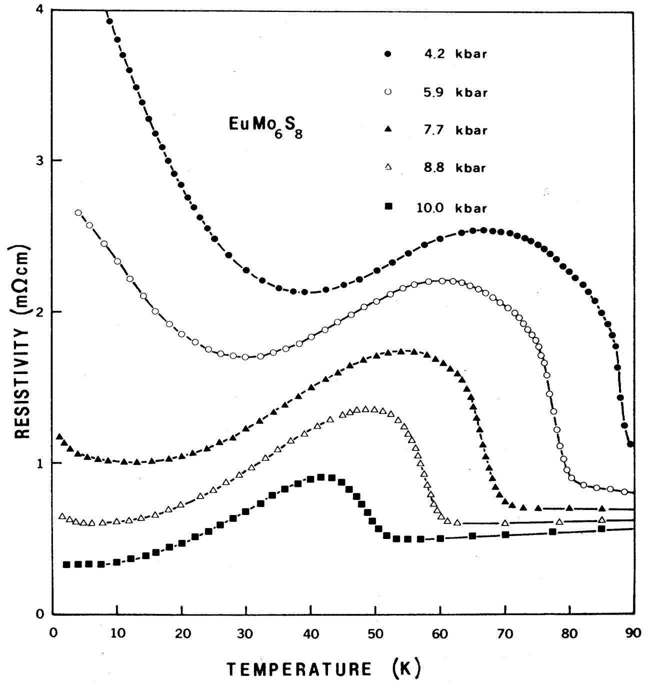

FIG. 1. Electrical resistivity vs temperature of $EuMo_6S_8$ (sample 1) at several pressures between 4.2 and 10 kbar.

The first feature in the resistivity that can be attributed to superconductivity appears above 10.5 kbar, but a pressure of at least 11.3 kbar is necessary to obtain a complete resistive transition. This result confirms the detailed studies in the pseudoternary system $La_{1.2-x}Eu_xMo_6S_8$ where the first diamagnetic change in the magnetic susceptibility of $EuMo_6S_8$ was observed at 11.7 kbar.[13] The temperature dependences of the electrical resistivity for pressures higher than 11.5 kbar are shown in Fig. 2. The anomaly in the resistivity at the structural transition is easily detectable up to 12.3 kbar, but as the pressure increases, the jump in the resistivity at T_s becomes gradually less sharp. We believe that this broadening of the resistivity anomaly is a consequence of a pressure gradient at the interfaces between crystallites. This conjecture is supported by the results of resistivity measurements on a part of the original sample after it had broken under pressure and terminated the series of measurements shown in Figs. 1 and 2. This smaller sample consists of fewer crystallites and the temperature dependences of the resistivity displayed in Fig. 3 show that the resistivity jumps at T_s at higher pres-

