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Effect of pressure on the electrical resistance of EuO

D. DiMarzio, M. Croft, and N. Sakai*
Physics Department, Rutgers University, Piscataway, New Jersey 08854

M. W. Shafer
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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The electrical resistivity of EuO has been measured from room temperature to 70 K and at pressures up to 250 kbar. A semiconductor-to-semiconductor transition is observed around 140 kbar at room temperature, and the conduction remains activated with a narrow gap up to 250 kbar. The magnetic transition temperature is observed to rise rapidly with pressure below 100 kbar but to saturate near 200 K in the 100–250-kbar range.

The electronic structure of EuO (NaCl-type crystal structure) consists of a filled 0-p valence band about 3.1 eV below an empty Eu $5d$ conduction band with the localized Eu $4f^7$ orbit lying in the band gap at $E_g = 1.14$ eV below the $5d$ band bottom. Formally, the Eu was in the strongly magnetic $J = \frac{7}{2}$ Eu^{2+} valence state at ambient pressure in this compound. E_g is strongly affected by the onset of ferromagnetic order below 69.3 K through an extraordinary 0.27-eV exchange-induced red shift of the $5d$ band bottom.[1] The magnetic activity of the $5d$ band bottom leads to a dramatic (up to 13 orders of magnitude for some stoichiometries) decrease in the electrical resistivity of EuO in the vicinity of its ferromagnetic ordering temperature. Pressure (volume reduction) also induces a decrease in E_g at the initial rate of 5 meV/kbar.[2] Here the pressure-induced increase of the t_{2g}-e_g crystalline field splitting of the $5d$ band is at the root of the pressure-induced downward movement of the t_{2g}-$5d$ band bottom.[2]

The close proximity of the $4f^7$ level to the $5d$ band bottom coupled with both the strong magnetic and volumetric reduction of the $4f^7$-$5d$ splitting sets the stage for a potentially rich competition between magnetism and a Eu valence instability in the high-pressure phase diagram of EuO. It is, after all, the closing of the analogous $4f^6$-$5d$ gap in SmS which induces a spectacular black to gold valence transition.[3] In EuO, promotion of electrons from the $4f^7$ level to the $5d$ band would entail the admixing of the Eu^{3+} $4f^6$ $J=0$ state and, hence, the creation of a mixed-valent material.

Previous high-pressure measurements on EuO have been motivated largely by the above-noted tennous balance of the Eu^{2+} valence state. Early pressure-volume work done by Jayaraman,[4] with an ungasketed diamond cell technique, yielded an isostructural volume collapse near 300 kbar along with the visual observation of a change in the materials reflectivity. Recently, Zimmer, Tokemura, Syassen, and Fisher[5] have reported a large increase in the number of free carriers near 130 kbar via optical reflectivity measurements. Zimmer *et al.*[5] have also reported the onset of a continuous volume collapse at 130 kbar. Both of these latter two measurements employed gasketed diamond anvil press techniques which presumably guaranteed superior pressure hydrostaticity. Regarding the ferromagnetic ordering temperature, McWhan, Sauers, and Jura[6] have measured a rapid pressure-induced enhancement of the ferromagnetic T_c to about 130 K by 70 kbar.

On the theoretical model side, Nolting[7] has presented a picture where the $4f^7$-$5d$ gap closes under pressure, but where a hybridization gap persists even after the volume collapse onsets. Like mixed valent SmB_6 (Ref. 8) and gold phase SmS,[3] Nolting predicts that the Fermi energy would lie in this hybridization gap yielding a small band-gap semiconductor at very high pressures. In discussing their data Zimmer *et al.*,[5] on the other hand, have ascribed their carrier concentration change and volume collapse near 130 kbar to a insulator-metal transition accompanying a continuous Eu valence change. In the Zimmer *et al.*[5] interpretation it is the presummed onset of ferromagnetic order at 300 K and 130 kbar which induces the red shift of the $5d$ band edge which in turn closes the remaining gap.

