PHYSICAL REVIEW B VOLUME 29, NUMBER 4 15 FEBRUARY 1984

Insulator-metal transition and valence instability in EuO near 130 kbar

H. G. Zimmer, K. Takemura, and K. Syassen
Physikalisches Institut III, Universität Düsseldorf, D-4000 Düsseldorf 1, Federal Republic of Germany

K. Fischer
Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, Federal Republic of Germany

(Received 18 August 1983; revised manuscript received 13 December 1983)

Optical reflection spectroscopy reveals an insulator-metal transition in EuO at 140 kbar ($T = 300$ K). The pressure-volume relation starts to exhibit "softening" near 130 kbar. Both observations indicate a continuous valence change commencing at a pressure considerably lower than predicted. The pressure dependence of the $4f$-$5d$ absorption edge suggests that the valence instability is driven by the onset of ferromagnetic ordering and the concomitant exchange splitting of conduction-band states.

The extensive research effort devoted to the semiconductor EuO was predominantly stimulated by those physical properties which are related to the magnetic moment of the half-filled $4f$ shell of divalent Eu ions.[1] The application of high pressure is expected to result in an instability of the $4f$ configuration going along with an insulator-metal (I-M) transition. Jayaraman[2] has reported a 5% isostructural volume anomaly in EuO at 300 kbar (relative volume $V_t/V_0 = 0.82$). The collapsed NaCl phase exhibits a "silvery luster"[2] indicating metallic behavior. Both observations represent characteristic features of a valence change in divalent rare-earth (RE) monochalcogenides.[3] Furthermore, a valence transition near $V_t/V_0 = 0.80$ appears to be consistent with the experimental volume dependence of the optical gap E_g between the localized $4f$ configuration and the bottom of the $5d$ conduction band [$E_g = 1.1$ eV at normal volume,[1] $dE_g/d\ln V = 5$ eV below 10 kbar (Ref. 4)]. Therefore it is believed[2] that EuO undergoes a first-order I-M or valence transition at 300 kbar. This behavior would resemble the valence instability in SmS near 6 kbar.

The primary motivation for a new high-pressure investigation of EuO is twofold: (i) One of the key parameters controlling the course of a valence change is the bulk modulus B. Since B for EuO near 300 kbar is four times larger compared with SmS below 6 kbar, a first-order transition is difficult to imagine within the framework of theoretical models[5] which have addressed the question of continuous versus discontinuous electronic transition in Sm chalcogenides. (ii) If the superexchange mechanism proposed by Goodenough[1] is adopted to extrapolate the experimental pressure dependence of the Curie temperature T_C,[6] one expects ferromagnetic order below 300 kbar at room temperature (see below for details). A valence transition in the ferromagnetic phase, however, would be strongly influenced by an intimate relationship between degree of valence change, dilution of magnetic moments during the transition from the $J = \frac{7}{2}$ to a nonmagnetic ground state, and exchange splitting of conduction-band states (see also Ref. 7). As a result, ferromagnetic ordering below 300 kbar is likely to exclude a discontinuous transition at 300 kbar.

We have measured high-pressure optical properties and the pressure-volume (PV) relation of EuO in the 400-kbar pressure range. Optical reflection spectra and PV data provide conclusive evidence for an I-M transition and the onset of a continuous valence change at the unexpectedly low pressure of ~ 130 kbar. No indication is found for a first-order transition below 370 kbar. The anomalous pressure dependence of optical properties in the vicinity of the transition suggests that the valence instability in EuO at 300 K is *initiated* by ferromagnetic ordering and the concomitant magneto-optical red shift of the $4f$-$5d$ absorption edge.

The high-pressure experiments were performed with the gasketed-diamond-anvil technique.[8] Optical measurements employed a micro-optical system described previously.[9] A conventional diffractometer was used for x-ray diffraction studies. Samples were embedded in silicon oil for x-ray measurements and in NaCl for optical studies. The optical reflectivity (hereafter denoted R_d) was measured at the sample-diamond interface. Pressures were determined from the ruby fluorescence shift.[8]

Figure 1 shows optical reflection spectra of EuO at high pressures. The maximum of R_d in the semiconducting phase [Fig. 1(a)] arises from transitions $4f^7$ to $5d$ conduction band,[1,10] with a contribution from excitonic or atomic-like transitions.[11,12] As expected, the maximum shifts to lower energy with increasing pressure. At 144 kbar the infrared reflectivity shows a drastic increase. An overall rise of R_d continues up to the highest pressure of 370 kbar [Fig. 1(b)]. Obviously, the increase of R_d above 140 kbar must be attributed to a free-carrier contribution in the dielectric response of EuO. From pressure scans of R_d at constant photon energy (0.6 eV) we locate the I-M transition at 140 kbar for a stoichiometric sample. From similar pressure scans for Eu-rich and O-rich material it is found that the sample-dependent variation in transition pressure is less than ±10 kbar for about ±2% deviation from stoichiometry.

