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MAGNETISM AND SUPERCONDUCTIVITY IN $Eu(Ho)Mo_6S_8$*

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ABSTRACT:

A variety of ambient and high pressure experimental results reveal the interplay between magnetism and superconductivity in Ho doped samples of the pressure induced superconductor, $EuMo_6S_8$. Ho concentrations up to 50 atomic percent of the rare earth ions were used. High resolution magnetic measurements are consistent with the crystalline electric field ground state for the Ho^{3+} ions being a magnetic doublet consisting largely of $J_z=\pm8$. The results of high pressure magnetization experiments reveal negligible effects of reduced lattice constant on the rare earth-rare earth interactions. Resistivity in a 10 atomic percent sample for P=10 kbar shows the suppression of a P=0 structural transition, metallic conductivity down to low temperatures, and finally superconductivity at 8 K. The upper critical field, $H_{c2}(T)$, for this sample was measured for P=7, 10 and 12 kbar and showed strong reentrant behavior ($dH_{c2}(T)/dT>0$ as $T\to0$ K). A minimum with field in the resistivity above H_{c2} was also observed at lowest temperatures. The $H_{c2}(T)$ data are compared with those of $EuMo_6S_8$ at high pressure, which shows positive curvature, and $HoMo_6S_8$, in which superconductivity is quenched by ferromagnetism at low temperatures.

The superconductivity of pure $EuMo_6S_8$, which is attained only at high hydrostatic pressures,(1) has recently been shown to be a bulk effect.(2) $EuMo_6S_8$ has a regular array of magnetic ions $(7\mu_B)$(3) (non-interacting at least for $T>0.5$ K(4)) and provides a good host for the introduction of other magnetic ions. The effects of the magnetic contribution of Ho^{3+} ions on the pressure induced superconductivity of $EuMo_6S_8$ is discussed here.(5) Electrical resistivity and normal state magnetization measurements at ambient and high pressures are presented. The upper critical field $H_{c2}(T)$ for the pressure induced superconductor $Eu_{0.9}Ho_{0.1}Mo_6S_8$ was found to be reentrant $(dH_{c2}/dT \rightarrow 0$ as $T \rightarrow 0$ K). At low temperatures ($T<2$ K) the electrical resistivity for $P \approx 7$ kbar showed a minimum with increasing field above H_{c2}.

The substitutional magnetic impurity Ho^{3+} is of particular interest because the two end members of the pseudoternary $Eu(Ho)Mo_6S_8$ series, namely $HoMo_6S_8$ and $EuMo_6S_8$, have greatly dissimilar superconducting-normal phase boundaries as a function of applied magnetic field. For $HoMo_6S_8$ the P=0 superconductivity (T_c=1.3 K) is quenched due to ferromagnetic alignment of the Ho^{3+} ions at about 0.5 K,(6) and $H_{c2}(T)$ reaches only about 0.3 T. For $EuMo_6S_8$ $H_{c2}(T)$ reaches as high as 26 T and the phase boundary is fit well by assuming a negative exchange interaction for the Eu^{2+} ions and the conduction electrons.(2,7)

The samples were obtained in the form of sintered clumps which were carefully cut into ingots for electrical resistivity measurements (including $H_{c2}(T,P)$). The leads were attached with conductive epoxy. The zero field transition temperatures measured with electrical resistivity agreed with those using ac susceptibility. High pressure critical field and electrical resistivity were carried out in small Berylco 25 pressure clamp devices having electrical lead access into the high pressure chamber. High pressure magnetization was carried out in non-magnetic Co-free beryllium copper clamps. During the sample preparation and measurements care was taken to prevent the introduction of oxygen into the samples and to prevent strains, because these broaden transition widths and/or alter the pressure dependent properties.(8)

The normal state magnetization, σ, vs applied field H_o to 9 T was measured at T=4.2 K for six $Eu_{1-x}Ho_xMo_6S_8$ samples (x=0,0.1,0.2,0.3, 0.4 and 0.5). Although the x=0 sample ($EuMo_6S_8$) attained near saturation in 9 T fields, and σ closely followed a Brillouin function for J=7/2, the approach to magnetic saturation in the Ho doped materials was much slower. Data for the x=0.5 sample is shown in Fig. 1, where the free ion saturation magnetic moment (47.9 emu/gm) is also indicated. The slow approach to saturation is attributed to the effect of crystalline electric field (CEF) splittings on the Ho^{3+} ion. (Eu^{2+} is an S-state ion, so that CEF splittings are zero to first order, and the Brillouin-like magnetization and an observed near-ideal Curie law susceptibility, θ<.2 K, support this.) All the σ vs H_o data can be fit well assuming a CEF doublet ground state with largely $J_z=\pm 8$ components for the Ho ions(9) and with the next excited CEF levels split up by many K so that only the lowest lying doublet is thermally populated at T=4.2 K. The fit to the data in Fig. 1 (solid line) is with no adjustable parameters. Although considerable anisotropy of σ is apparent for

