

Pressure-volume relationship and pressure-induced electronic and structural transformations in Eu and Yb monochalcogenides

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The pressure-volume relationships for EuSe, EuS, YbSe, and YbS have been obtained from high-pressure x-ray-diffraction studies to nearly 300 kbar. Like EuTe, EuSe and EuS exhibit normal compression and undergo the NaCl-to-CsCl-type transition at about 145 and 215 kbar. The compression curves of YbSe and YbS are anomalous in the 150–200-kbar region, which we believe is because of a change in the valence state of Yb from 2^+ towards the 3^+ state. Among the Eu monochalcogenides EuO is the only substance that shows a valence transformation (≈ 300 kbar) followed by a NaCl-to-CsCl-type transition (≈ 400 kbar). However, all the Yb monochalcogenides undergo the valence transformation continuously with pressure. The bulk moduli evaluated from the experimental P - V data and the measured pressure coefficients of the energy gap between the $4f$ level and the conduction-band edge from optical-absorption studies of divalent rare-earth monochalcogenides are compared. These data are used to rationalize the occurrence or nonoccurrence of the valence transitions in this series of compounds.

I. INTRODUCTION

Recent pressure studies on Sm monochalcogenides,^{1,2} EuO,³ TmTe,^{2,4} and YbTe^{2,5} have shown that the rare-earth ions in these compounds undergo a pressure-induced valence change from 2^+ towards the 3^+ state, due to $4f$ electron promotion. In SmTe and EuO, in addition to the above electronic transition, a pressure-induced structural transition from the NaCl-type to the CsCl-type structure, and in EuTe only this latter transition, has been reported.

Pressure-volume studies have been particularly valuable in establishing the occurrence or nonoccurrence of the electronic transition mentioned above, since property changes such as resistivity variation with pressure,¹ although very important, can be influenced by the presence of impurities and cannot be taken as conclusive evidence for the occurrence of such a transition. Compressibility, on the other hand, reflects the bulk property of the material and valence transitions of the type that we are interested in are clearly seen as anomalous compression regions in the pressure-volume relationship,² especially since the size changes involved in the rare-earth ions at the latter transition are strikingly large. As a part of our program of investigating the behavior of divalent rare-earth monochalcogenides under pressure, we have studied the pressure-volume relationship in EuSe, EuS, YbSe, and YbS, using high-pressure x-ray-diffraction techniques to nearly 300 kbar. We have obtained strong evidence for the occurrence of a pressure-induced valence change in the Yb com-

pounds. EuSe and EuS show no evidence for an electronic transition, but they undergo the NaCl-to-CsCl transition. We have also made some qualitative observations on the optical reflectivity changes with pressure in these materials. These results will be presented and discussed along with EuTe, EuO, and YbTe, the pressure-volume behavior of which were briefly reported in earlier communications.^{1–3,5}

II. EXPERIMENTS AND RESULTS

The pressure-volume data up to nearly 300 kbar were obtained from lattice-parameter measurements, using a diamond-anvil high-pressure x-ray apparatus.⁶ The diffraction patterns were recorded with the two-film cassette introduced by Singh,⁷ for better accuracy in the lattice-parameter measurements. Below 50-kbar pressure, lattice-parameter data were also collected with an opposed-tungsten-carbide-anvil high-pressure x-ray camera.⁸ Pressures were estimated using NaCl or Ag as internal standards. The latter proved better for use above 50 kbar, as NaCl extrudes excessively at higher pressures resulting in too weak a diffraction pattern. The theoretical equation of state for NaCl⁹ and the experimental equation of state for Ag¹⁰ have been used in converting the volume to pressure.

The samples used in the present study were made by techniques referred to in earlier publications.^{1,2,5} The NaCl-type structure and the lattice parameters were checked with the published values. In Table I these are given.

TABLE I. Lattice parameters and bulk moduli of divalent rare-earth monochalcogenides.

Substance	Lattice parameter a (Å)	Bulk modulus B_0 (kbar)	M/ρ (cm ³)	Bulk modulus B_0 (kbar) other work
EuTe	6.60	400 ± 50	43.3	400 ± 30 ^a 360 ± 50 ^{b,c}
EuSe	6.19	520 ± 50	35.7	526 ± 100 ^a 476 ± 50 ^{b,c}
EuS	5.97	610 ± 50	32.0	555 ± 55 ^a 500 ± 75 ^{b,c}
EuO	5.14	1100 ± 50	20.45	900 ± 150 ^a 900 ± 100 ^{b,c}
YbTe	6.36	460 ± 50	38.75	
YbSe	5.93	610 ± 50	31.42	610 ^d
YbS	5.68	720 ± 50	27.55	740 ^d
TmTe	6.34	460 ± 50	38.33	465 ^d
SmTe	6.60	400 ± 50	43.2	400 ^d
SmSe	6.22	400 ± 50	35.86	520 ^d
SmS	5.97	151	32.0	600 ^d 476 ± 50 ^e

^aReference 12.^bAdiabatic values.^cReference 13.^dFrom Fig. 7.^eReference 15.