Figure 2 shows the PV relation of EuO as determined from x-ray diffraction. For comparison, we also show the PV relation of SrO (Ref. 13) (marked 2+) after a constant pressure of 8 kbar has been subtracted in order to match the normal pressure lattice constants [$a_0(\mathrm{EuO}) = 5.143$ Å, $a_0(\mathrm{SrO}) = 5.160$ Å]. Below 100 kbar, the PV data for EuO and "SrO" agree within experimental uncertainty. Near 130 kbar ($V/V_0 = 0.89$), the PV relation of EuO starts to deviate from the SrO curve, which provides the reference for EuO, if it would remain truly divalent. The volume difference between EuO and SrO increases with pressure and amounts to 5% at 350 kbar. At this pressure, the volume of EuO agrees with Jayaraman's[2] data. However,

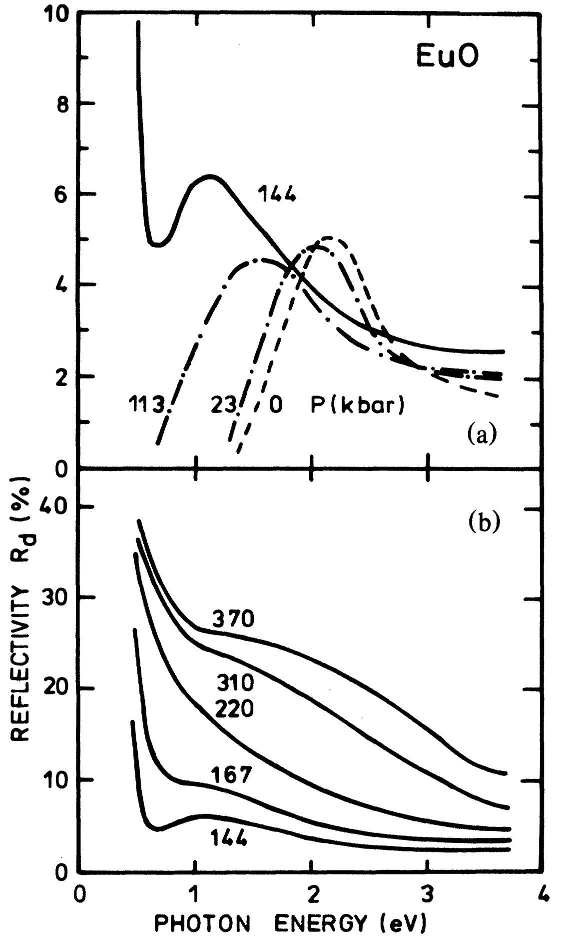

FIG. 1. Reflection spectra of EuO at high pressures. Dash-dotted and solid lines correspond to semiconducting and metallic phase, respectively. The reflectivity is measured at the sample-diamond interface. R_d at normal pressure (dashed line) is calculated from optical constants of Ref. 10.

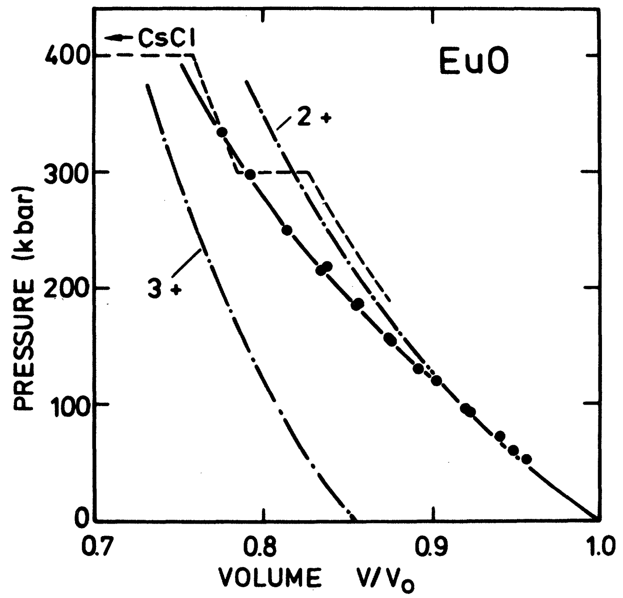

FIG. 2. PV relation of EuO at room temperature. The solid line is a guide to the eye through the present data points. The dashed line represents previous results of Jayaraman (Ref. 2). The dash-dotted lines correspond to PV relations for divalent and trivalent EuO. According to Ref. 2, a NaCl to CsCl structural transition occurs at 400 kbar.

there is no discontinuity at 300 kbar.[14] Also, our value of B_0 (B at 1 bar) is 970 kbar, i.e., somewhat lower compared with $B_0 = 1100$ kbar in Ref. 2 and in closer agreement with ultrasonic data.[1] The present results from reflectivity as well as x-ray measurements lead to the unambiguous conclusion that EuO undergoes a continuous valence transition, starting near 130 kbar.

