

(Utrecht) 36, 457 (1967).<sup>9</sup>A. Weijland and J. M. J. van Leeuwen, *Physica* (Utrecht) 38, 35 (1968).<sup>10</sup>C. Bruin, to be published.<sup>11</sup>M. H. Ernst and A. Weyland, *Phys. Lett.* 34A, 39 (1971).

## Pressure-Induced Electronic Collapse and Semiconductor-to-Metal Transition in EuO

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Pressure-volume data for EuO to 400 kbar are presented. An electronic collapse in the Eu ion involving the promotion of a  $4f$  electron to the  $5d$  state occurs near 300 kbar at room temperature. The structure remains NaCl type in this transformation. The transition appears to be first order and is from semiconductor to the metallic state. The collapsed NaCl phase undergoes a phase change to the CsCl-type structure near 400 kbar.

We have investigated the pressure-volume relationship in EuO to 400 kbar at room temperature, with a view to finding out if a pressure-induced electronic collapse due to the promotion of a  $4f$  electron to the  $5d$  state occurs in the Eu ion. Such a transition does not seem to take place in EuTe,<sup>1</sup> EuSe, and EuS<sup>2</sup> at pressures up to 300 kbar. In EuO we have found strong evidence for such an electronic transition near 300 kbar. The transition is isostructural (NaCl type to NaCl') but the lattice parameter contracts rapidly near this pressure. The high-pressure phase exhibits a *silvery luster* indicating that it is metallic in nature and hence the transition is from semiconductor to metal. This is the first time a  $4f$ - $5d$  electronic collapse has been observed in a europium chalcogenide and the finding has interesting consequences.

Pressure-volume data to 400 kbar were obtained using a high-pressure diamond-anvil x-ray camera,<sup>3,4</sup> with Ag as the internal standard. Pressures were computed from the recent data of Liu and Bassett<sup>5</sup> for silver. The latter have compared Ag with NaCl up to 300 kbar. The bulk modulus  $B_0$  and its pressure derivative  $B_0'$  obtained by Liu and Bassett were used in the Birch equation of state to extrapolate the pressure scale above 300 kbar. The pressures are believed to be true within  $\pm 20$  kbar in the higher pressure range and  $\pm 10$  kbar below 300 kbar.

In Fig. 1 the pressure-volume data for EuO are presented. In a previous study McWhan, Souers, and Jura,<sup>6</sup> have obtained  $P$ - $V$  data on EuO to 80 kbar and fitted their experimental points to a curve calculated with  $B_0 = 1170$  and  $B_0' = 4$  in the Birch equation of state. Subsequently McWhan revised the value of  $B_0$  to 1130 kbar.<sup>7</sup> In Fig. 1 the

solid curve represents the calculated  $P$ - $V$  relationship using  $B_0 = 1130$  kbar and a  $B_0'$  of 3.75, in the Birch equation of state. The present data, which extend to very much higher pressures than those of Ref. 6, give a better fit with a  $B_0'$  of 3.75. Up to about 280 kbar our experimental points follow the calculated curve closely. Within a narrow pressure interval the volume drops rather abruptly by about 4%. However, there is no change in the structure; the NaCl-type structure remains NaCl. The lattice-parameter contraction suggests that the atomic volume of one of the ions decreases. We ascribe this rather rapid volume decrease without change of structure to a change in the valence state of the Eu ion from divalent to trivalent due to  $4f \rightarrow 5d$  electron promotion. Figure 1 also shows a further abrupt decrease in volume near 400 kbar. This volume decrease is associated with the transition of the collapsed

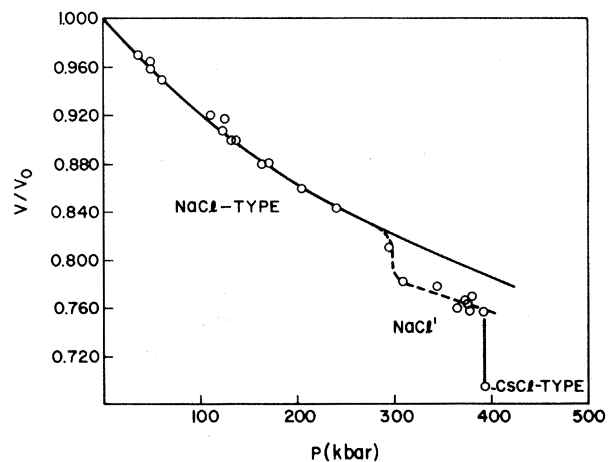


FIG. 1. Pressure-volume relationship for EuO.

NaCl phase to the CsCl-type structure ( $a_{\text{NaCl}} = 4.74 \text{ \AA}$ ;  $a_{\text{CsCl}} = 2.92 \text{ \AA}$ ;  $\Delta V_{\text{trans}} = 6.5\%$ ).