$x>0$, we observed very little deviation from a Curie-Weiss law in high resolution susceptibility measurements. This is due to random orientations of the crystallites with respect to the applied field, as shown by Dunlap.(10) The fit to the data in Fig. 1 is averaged for random orientation of the crystallites with the external field. High resolution σ vs H_o measurements were also performed on the $x=0.5$ sample down to 1.5 K in order to search for hysteresis. None was observed to within 1%, so all samples were paramagnetic in the temperature range covered. This sample was also subjected to 5.5 kbar hydrostatic pressure and σ measured at 4.2 K. These data are also included in Fig. 1, where it is seen that no significant differences exist; thus the moment change under pressure is negligible: $(1/\sigma)(d\sigma/dP)<1.8 \times 10^{-3}$ kbar^{-1}.

The electrical resistivity, ρ, vs T and its pressure dependence are shown in Fig. 2 for $Eu_{0.9}Ho_{0.1}Mo_6S_8$. At P=0 a sintered high purity $EuMo_6S_8$ sample also showed an increase in ρ with decreasing T, but the relative value attained was much larger: $R(4\ K)/R(300\ K)\simeq 20$. Two possible sources for the smaller change in the $x=0.1$ sample are: first a decrease in the extent of the structural distortion caused by the introduction of smaller Ho^{3+} ions into the lattice (the c-axis is reduced(11)), and secondly an increase of conduction electron concentration introduced by the trivalent impurity. The high pressure data in Fig. 2 clearly show the metallic behavior of the system and the superconducting transition at about 8 K. Only about 5 kbar is needed to produce metallic conductivity in the $x=0.1$ sample, whereas about 12 kbar is needed in pure $EuMo_6S_8$.

Measurements of the superconducting upper critical field, $H_{c2}(T)$, on the x=0.1 sample were made in order to compare the phase boundary with those of the two end members of the pseudoternary series. The phase boundary is far more similar to that of $HoMo_6S_8$(6) than that of $EuMo_6S_8$(2); data for three pressures is shown in Fig. 3. The pressure dependence of the data on the high temperature side of the $H_{c2}(T)$ peak results from the pressure dependence of T_c previously reported.(5) However, the pressure dependence on the low temperature side indicates a change in the exchange interaction with pressure. One feature, evident for all three pressures, is the linear dependence of $H_{c2}(T)$ with T below the peak. The 12 kbar data, if extrapolated to zero field, indicates a transition back to the normal state at about 0.5 K. Semiquantitative fits to the 10 kbar data of Fig. 3 were obtained using an abbreviated form(12) of the multiple pairbreaking equation(13) with net positive magnetic impurity-conduction electron exchange; ($a=4 \times 10^{-5}$ in Eq. 3.81 of Ref. 15, and c=90, an effective Curie constant).

In Fig. 4 we show ρ vs H_o to 15 T for the x=0.1 sample at P= 7 kbar. For T<3 K ρ rises rapidly, decreases above H_{c2} and then increases again. The shallow minimum may be due to a strongly temperature dependent magnetoresistivity in the normal state. However, an alternative explanation is precursive field-induced superconductivity, which has been recently reported in another $EuMo_6S_8$-based hot pressed sample.(14) Negative exchange is essential for the observation of this interesting phenomenon. The resistivity to 15 T at high pressures and lower temperatures for the x=0.1 sample substantiated this shallow minimum and showed strong temperature dependence:

the depth of the minimum increased by a factor of four between 1.0 K and 0.5 K. This is being investigated further.