The PV relation for trivalent EuO in Fig. 2 represents an empirical Birch equation assuming $a_0 = 4.95$ Å,[15] $B_0 = 1.5$ Mbar,[16] and $B_0' = 6$.[17] If this construction of the trivalent PV relation is valid, the valence of EuO at 350 kbar estimated from a lattice parameter scaling is 2.5. Thus EuO is still far from the trivalent state at 350 kbar and the valence instability extends over an extremely large pressure range.

We now turn to the apparent discrepancy between V_t/V_0 estimated from the volume dependence of E_g ($V_t/V_0 \simeq 0.80$) and the experimental value $V_t/V_0 = 0.89$. Figure 3 shows E_g versus volume data corresponding to a pressure range of 100 kbar (above 100 kbar, E_g has dropped below the spectral range accessible in this experiment). Also shown in Fig. 3 is the volume dependence of $E_{\max}$, where $E_{\max}$ corresponds to the maximum of the imaginary part of the dielectric constant as obtained from an analysis of the weak reflection bands in Fig. 1(a). $E_g(V)$ may be described by assuming an inverse four-thirds volume dependence[18] for the width of $5d$ states, i.e.,

$$E_g(V) = E_g(V_0) - \beta[(V/V_0)^{-4/3} - 1] ,$$

with $\beta = 4.2$ eV for EuO. The initial volume coefficient

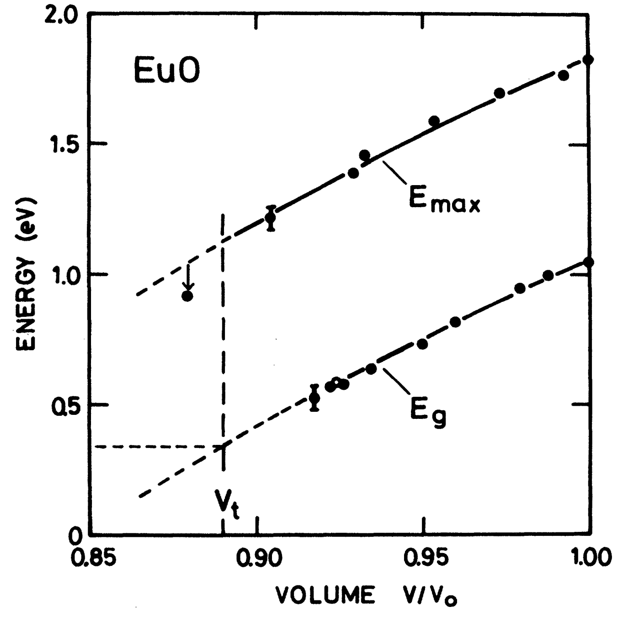

FIG. 3. Volume dependence of the optical gap E_g and the energy $E_{\max}$.

$dE_g/d\ln V=5.6$ eV is slightly larger compared with previous results.[4] Extrapolation of E_g to 130 kbar yields a gap of 0.33 eV. This large value of E_g is inconsistent with the prevailing picture[3] in which $E_g < 0.1$ eV near the onset of a continuous valence change. We are therefore forced to consider a mechanism which explains the rapid decrease of E_g between 100 and 130 kbar, but does not require a volume anomaly. Furthermore, we have to take into account that the reflectivity maximum of the semiconducting phase persists in the metallic phase [see Fig. 1(a), spectrum of 144 kbar] with a small deviation (-0.15 eV) of $E_{\max}$ from the extrapolated curve in Fig. 3.

The explanation is based on a model in which, for $V > V_t$, the optical-absorption edge arises from transitions to delocalized $5d$ states (leaving behind a $4f^6$ configuration) as well as narrow $4f^65d$ states (see also Ref. 11). If one assumes ferromagnetic ordering near V_t, transitions to delocalized states undergo a magneto-optical red shift E_r.[1] More localized $4f^65d$ states, being predominantly responsible for the reflection band at 144 kbar, are less affected by the exchange splitting. In EuO at normal volume, E_r amounts to -0.27 eV.[1] This is roughly the energy needed to close the gap near 130 kbar.