III. EUROPIUM MONOCHALCOGENIDES

The pressure-volume data for EuSe and EuS are reproduced in Figs. 1 and 2. The solid line represents the computer fit to the data points using a second-degree polynomial. In Fig. 3 the data for all the Eu monochalcogenides are presented for ready comparison. From Figs. 1 and 2 it is clear that the compression curves for EuSe and EuS are normal, compressibility decreasing with

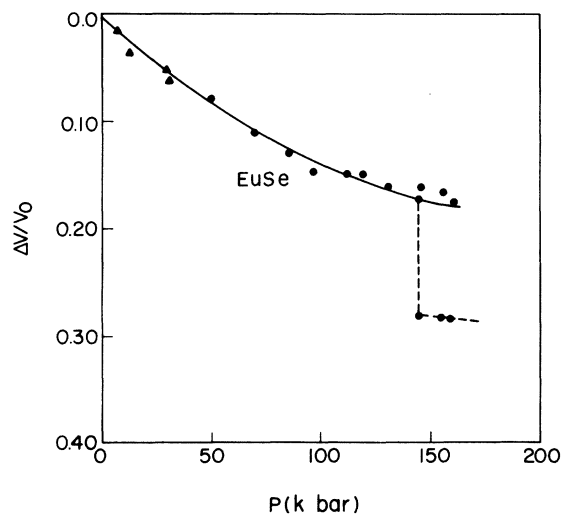


FIG. 1. Pressure-volume data for EuSe. Solid line is the computer fit to the data points. The discontinuity in volume is due to NaCl-CsCl transition.

increasing pressure. The discontinuous volume changes at 145 and 215 kbar for EuSe and EuS, respectively, are due to a transition from the NaCl- to CsCl-type structure. From Fig. 3 it is evident that EuTe also exhibits normal compressibility and undergoes the latter transition near 110 kbar. Europium oxide is the only Eu chalcogenide that shows an isostructural transition near 300 kbar and the NaCl-to-CsCl-type transition near 400 kbar.

IV. YTTERBIUM MONOCHALCOGENIDES

Pressure-volume data for YbSe and YbS are reproduced in Figs. 4 and 5, and in Fig. 6 the data for all three Yb chalcogenides are presented. The solid lines in Figs. 4 and 5 are polynomial fits to

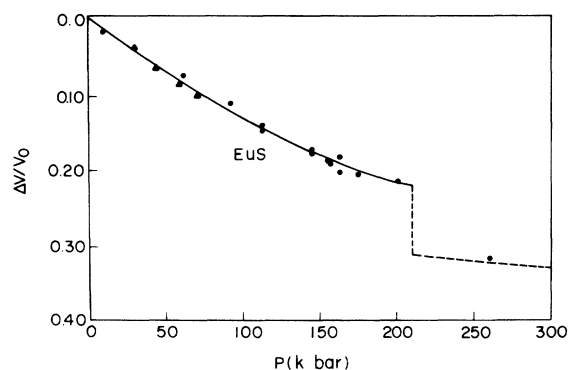


FIG. 2. Pressure-volume data for EuS. Solid line is the computer fit to the data points. The discontinuity in volume is due to NaCl-CsCl transition.

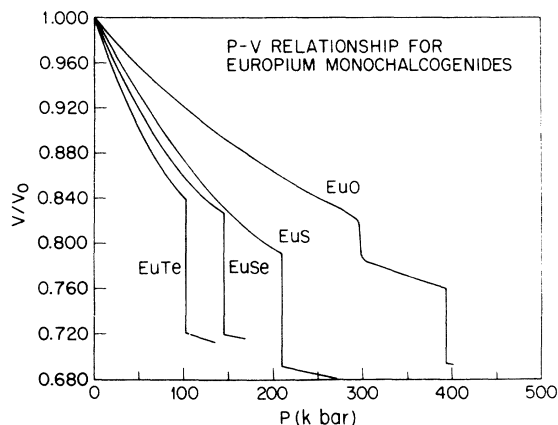


FIG. 3. P - V relationship for the Eu monochalcogenides.

the data points. The Yb chalcogenides exhibit anomalous compressibilities in the 150-200-kbar region but the structure remains NaCl type in the entire pressure range investigated. This anomalous compression we believe is due to a pressure-induced change in the valence state of Yb from the 2^+ state towards the 3^+ state.