Thus several crucial questions are raised by previous work: (1) What is the character of the 130-kbar transition observed by Zimmer *et al.*?[5] (2) What is the behavior of the high-pressure magnetic ordering (temperature) energy scale, and, specifically, how does it connect to the 130-kbar anomaly? (3) What is the high-pressure behavior of the electronic gap E_g, and is the phase above 130 kbar metallic or semiconducting? In order to provide insight into these questions, we have performed high-pressure dc resistance measurements on EuO.

In our experiment we used very nearly stoichiometric EuO (oxygen vacancies <0.03 mol%). It was prepared by reacting Eu metal with Eu_2O_3 at approximately 1800 °C. Small pieces (typically $0.1\times0.05\times0.005$ mm^3) of EuO where chipped off of a single crystal and used in the high-pressure cell. Since concentration gradients are a usual difficulty with melt-grown crystals, we performed experiments on a number of different pieces of EuO from one crystal to eliminate any atypical behavior in resistance. Pressure was generated by a diamond anvil cell with quasihydrostatic pressure in the range of 40 to 250 kbar.[9] Resistance was measured by a modified two-probe method. The sample bridged two precompressed platinum leads at the center of the diamond face, and was surround-

ed by a pressure transmitting medium of polyvinylidene chloride film. External pressure to the cell was generated by a hydraulic gas press. Sample pressures were initially determined by the ruby fluorence method and subsequently by fixed-point measurements. Variations on the pressure calibration were less than 10 kbar. Temperatures were measured by a silicon diode thermometer.

In Fig. 1 we show the resistance (R) of EuO as a function of pressure at room temperature. If we assume an activated behavior of resistance given by

$$R = R_0 \exp[E_g(P)/2k_BT] \ , \tag{1}$$

where R_0 is a normalizing constant, k_B is the Boltzmann constant, T is the temperature, and only E_g depends on pressure, then we can express E_g by

$$E_g = 2k_BT \ln[R(P)/R_0] \ . \tag{2}$$

In this simple model we assume that the pressure dependence of R_0, which for intrinsic behavior depends on powers of electron and hole effective masses, is much slower than the pressure dependence of the exponential term in Eq. (1).[10,11] If one assumes that at $P=0$, $E_g = 1.14$ eV then one can use Fig. 1 as a plot of E_g vs P as indicated by the left-hand scale. A linear fit of the low-pressure region gives

$$d(\ln R)/dP = -0.0988/\text{kbar} \ .$$

Assuming a linear dependence of E_g on P [Eq. (2)] we get

$$dE_g/dP = -5.0\times10^{-3} \text{ eV/kbar} \ ,$$

which is in agreement with the above-noted previous results (see dashed line in Fig. 1). Interestingly, our experimental results at very high pressures appear to agree well with the quantitative hybridization-gap predictions of Nolting (dashed-dotted line in Fig. 1).

Perhaps the most important feature of our pressure-dependent resistivity (in Fig. 1) is the occurrence of a rapid (though modest) drop in the resistance (and hence of E_g) in a 20-kbar range centered on $P=140$ kbar.

This gap anomaly is in the same pressure range that Zimmer *et al.*[5] report their transition. Above 150 kbar the resistance levels off, however, and from an approximate sample size (Pt lead gap ≈ 0.01 mm) for this run we get a resistivity of about 0.08 Ω cm. This indicates that the sample is still nonmetallic up to 250 kbar. Thus our results are consistent with a sudden though moderate drop in E_g near $P_1 = 140$ kbar, but with the persistence of a narrow gap up to 250 kbar.