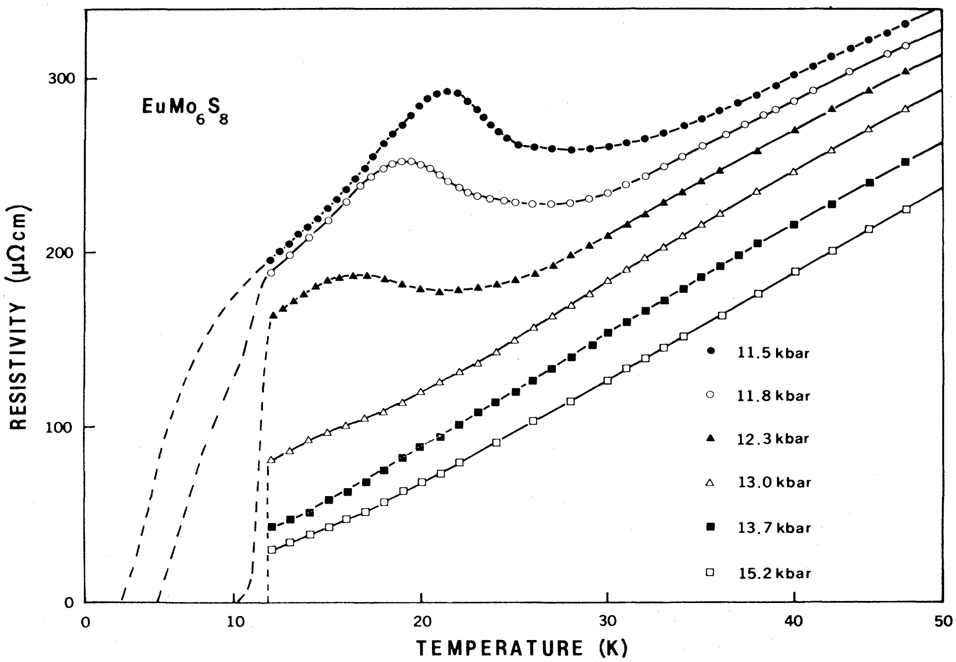

FIG. 2. Electrical resistivity vs temperature of $EuMo_6S_8$ (sample 1) at several pressures between 11.5 and 15.2 kbar. Dashed lines represent the resistive superconducting transition.

sures are much sharper than in Fig. 2. Most of the remaining results presented in this paper have been obtained on this smaller part (sample 2) of the original sample (sample 1).

Referring now to Fig. 3, the resistive superconducting transitions are very broad, as long as the structural transition is present. At 12.7 kbar the first significant diamagnetic change in the ac susceptibility can be detected in accordance with the resistive transition. Above 13 kbar the structural transition completely disappears and the superconducting transition becomes very sharp ($\Delta T_c = 0.03$ K for the resistive transition) with T_c reaching 12.2 K at 13.2 kbar. This new result clearly demonstrates that superconductivity does not appear by accident, but instead is associated with the disappearance of the structural transition. Typical resistive and inductive transitions are shown in Fig. 4 where both of the transitions were recorded at the same time. The inductive transition is completed within less than 0.6 K, and in contrast to previously reported results on sintered $EuMo_6S_8$ samples it has a magnitude that remains constant for pressures above 13.2 kbar. The values of T_c given in Fig. 4 are lower than the actual values by 0.2—0.3 K since a dc current was used for this experiment.

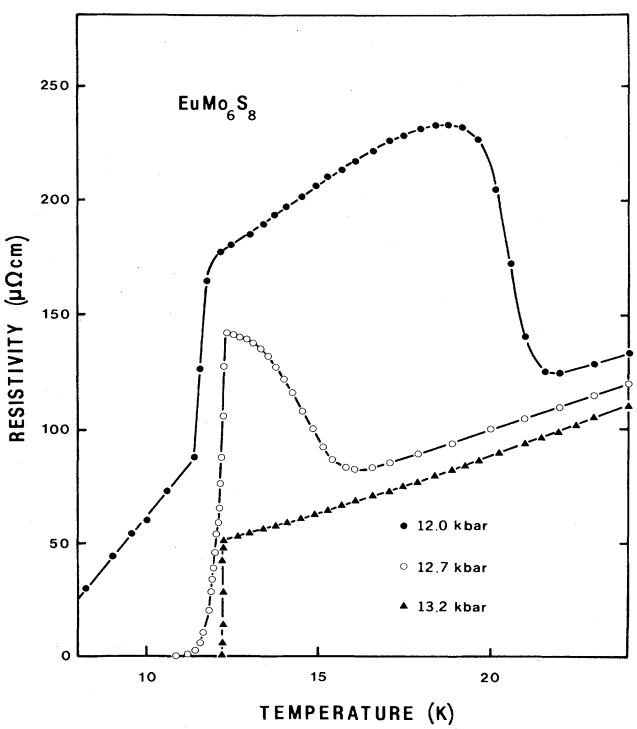

FIG. 3. Electrical resistivity vs temperature of $EuMo_6S_8$ (sample 2) in the vicinity of T_c at 12.0, 12.7, and 13.2 kbar.