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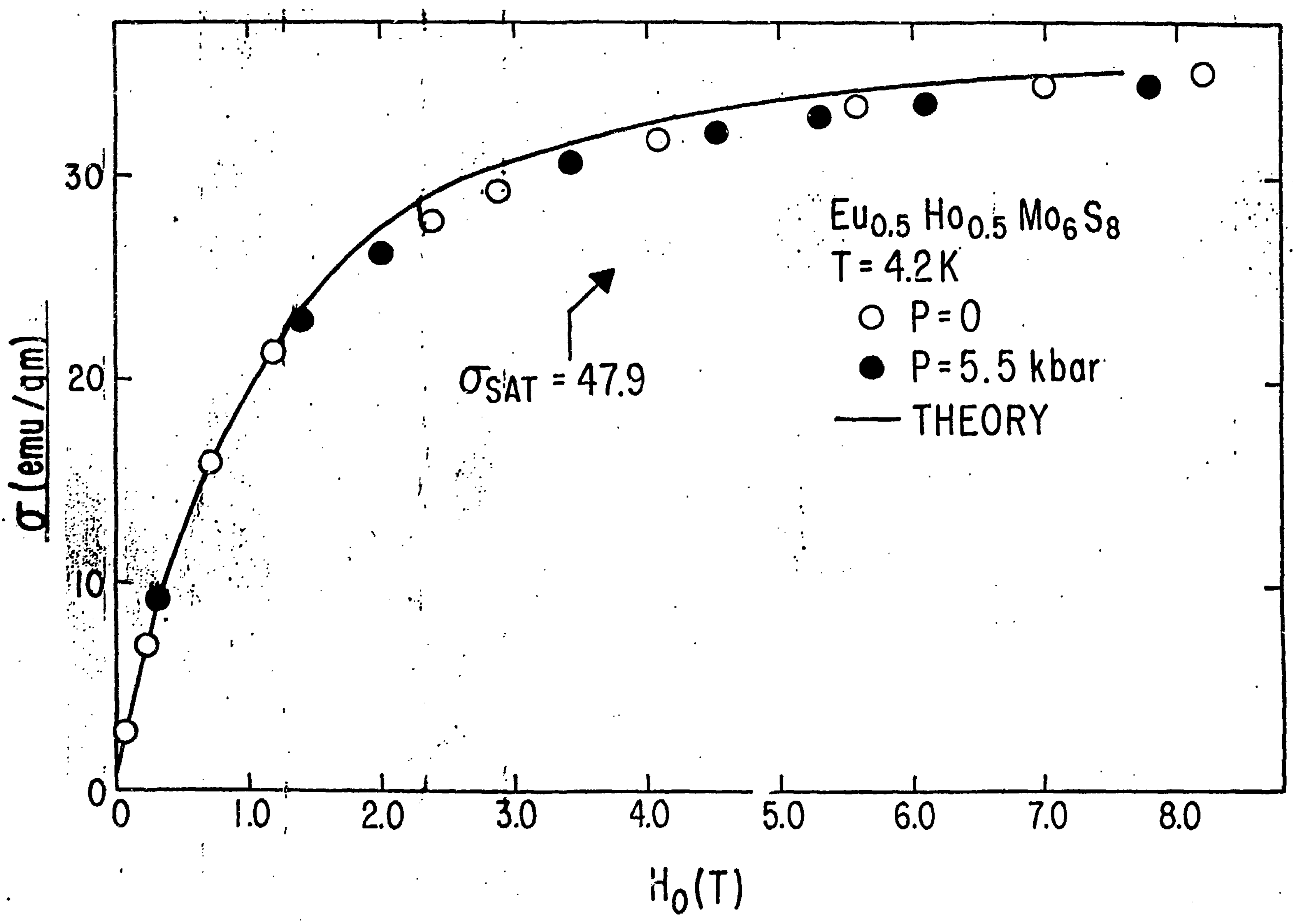
FIGURE CAPTIONS