Is ferromagnetic ordering at 130 kbar (room temperature) a realistic assumption? According to McWhan, Sours, and Jura,[6] T_c increases nonlinearly to 125 K at 80 kbar ($T_C=69$ K at 1 bar). Within the superexchange model proposed by Goodenough[1] the ferromagnetic exchange integral $\bar{J}_1$ and therefore also T_C are roughly proportional to $(b/U_{fd})^2$, where b is an overlap integral and U_{fd} is the energy separation $4f^7-5d(t_{2g})$. If one identifies U_{fd} with $E_{\max}$ and assumes that $b \propto d$-band width, one obtains a smooth fit to the experimental[6] volume dependence of T_C. Extrapolation to V_t/V_0 yields $T_C=220$ K. T_C of EuO at normal pressure may be enhanced by a factor of 2 in the presence of free carriers with densities in the order of 10^{20} cm^{-3}.[1] In addition to the superexchange mechanism, free carriers contribute a basically Ruderman-Kittel-Kasuya-Yosida–type interaction between $4f$ spins. Thus, with a source for free carriers, one expects T_C to be considerably higher than 220 K near 130 kbar.

One possible process for free-carrier generation may be the ionization of unidentified deep donor levels. A more important mechanism, however, originates from an instability near V_t, where the extrapolated value of E_g is close to E_r: Spin-correlation results in a red shift of E_g, followed by efficient thermal excitation of electrons across the reduced gap, a stabilization of magnetic order with E_r approaching it's maximum value, and, finally, the onset of the valence instability. This bootstrap mechanism is possible only if ferromagnetism and $4f$ instability coexist in the vicinity of the transition. Theoretical investigations[19] seem to support this coexistence. Dilution of magnetic moments during the course of the valence change decelerates the further progression of the transition with increasing pressure.

The present results provide the first experimental indication for a unique type of electronic and magnetic phase transition in RE monochalcogenides. The interplay of room-temperature ferromagnetic ordering and $4f$ instability near $V_t/V_0=0.89$ turns out to be a direct consequence of the generally accepted understanding[1] of optical and magnetic properties of EuO at normal volume. An investigation of the magnetic phase diagram of EuO at pressures extending beyond 100 kbar would be a valuable complement to the present study.

We gratefully acknowledge several discussions with Professor W. Nolting. One of us (K.T.) expresses his thanks to the Alexander von Humboldt–Stiftung for a research fellowship.

---

[1] P. Wachter, in *Handbook on the Physics and Chemistry of the Rare Earth,* edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, New York, 1979), Vol. 1, p. 507.

[2] A. Jayaraman, Phys. Rev. Lett. 29, 1674 (1972); see also A. Jayaraman, A. K. Singh, A. Chatterjee, and S. K. Devi, Phys. Rev. B 9, 2513 (1974).

[3] For a review see, e.g., J. M. Lawrence, P. R. Riseborough, and R. D. Parks, Rep. Prog. Phys. 44, 1 (1981).

[4] P. Wachter, Solid State Commun. 7, 693 (1969); see also M. R. Oliver, J. A. Kafalas, J. O. Dimmock, and T. P. Reed, Phys. Rev. Lett. 19, 1064 (1970).

[5] See, e.g., L. L. Hirst, J. Phys. Chem. Solids 35, 1285 (1974); C. M. Varma and V. Heine, Phys. Rev. B 11, 4763 (1975); S. D. Mahanti, T. A. Kaplan, and M. Barma, Phys. Lett. 58A, 43 (1976).

[6] D. B. McWhan, P. C. Sours, and G. Jura, Phys. Rev. 143, 385 (1966).

[7] W. Nolting, J. Phys. C 15, 733 (1982); Z. Phys. B 49, 87 (1983).

[8] A. Jayaraman, Rev. Mod. Phys. 55, 65 (1983).

[9] K. Syassen and R. Sonnenschein, Rev. Sci. Instrum. 53, 644 (1982).

[10] G. Güntherodt, Phys. Condens. Matter. 18, 37 (1974).

[11] T. A. Kaplan, S. D. Mahanti, and M. Barma, in *Valence Instabilities and Related Narrow Band Phenomena,* edited by R. D. Parks (Plenum, New York, 1977), p. 153.

[12] O. V. Farberovich and S. V. Vlasov, Phys. Status Solidi B 105, 755 (1981).

[13] L. Liu and W. A. Bassett, J. Geophys. Res. 78, 8470 (1973).

[14] The difference in experimental results can presumably be attributed to experimental uncertainties in the earlier experiment (Ref. 2) which employed the ungasketed-diamond-cell technique.

[15] J. M. Leger, N. Yacoubi, and J. Loriers, J. Solid State Chem. 36, 261 (1981).

[16] A. Jayaraman, B. Battlogg, R. G. Maines, and H. Bach, Phys. Rev. B 26, 3347 (1982).

[17] B_0' ($=dB/dP$ at V_0) is chosen such that $B_0'(3+) > B_0'(2+)$, where $B_0'(2+)=4.3$.

[18] Systematic trends among the Eu chalcogenides (see Ref. 1) suggest that the volume dependence of the d-band width is weaker compared with Heine's inverse five-thirds law.

[19] W. Matlak and W. Nolting, Solid State Commun. 47, 11 (1983).