Figure 2 shows our resistance versus temperature results for various pressures for EuO. The dominant feature in the temperature-dependent resistivity is the large peak (at a temperature T_p) which occurs above the ferromagnetic ordering temperature (T_c). One explanation for this large resistivity peak could lie with short-range order effects above the ferromagnetic T_c. Suppose one has a thermodynamic fluctuation of a local region into the ferromagnetic state with the surroundings being paramagnetic. The states at the bottom of the $5d$ band in this local region would be pulled down by the magneto-optic red shift. Hence the low-lying conduction band states in this region would have no equienergetic states in the surrounding paramagnetic region into which they could tunnel. The conduction electrons would therefore tend to be bound within the fluctuating regions (i.e., they would have their mobility reduced). This would provide a mechanism for the strong resistivity increase upon approaching T_c from high T. As one approaches the ferromagnetic T_c more closely, correlations between fluctuating ordered regions increase until ordered region → ordered-region electron motion brings the resistivity rapidly down. Below the ferromagnetic T_c the resistivity drops many orders of magnitude depending on pressure. Within this argument the temperature of the peak T_p should be correlated with the ferromagnetic ordering temperature T_c on the high-temperature side.

Under pressure T_p moves to higher temperatures and the preordering peak height is tremendously reduced (see Fig. 2). We believe that the increase in T_p is associated with a pressure-induced increase in the ferromagnetic T_c.

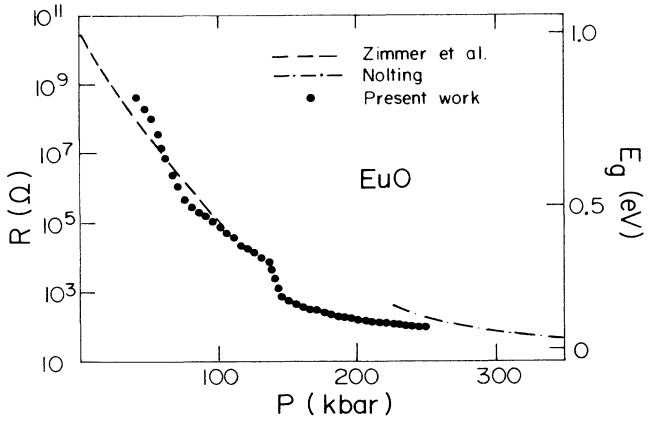

FIG. 1. Resistance R as a function of pressure at room temperature. The dashed line is from Zimmer *et al.* (Ref. 5). Optical measurements and the dash-dotted line is from Nolting's calculations (Ref. 7). The right-hand scale is the effective $4f^7$-$5d$ energy gap derived from Eq. (2).

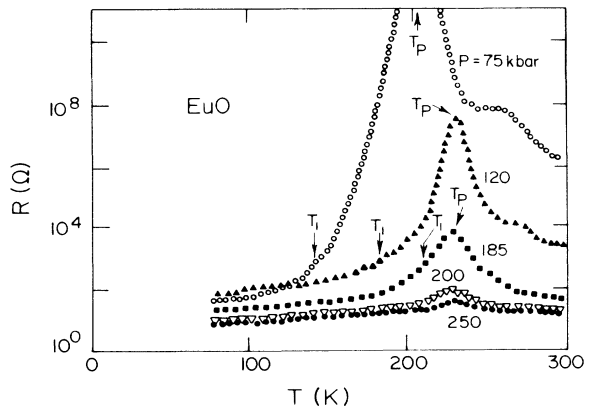

FIG. 2. Resistance R as a function of temperature for various pressures. T_p is the peak temperature and T_I is the inflection point.

This will be discussed at greater length below. The degradation of the height of the resistance peak with pressure is presumably linked to the large increase in the conductivity and carrier concentration of the paramagnetic (high-temperature) state. This linkage is empirically supported by the comparable ordered state (e.g., $T \approx 80$ K) resistance at all pressures.

In analogy with extensive ambient pressure studies on EuO we associate the onset of ferromagnetic order with a small shoulder or inflection point on the left-hand side of the large resistivity peak. This subtle anomaly is best viewed in expanded plots of the data and in numerical derivative curves taken from the data. Like the peak temperature the inflection-point temperature (T_I) shows a systematic increase under pressure. Both the T_p and T_I pressure variations indicate that the magnetic ordering temperature saturates near 200 K for pressures above 120 kbar. Certainly the presence of ferromagnetic order at room temperature below 250 kbar can be ruled out.