For the Sm ion, an electronic collapse involving a valence change from the  $2^+$  towards the  $3^+$  state due to  $4f \rightarrow 5d$  electron delocalization has been reported in SmTe, SmSe, and SmS.<sup>8,1</sup> Such a transition exhibits large changes in conductivity,<sup>8</sup> anomalous pressure-volume behavior, and a dramatic change in the reflectivity. In SmS this is a discontinuous event and the sample suddenly changes its reflectivity from black to a bright golden yellow color.<sup>9</sup> The high-pressure phases show positive temperature coefficients of resistivity and all exhibit metallic conductivity. However, recent pressure-volume studies on EuTe,<sup>1</sup> EuSe, and EuS<sup>2</sup> and optical observation in the diamond-anvil camera to 300 kbar pressure have failed to show any evidence for such an electronic transition in these, although a previous study by Rooymans<sup>10</sup> claimed observation of a valence transformation in EuTe near 30 kbar. EuTe, EuSe, and EuS exhibit a perfectly normal compression curve, compressibility decreasing pressure, and undergo the NaCl-to-CsCl-type transition at about 100, 140, and 190 kbar, respectively.

Eu monochalcogenides are all semiconductors, and optical absorption studies have established that the energy gap between the localized  $4f$  state and the  $6s$ - $5d$  conduction band edge decreases systematically<sup>11</sup> in the sequence EuTe (2.0 eV), EuSe (1.85 eV), EuS (1.64 eV), and EuO (1.12 eV) (the values are for 300°K). For all these compounds it has been found that the above gaps decrease with pressure.<sup>12</sup> The published values<sup>12</sup> are  $-12$ ,  $-8.4$ ,  $-7.9$ , and  $-4.4$  meV/kbar for EuTe, EuSe, EuS, and EuO, respectively. If these values are converted to deformation potentials and are used to estimate the volume at which the energy gap between the  $4f$  level and the conduction band should vanish, one obtains  $V/V_0$  of 0.61, 0.63, 0.75, and 0.78 for EuTe, EuSe, EuS, and EuO, respectively, in the NaCl phase. It may be seen from Fig. 1 that for EuO it is precisely near a  $V/V_0$  of 0.78 that the electronic collapse occurs. The rather rapid change in  $V/V_0$  from about 0.82 to 0.78 within a narrow pressure interval strongly suggests that the transition may be of first order, since the energy gap between  $4f$  and the  $6s$ - $5d$  conduction band should still be quite substantial at a  $V/V_0$  of 0.82. The gap at this volume is estimated to be about 0.2 eV. The collapse of this gap to zero within a very narrow pressure range must there-

fore mean a first-order  $4f \rightarrow 5d$  electronic transition. Qualitatively we observe a large hysteresis of the transition, which further strengthens this picture. For EuTe, EuSe, and EuS a transformation to the CsCl structure takes place before the above  $V/V_0$ 's are reached in their NaCl phases. The competing NaCl-to-CsCl transition is probably the reason why in these Eu monochalcogenides the  $4f \rightarrow 5d$  electronic collapse does not appear in their NaCl structure. Whether such a collapse can occur in the CsCl structure at very high pressures is still an open question.

Since one  $4f$  electron per EuO may be expected to be released in the valence transformation of Eu in EuO, the high-pressure phase should have a carrier density of  $3.74 \times 10^{22}/\text{cm}^3$  (calculated from the lattice constant of 4.743 Å at 310 kbar and assuming that one  $4f$  electron per EuO is delocalized). The high-pressure phase should therefore be metallic in nature. We have not measured the resistivity under pressure in EuO but have obtained evidence for the metallic nature of the high-pressure phase. The latter phase of EuO exhibits a *silvery luster*, as observed in the diamond-anvil camera by reflecting white light off the pressurized sample. This qualitative observation, we believe, is strong evidence for the metallic nature of the high-pressure phase and is quite in line with what one might expect for the reflectivity of a system with a carrier density  $N = 3.74 \times 10^{22}$  electrons/cm<sup>3</sup>. In a metal, all frequencies below the plasma cutoff frequency  $\omega_p$  are totally reflected. From the expression  $\omega_p^2 = 4\pi Ne^2/m^*$ , one obtains for the high-pressure phase of EuO  $\omega_p = 10.4 \times 10^{15}$ , on the assumption that the effective-mass ratio  $m^*/m_0 = 1$ . The plasma cutoff edge corresponding to this frequency would be about 7 eV. One therefore expects the entire visible spectrum to be totally reflected. In this circumstance the high-pressure phase of EuO should appear *silvery* and this is actually observed. The true plasma edge can be modified by the presence of interband transitions. Whether such a situation exists for EuO is a matter of detail, which cannot be discussed until quantitative reflectivity data are obtained. Unfortunately, this is difficult in the present case because of the extremely high-pressure transition.