A summary of the experimental results for the influence of pressure on the structural and superconducting transitions is presented in Fig. 5. The temperature dependence of the structural transition versus pressure is strongly nonlinear and there is a critical pressure just below 13 kbar where the structural transition is completely suppressed by pressure. Above 12.7 kbar the jump at the structural transition is masked by the superconductivity, but it appears from the behavior of T_s close to 13 kbar that T_s goes to zero with an infinite slope. Since the structural transition is of first order,[4] the slope dT_s/dP, the latent heat L, and the volume change ΔV at the structural transition must be related through the Clausius-Clapeyron equation $dT_s/dP = L/(T\Delta V)$. In Fig. 5 we estimate that $(dT_s/dP)_{P=0} = 4.5$ K/kbar, while

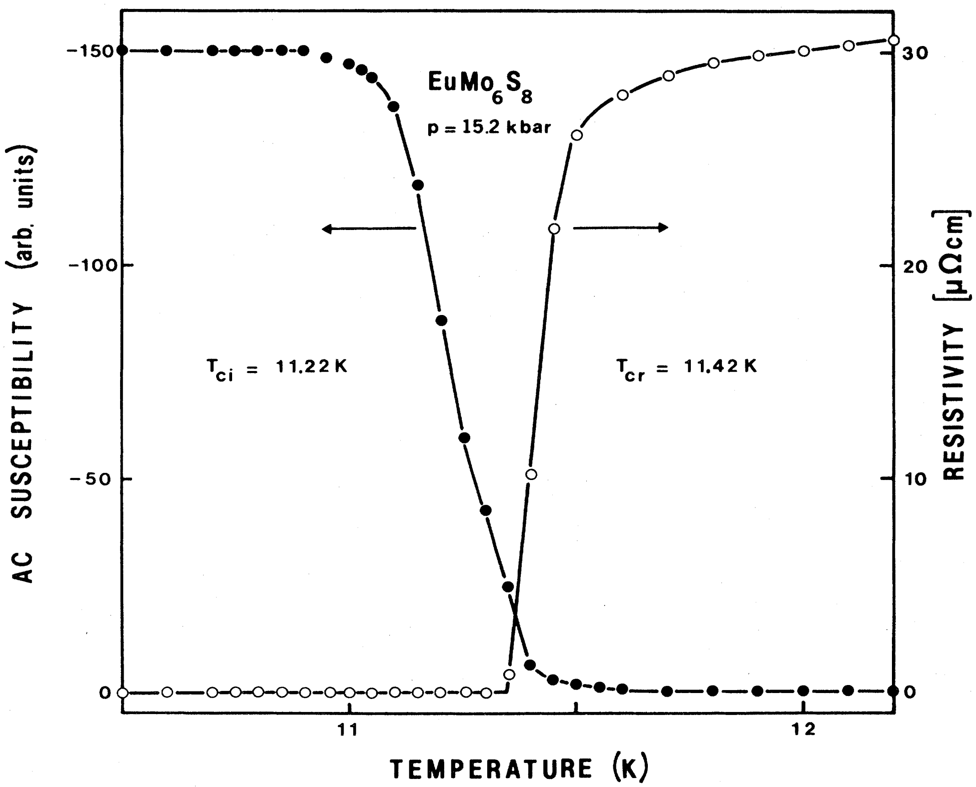

FIG. 4. Resistive and inductive superconducting transition curves of $EuMo_6S_8$ (sample 1) at 15.2 kbar. (Note that the resistive transition was measured with a dc current—see text.)

from previously reported specific-heat results, $L = 46$ J/K g-at.[5] Unfortunately, there are no accurate results for the volume change ΔV at the structural transition, and therefore it is impossible to compare our measurement of dT_s/dP with the value determined from this fundamental thermodynamic relation. However, we can estimate the volume change ΔV from the Clausius-Clapeyron equation and deduce that $\Delta V \simeq 0.5$ Å^3. This very small volume change agrees with the observation that the structural transition mainly affects the position of the six molybde-

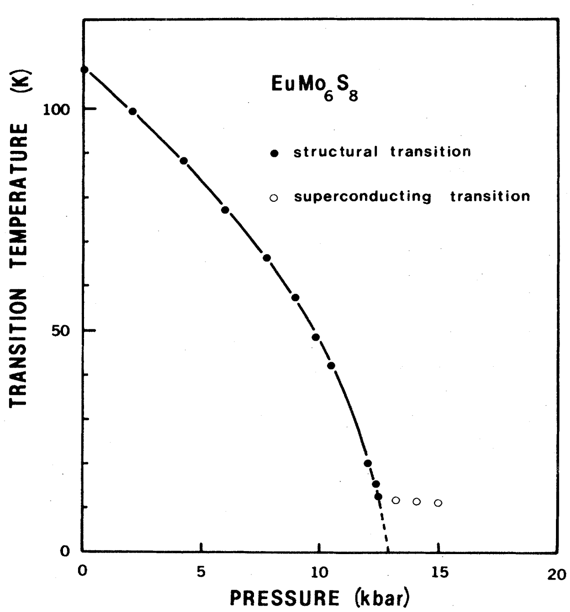

FIG. 5. Structural and superconducting transition temperatures vs pressure for $EuMo_6S_8$ (samples 1 and 2).