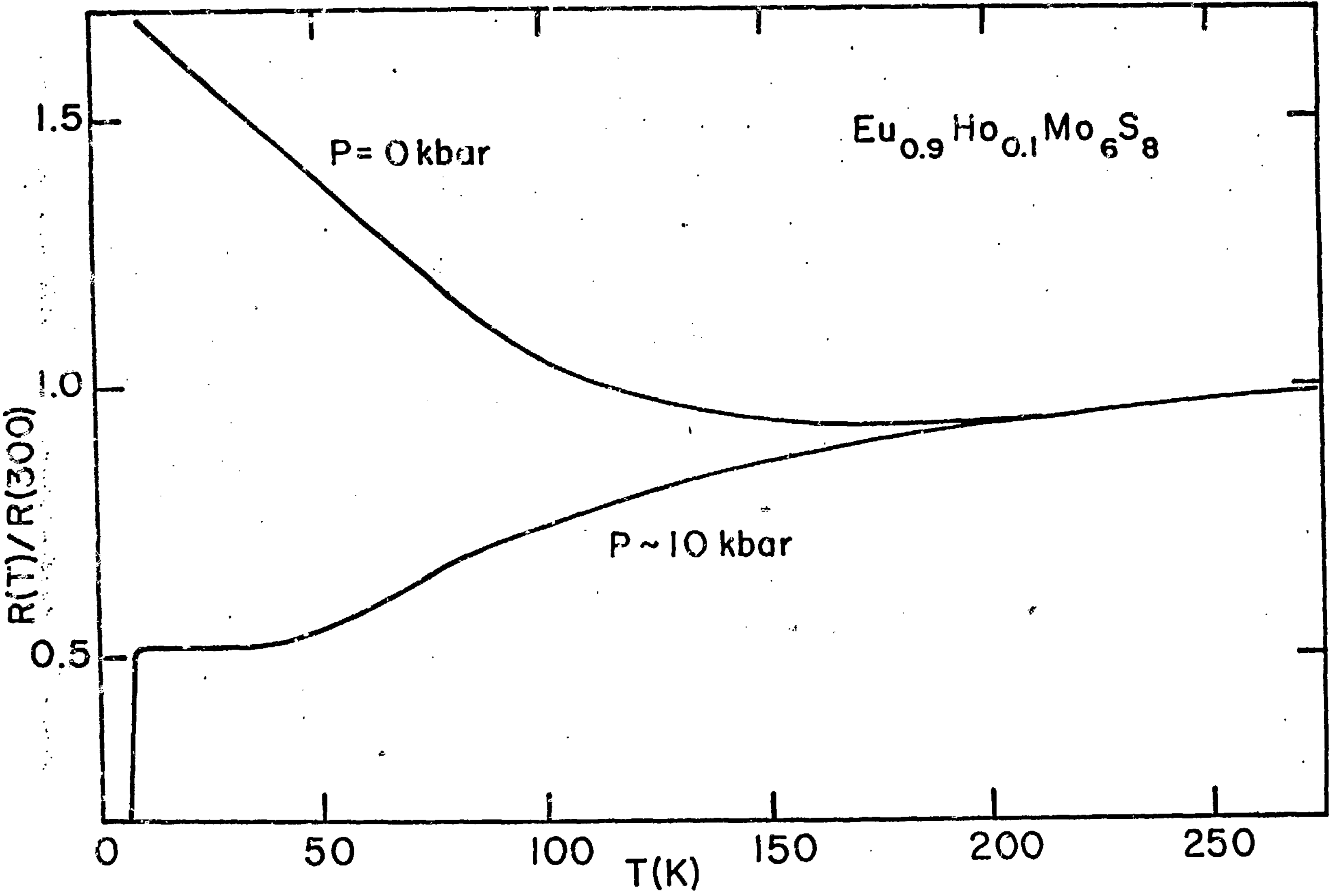
Fig. 1: Magnetization vs applied magnetic field at T=4.2 K for $Eu_{0.5}Ho_{0.5}Mo_6S_8$ at P=0 and P=5.5 kbar hydrostatic pressure. The solid line is a fit to the data incorporating crystalline electric field effects on the Ho ions. The saturation magnetic moment for free ions (47.9 emu/gm) is indicated.