That the NaCl-to-CsCl transition is a ubiquitous phenomenon<sup>1</sup> for the rare-earth monochalcogenides is again proved by EuO. Thermodynamically speaking it appears to compete with the electronic collapse, lowering its free energy much

faster with pressure, and it appears to win in the competition in all the Eu monochalcogenides with the exception of EuO. EuO is thus the first Eu chalcogenide to exhibit a valence transformation from the  $2^+$  towards  $3^+$  state due to  $4f$ -to- $5d$  electron delocalization, prior to the CsCl transformation. Qualitative optical observation shows that the CsCl form of EuO is also metallic in nature. *Per contra*, the CsCl phases of EuTe, EuSe, and EuS do not exhibit any metallic reflectivity to about 350 kbar pressure,<sup>13</sup> which suggests that there is no significant change in the valence state of Eu in these cases up to the above pressure.

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<sup>1</sup>A. Chatterjee, A. K. Singh, and A. Jayaraman, *Phys. Rev. B* **6**, 2285 (1972).

<sup>2</sup>A. Jayaraman, unpublished.

<sup>3</sup>W. A. Bassett, T. Takahashi, and P. W. Stook, *Rev. Sci. Instrum.* **38**, 37 (1967).

<sup>4</sup>We believe that 400 kbar pressure attained in the present study is a new record of highest pressure for the diamond-anvil camera.

<sup>5</sup>L. Liu and W. A. Bassett, to be published.

<sup>6</sup>D. B. McWhan, P. C. Souers, and G. Jura, *Phys. Rev.* **143**, A385 (1966).

<sup>7</sup>D. B. McWhan [*J. Chem. Phys.* **44**, 3528 (1966)] has suggested  $1030 \pm 130$  kbar as his estimate for  $B_0$  for EuO.

<sup>8</sup>A. Jayaraman, V. Narayanamurti, and E. Bucher, *Phys. Rev. Lett.* **25**, 4130 (1970).

<sup>9</sup>The metallic phase of SmS exhibits a golden yellow luster: J. L. Kirk, K. Vedam, V. Narayanamurti, A. Jayaraman, and E. Bucher, *Phys. Rev. B* **6**, 3023 (1972).

<sup>10</sup>C. J. M. Rooymans, *Ber. Bunsenges. Phys. Chem.* **70**, 1036 (1966), and *Solid State Commun.* **3**, 421 (1965).

<sup>11</sup>J. O. Dimmock, *IBM J. Res. Develop.* **14**, 301 (1970), and references cited therein. Also S. J. Cho, *Phys. Rev. B* **1**, 4589 (1970).

<sup>12</sup>P. Wachter, *Solid State Commun.* **7**, 693 (1969).

<sup>13</sup>A. Jayaraman, unpublished.

## Experimental Evidence of the Anomalous Hall Effect in a Nonmagnetic Semiconductor

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The anomalous Hall effect is measured in InSb at low temperature. In this nonmagnetic semiconductor the polarization of the conduction electrons is obtained by application of an external magnetic field  $B_0$ . The spin-dependent Hall effect is separated from the much larger ordinary Hall effect by magnetic resonance of the conduction electrons. Two physical mechanisms responsible for the anomalous Hall effect are separated and the experimental results agree within a factor of 2 with the theoretical predictions without any adjustable parameter.

The discovery of a strong anomalous Hall effect in ferromagnetic materials initiated an abundant literature on the theory of the spin-dependent Hall effect,<sup>1</sup> but this theory was obscured for a long time by the extreme complexity of the ferromagnetic systems at finite temperatures. The theories conflicted in the interpretation of the physical mechanisms responsible for the effect, although most of them agreed on the importance of the spin-orbit interaction. Recently,<sup>2</sup> the consideration of much simpler physical systems like III-V semiconductors has somewhat clarified the situation, acknowledging for the most part the validity of the pioneering work of Luttinger.<sup>3</sup> However, an experimental study of the anomalous Hall effect in one of those simple

nonmagnetic systems, permitting a direct comparison with the theory, was still lacking. In this work we present the first anomalous Hall effect obtained in a semiconductor, thus providing experimental evidence of the validity of the theoretical model. In this material there is no spontaneous magnetization, and the polarization of the conduction electrons is obtained by application of an external magnetic field  $B_0$ . The experimental difficulty is to separate unambiguously the small spin-dependent Hall effect, corresponding to the equilibrium polarization, from the much larger ordinary Hall effect. This is achieved by observing the effect on the Hall voltage of a change of the electronic spin polarization. This change is obtained by a magnetic res-