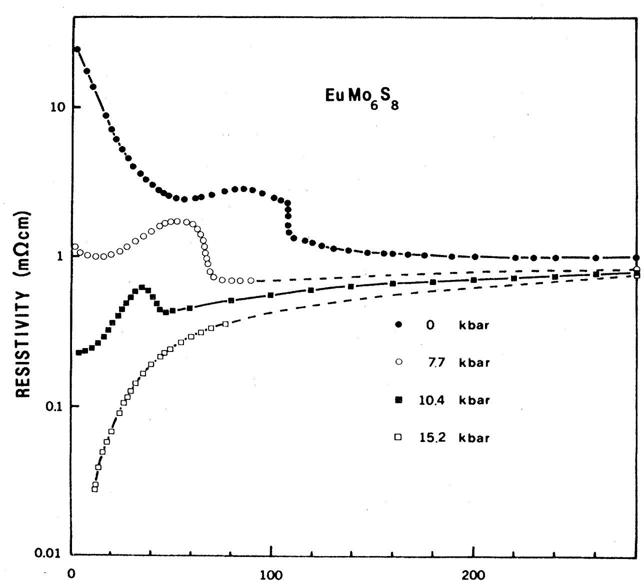

FIG. 6. Typical electrical resistivity vs temperature curves for $EuMo_6S_8$ (sample 1) at four pressures between 0 and 15.2 kbar.

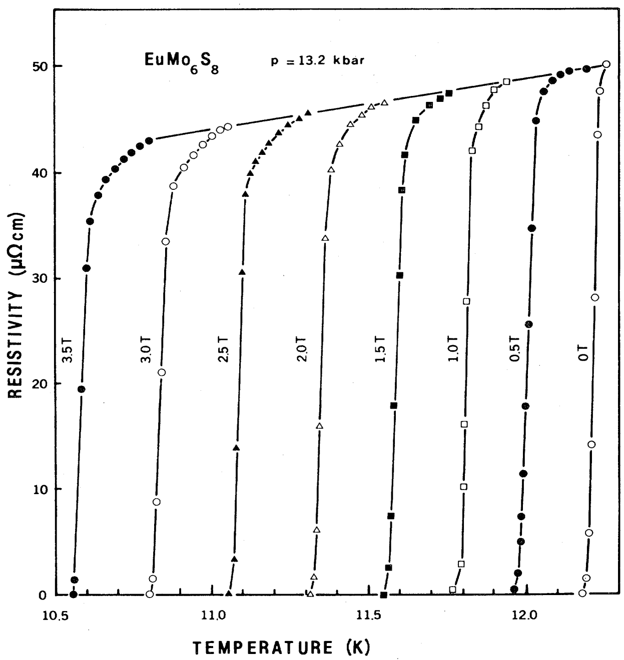

FIG. 7. Resistive superconducting transitions of $EuMo_6S_8$ (sample 2) in various applied magnetic fields at 13.2 kbar.