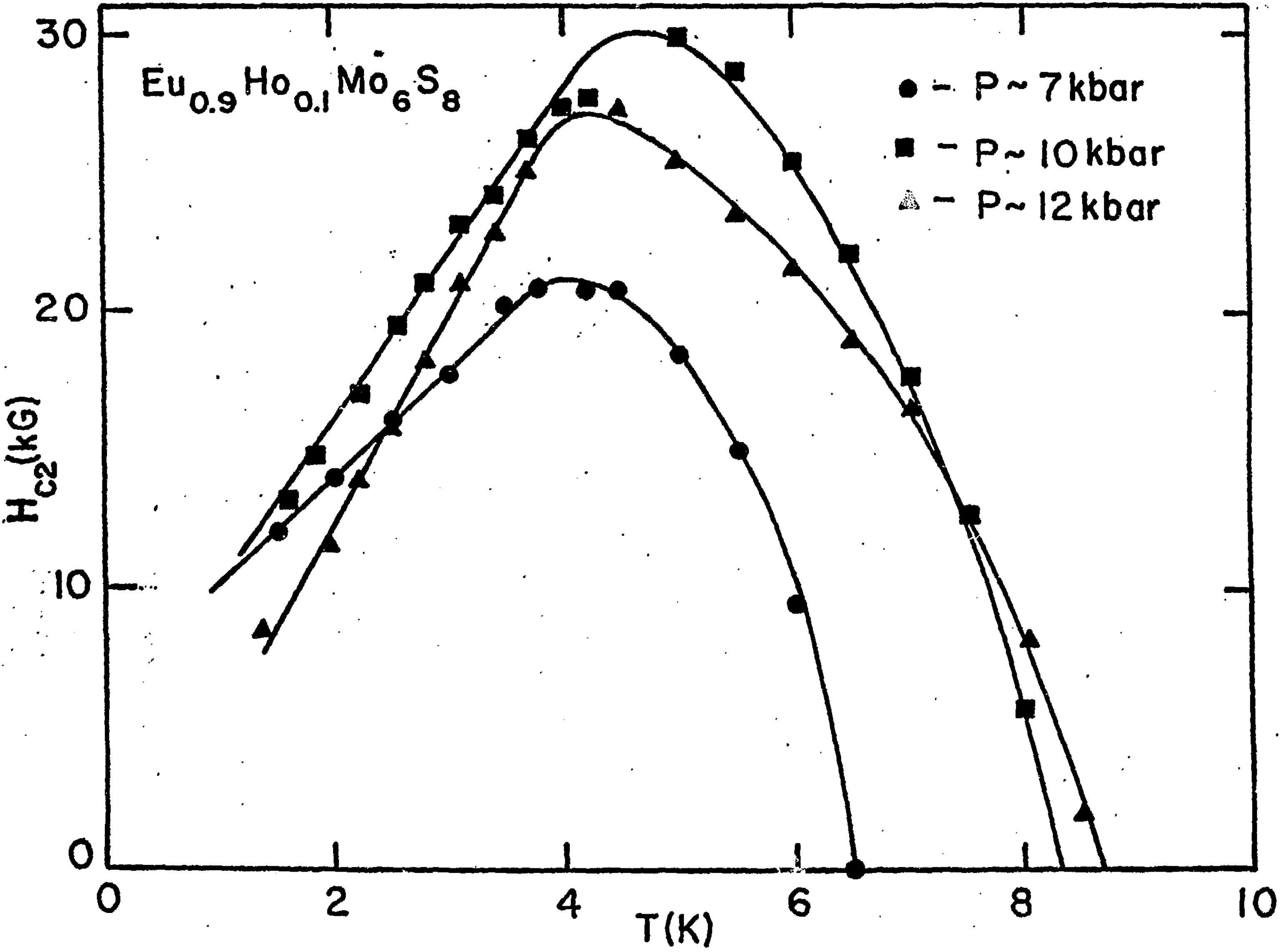
Fig. 2: Normalized electrical resistivity vs temperature for the pressure induced superconductor $Eu_{0.9}Ho_{0.1}Mo_6S_8$ for P=0 and P=10 kbar hydrostatic pressure. The superconducting transition is at about 8 K.