Assuming an intrinsic semiconductor condition holds for the $4f^7$-$5d$ system one can extract a rough estimate for E_g from the temperature dependence of the resistivity well above T_p. Doing so one finds an E_g variation that is consistent with that in Fig. 1. Approximate sample sizes for Fig. 2 give room-temperature resistivity values also consistent with Fig. 1.

We summarize our resistivity results in the T-P diagram of Fig. 3. The $R(P)$ nonlinearity (at 300 K) occurring at $P = 140$ kbar is indicated by a hatched region. We associate this with a continuous but nonlinear passage from a region, A ($P < 130$ kbar), where the $4f^7$-$5d$ gap closing is dominated by the crystal-field downshift of the $5d$ band to a region, B ($P > 150$ kbar), where a small hybridization gap is stabilized. One should note that the peak temperatures (T_p) and inflection-point temperatures (T_I) from the resistivity curves match well to the previous lower-pressure variation of the ferromagnetic transition temperatures T_c. (Recall again that we have associated T_I with T_c and T_p with tracking T_c on the high-temperature side.) From these associations we derive several inferences. The ferromagnetic T_c rises rapidly as the region $A \rightarrow$ region B borderline is approached and saturates near 200 K in region B. That is, while the gap E_g is closing rapidly T_c rises rapidly, but when E_g saturates at its high-pressure hybridization value, T_c also saturates. Even up to 250 kbar ferromagnetism persists with T_c on the order of 200 K. This is despite the fact that in this hybridization-gap regime some valence mixing presumably occurs.

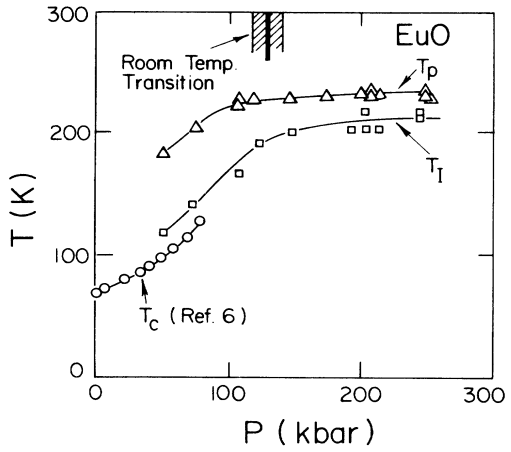

FIG. 3. EuO phase diagram from the previous data. T_c at lower pressures is from McWhan's results (Ref. 6).

Our work favors the identification of the $P > 140$-kbar region of EuO as a hybridization-gap mixed-valent semiconductor phase. Further, we see the ferromagnetic ordering temperature saturating above 200 K. Thus ferromagnetic order cannot be the explanation for the transition at 130 kbar at room temperature. Indeed, Farrell and Taylor[12] have reported high-pressure room-temperature Mössbauer effect measurements which support a pressure-induced increase of Eu valence in EuO around 130 kbar but with no magnetic ordering. In addition, Taylor and Farrell[13] report a magnetic ordering temperature at 200 K at 250 kbar via Eu magnetic hyperfine field measurements, which agree well with our results. In metallic compounds, like $Eu(Pd_{1-x}Au_x)_2Si_2$ a magnetically ordered ground state persists up to an Eu valence of about 2.3.[13] However, Farrell and Taylor[12] report a lesser degree of valence mixing up to 250 kbar in EuO. These results motivate further investigation of the nature of the transition at 140 kbar, along with pressure measurements above 250 kbar in search of a fully collapsed metallic, and nonmagnetic phase for EuO.

*Present address: Martin Marietta Laboratories, 1450 South Rolling Road, Baltimore, MD 21227.

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