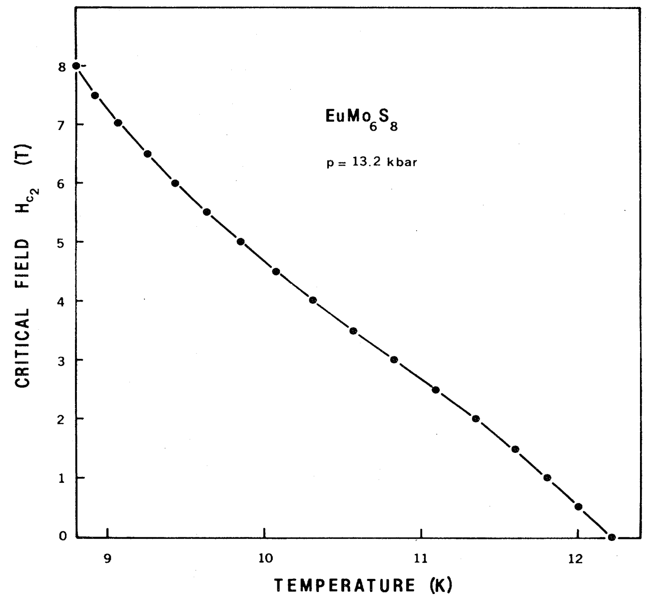

FIG. 8. Upper critical field vs temperature for $EuMo_6S_8$ (sample 2) at 13.2 kbar. Line through the data is a guide for the eye.

num atoms leaving the volume of the unit cell almost unchanged. The superconducting critical temperatures T_c displayed in Fig. 5 were obtained from resistive transitions, and we have selected only those above ~ 13 kbar where they were very sharp. As expected for a Chevrel-phase compound, T_c is very sensitive to pressure and decreases at a rate of $dT_c/dP = -0.18$ K/kbar. This value for dT_c/dP agrees with other results obtained for both the isoelectronic compounds $SnMo_6S_8$ and $PbMo_6S_8$.[21] An extrapolation of T_c to zero pressure gives $T_c = 14.6$ K. This value coincides precisely with the best T_c data obtained for $SnMo_6S_8$ and $PbMo_6S_8$, confirming the supposition that $EuMo_6S_8$ in the rhombohedral phase certainly has a high density of states at the Fermi level.

Figure 6 displays four typical temperature dependences of the resistivity at constant pressure. At room temperature the resistivity decreases almost linearly with pressure from 1 mΩ cm at ambient pressure to 0.75 mΩ cm at 15 kbar. But at low temperatures, the influence of pressure on the resistivity is enormous. At 1.2 K pressure decreases the resistivity from 24 mΩ cm at ambient pressure to 28 $\mu\Omega$ cm at 15 kbar, where the latter value is the *upper limit* of the residual resistivity (see discussion below). This amounts to 3 orders of magnitude change in resistivity at 1.2 K and a change in the behavior of the resistivity versus temperature from semiconductorlike to metallic character. At 15 kbar the resistivity ratio $\rho(300\ \mathrm{K})/\rho(12\ \mathrm{K})$ is about 27, but the resistivity below 12 K continues to decrease linearly with temperature as seen in Fig. 7 where the resistive transition with magnetic field is shown. This implies that the residual resistivity is smaller than 28 $\mu\Omega$ cm and thus the actual value for the resistivity ratio for this sample must be larger than 27.

Finally, we made resistive measurements of the upper critical field $H_{c2}(T)$ of $EuMo_6S_8$ at 13.2 kbar. To avoid complications from surface superconductivity the measurements were made with the current perpendicular to the magnetic field. Typical resistive superconducting transitions at constant magnetic field up to 3.5 T are displayed in Fig. 7. All of the transitions are extremely sharp, and the definition of H_{c2} has no influence on the temperature dependence of H_{c2} which is shown in Fig. 8. Only a small portion of the H_{c2}-vs-T curve was experimentally accessible due to the very high value of H_{c2}. This makes a detailed analysis difficult, but some important qualitative features can be obtained from these $H_{c2}(T)$ data. First of all, the initial slope of the critical field dH_{c2}/dT cannot be accurately determined, since $H_{c2}(T)$ is nonlinear close to T_c. Nevertheless, 2.5 T/K seems to be the lower limit for dH_{c2}/dT and, as a consequence, the orbital critical field is certainly higher than 21 T. The negative curvature of H_{c2} close to T_c is most likely due to large paramagnetic limiting produced by the mean exchange interaction between the conduction-electron spins and the localized magnetic moments of the Eu ions. At lower temperature, the curvature of $H_{c2}(T)$ becomes positive indicating that the exchange interaction is negative. Such behavior of H_{c2} is expected for $EuMo_6S_8$, since the compensation effect proposed by Jaccarino and Peter[22,23] has been observed in the isoelectronic series $Pb_{1-x}Eu_xMo_6S_8$,[24,25] $Sn_{1-x}Eu_xMo_6S_8$,[24,25] and $Yb_{1-x}Eu_xMo_6S_8$.[14] Nevertheless, taking into account the exchange interaction obtained in these series, the expected behavior of $H_{c2}(T)$ for $EuMo_6S_8$ should have a pseudoreentrant curve. For example, below a certain temperature the critical field should decrease with decreasing temperature as a result of the large increase of the paramagnetic limitation when the temperature is lowered. Since this kind of temperature dependence for H_{c2} was not observed, we conclude that pressure also changes the magnetic interaction either by decreasing the absolute value of the exchange interaction or by increasing the positive component of the exchange interaction. This mechanism has already been proposed as an explanation for the pressure dependence of $H_{c2}(T)$ in $EuMo_6S_8$.[26] New experiments are presently in progress to establish the role of pressure on the exchange interaction in this compound.