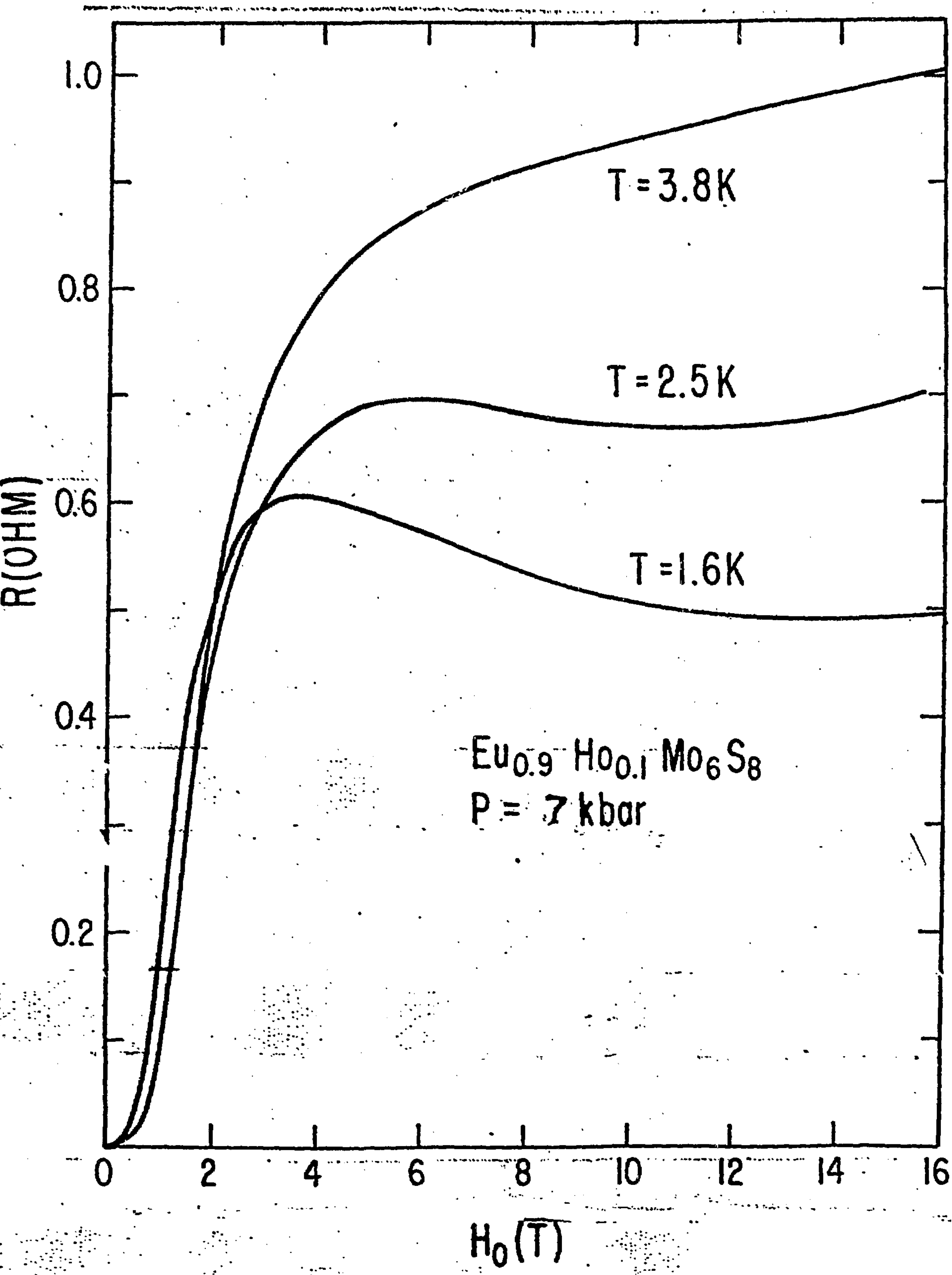
Fig. 3: Upper critical field for three pressures for the pressure induced superconductor $Eu_{0.9}Ho_{0.1}Mo_6S_8$.

Fig. 4: Electrical resistivity vs applied field for $Eu_{0.9}Ho_{0.1}Mo_6S_8$ at three temperatures. The high field minimum appearing at low temperatures may be due to precursive field-induced superconductivity. Data were taken at about 7 kbar.


σ (emu/gm)
0
10
20
30
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
H_0(T)
σ_{SAT} = 47.9
$Eu_{0.5}Ho_{0.5}Mo_6S_8$
T = 4.2K
○ P = 0
● P = 5.5 kbar
— THEORY


R(T)/R(300)
1.5
1.0
0.5
P= O kbar
$Eu_{0.9}Ho_{0.1}Mo_6S_8$
P ~ 10 kbar
0
50
100
150
200
250
T(K)


$Eu_{0.9}Ho_{0.1}Mo_6S_8$
● – P ~ 7 kbar
■ – P ~ 10 kbar
▲ – P ~ 12 kbar
H_{c2}(kG)
T(K)
0
10
20
30
0
2
4
6
8
10


1.0
0.8
0.6
0.4
0.2
R(OHM)
0
2
4
6
8
10
12
14
16
H_0(T)
T = 3.8K
T = 2.5K
T = 1.6K
$Eu_{0.9}Ho_{0.1}Mo_6S_8$
P = 7 kbar