CONCLUSIONS

The high metallurgical quality of the sample that was investigated in this work made it possible to accurately assess several aspects of the behavior of $EuMo_6S_8$ under pressure. Specifically, the shape of the T_s-vs-P curve, the correlation between the disappearance of T_s and the appearance of T_c near 13 kbar, and the variations of T_c with P above ~ 13 kbar and H_{c2} with T at 13.2 kbar could all be established quantitatively.

The extreme change in the resistivity under pressure from semiconducting to very metallic character definitively excludes impurities as the source of pressure-induced superconductivity in $EuMo_6S_8$. Further support for this assertion is provided by the apparent competition between the low-temperature triclinic structure and superconductivity, as evidenced by the correlation between the disappearance of T_s and the appearance of T_c near ~ 13 kbar. Moreover, the high value $T_c = 12.2$ K at 13.2 kbar is the highest *pressure-induced* superconducting transition ever observed up to now, and therefore cannot reasonably be attributed to any known elements or alloys. In addition, superconducting properties such as the extrapolated value of $T_c = 14.6$ K at ambient pressure, the rate of depression of T_c with pressure, $dT_c/dP = -0.18$ K/kbar, and the extremely high value of H_{c2} are all reminiscent of Chevrel-phase compounds, rather than any conceivable impurity phases. As a final point, perhaps the most striking evidence for bulk superconductivity of $EuMo_6S_8$ is the anomalous temperature dependence of H_{c2}. Here, the characteristic positive curvature of H_{c2} vs T is a result of the microscopic interaction between the spins of the conduction electrons and the Eu magnetic moments which has been well documented in the pseudoternary Chevrel-phase systems $M_{1.2-x}Eu_xMo_6S_8$ where M=Sn,[24,25] Pb,[24,25] La,[13] and Yb (Ref. 14) where bulk superconductivity is incontrovertible. From these results we conclude that pressure-induced superconductivity is an intrinsic property of $EuMo_6S_8$, rather than an impurity phase. Experiments are presently in progress to demonstrate directly the bulk nature of superconductivity in $EuMo_6S_8$ under pressure.

All of the results presented in this paper are in qualitative agreement with previous experiments on sintered $EuMo_6S_8$ samples. In the investigations on sintered samples, sample inhomogeneities spread the structural transition over a range of temperatures[27] which explains why superconductivity is observed at lower pressure ~ 7 kbar in the sintered samples and why the magnitude of the ac superconducting transition signal varies with pressure below ~ 13 kbar. The reason for the large disparity in the values of T_s at ambient pressure reported previously, is most certainly a consequence of deviations in stoichiometry with respect to either the Eu or S concentration. These deviations provide a reasonable explanation of the anomalous transport phenomena obtained in several samples of $EuMo_6S_8$ that had been prepared by different methods.[28]

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[1] Ø. Fischer, A. Treyvaud, R. Chevrel, and M. Sergent, Solid State Commun. 17, 72 (1975).

[2] M. B. Maple, L. E. DeLong, W. A. Fertig, D. C. Johnston, R. W. McCallum, and R. N. Shelton, in *Valence Instabilities and Related Narrow Band Phenomena,* edited by R. D. Parks (Plenum, New York, 1977), pp. 17—29.

[3] M. B. Maple, M. S. Torikachvili, R. P. Guertin, and S. Foner, in *The Rare Earths in Modern Science and Technology,* edited by S. J. McCarthy, H. B. Silber, and J. J. Rhyne (Plenum, New York, 1982), Vol. 3, pp. 301—313.

[4] R. Baillif, A. Dunand, J. Muller, and K. Yvon, Phys. Rev. Lett. 47, 672 (1981).

[5] R. Baillif, A. Junod, B. Lachal, J. Muller, and R. Yvon, Solid State Commun. 40, 603 (1981).

[6] D. W. Harrison, K. C. Lim, J. D. Thompson, C. Y. Huang, P. D. Hambourger, and H. L. Luo, Phys. Rev. Lett. 46, 280 (1981).

[7] C. W. Chu, S. Z. Huang, C. H. Lin, R. L. Meng, M. K. Wu, and P. H. Schmidt, Phys. Rev. Lett. 46, 276 (1981).

[8] R. N. Shelton and A. R. Moodenbaugh, Phys. Rev. B 24, 2863 (1981).

[9] R. W. McCallum, W. A. Kalsbach, T. S. Radhakrishnan, F. Pobell, R. N. Shelton, and P. Klavins, Solid State Commun. 42, 819 (1982).

[10] W. A. Kalsbach, R. W. McCallum, U. Poppe, F. Pobell, R. N. Shelton, and P. Klavins, in *Superconductivity in d- and f-Band Metals 1982,* edited by W. Buckel and W. Weber (KGK, Karlsruhe, 1982), p. 185.

[11] C. W. Chu, M. K. Wu, R. L. Meng, T. H. Lin, V. Diatschenko, and S. Z. Huang, in *Physics of Solids under High Pressure,* edited by J. S. Schilling and R. N. Shelton (North-Holland, New York, 1981), pp. 357-363.

[12] K. C. Lim, J. D. Thompson, D. W. Harrison, C. Y. Huang, and H. L. Luo, J. Appl. Phys. 52, 2177 (1981).

[13] M. S. Torikachvili, M. B. Maple, R. P. Guertin, and S. Foner, J. Low Temp. Phys. 49, 573 (1982).

[14] M. S. Torikachvili, J. Beille, S. E. Lambert, and M. B. Maple, in *Superconductivity in d- and f-Band Metals 1982,* edited by W. Buckel and W. Weber (KGK, Karlsruhe, 1982), p. 241.

[15] R. C. Lacoe, S. A. Wolf, P. M. Chaikin, C. Y. Huang, and H.

L. Luo, Phys. Rev. Lett. 48, 1212 (1982).
[16]P. D. Hambourger, J. C. Ho, C. Y. Huang, and H. L. Luo, Phys. Rev. B 26, 1446 (1982).
[17]M. Decroux, H. W. Meul, C. Rossel, Ø. Fischer and R. Baillif, in *Superconductivity in d- and f-Band Metals 1982,* edited by W. Buckel and W. Weber (KGK, Karlsruhe, 1982), p. 167.
[18]R. Baillif, Ph.D. thesis, University of Geneva, 1982 (unpublished).
[19]M. Ishikawa (private communication of unpublished results).
[20]T. F. Smith, C. W. Chu, and M. B. Maple, Cryogenics 9, 53 (1969).
[21]R. N. Shelton, in *Superconductivity in d- and f-Band Metals,* edited by D. H. Douglas (Plenum, New York, 1976), p. 137.
[22]V. Jaccarino and M. Peter, Phys. Rev. Lett. 9, 290 (1962).
[23]M. Decroux, Diploma thesis, University of Geneva, 1975 (unpublished).
[24]Ø. Fischer, M. Decroux, S. Roth, R. Chevrel, and M. Sergent, J. Phys. C 8, L474 (1975).
[25]M. Decroux and Ø. Fischer, in *Superconductivity in Ternary Compounds: Superconductivity and Magnetism,* edited by M. B. Maple and Ø. Fischer (Springer, New York, 1982), Vol. 34, pp. 57–98.
[26]C. Y. Huang, D. W. Harrison, S. A. Wolf, W. W. Fuller, H. L. Luo, and S. Maekawa, Phys. Rev. B 26, 1442 (1982).
[27]B. Lachal, R. Baillif, A. Junod, and J. Muller, Solid State Commun. 45, 849 (1983).
[28]H. W. Meul, M. Decroux, R. Odermatt, R. Noer, and Ø. Fischer, Phys. Rev. B 26, 6431 (1982).