V. DISCUSSION

A. Compressibilities

The pressure-volume relationship of EuTe was first investigated by Rooymans.¹¹ He reported a volume discontinuity and an isostructural transition near 30 kbar which was attributed to a valence change of Eu from the divalent to the trivalent state. Our compression measurements on EuTe, however, do not show any evidence for such a transition and the compressibility of EuTe is perfectly normal up to 110 kbar. The discontinuous volume

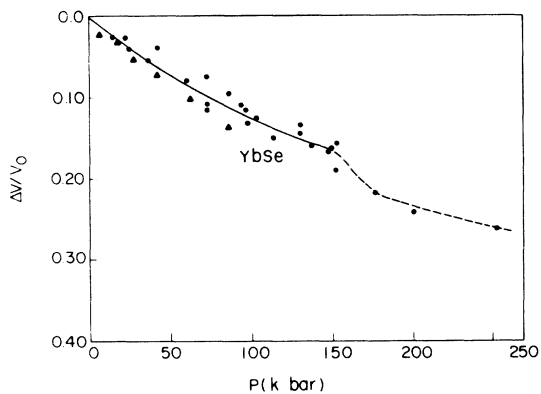


FIG. 4. Pressure-volume data for YbSe. The solid line is computer fit to the data points. The anomalous P - V relationship in the 150-200-kbar region is due to valence change of the Yb from 2^+ towards the 3^+ state.

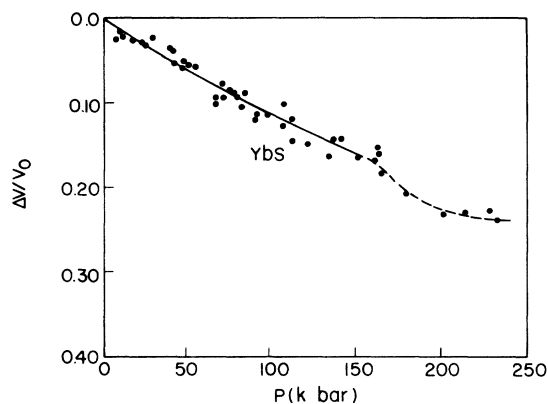


FIG. 5. Pressure-volume data for YbS. The solid line is the computer fit to the data points. The anomalous P - V relationship in the 150-200-kbar region is due to valence change of the Yb from 2^+ towards the 3^+ state.

change at 110 kbar, as pointed out, is due to the NaCl-to-CsCl transition. The P - V relationships presented for EuSe and EuS in this work show that their compression curves are also perfectly normal. The only phase transformation encountered in the pressure range investigated is the NaCl to CsCl type near 145 and 210 kbar for EuSe and EuS, respectively.

In Fig. 7 we present the pressure-volume data for the Sm chalcogenides, for the sake of completeness of our discussion of the behavior of divalent rare-earth monochalcogenides under pressure. In an earlier publication² we discussed at length the anomalous P - V relationships in these

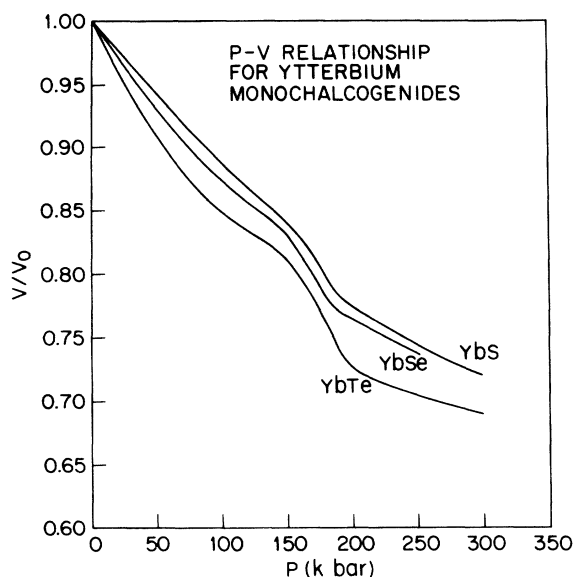


FIG. 6. P - V relationship for the Yb monochalcogenides.

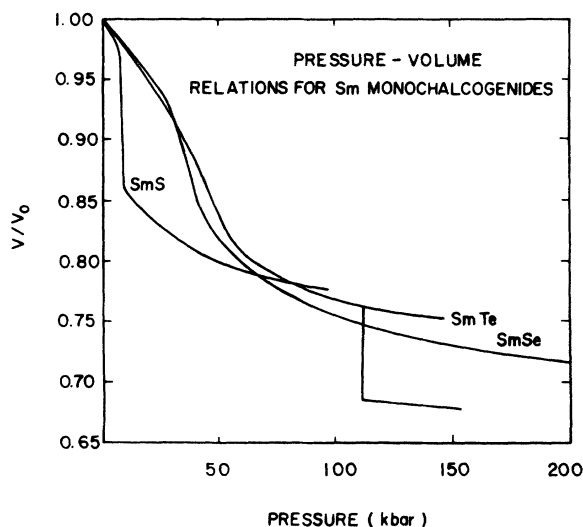


FIG. 7. P - V relationships for the Sm monochalcogenides.

compounds and their significance. Stated briefly, the anomalous compressibility of SmTe and SmSe in the 1–60-kbar region and the discontinuous volume change at 6.5 kbar in SmS are due to a pressure-induced valence change of the Sm ion from the 2^+ state towards the 3^+ state. This valence transformation is found to be a first-order transition in SmS while in SmTe and SmSe it takes place continuously with pressure; the structure, however, remains unchanged as the NaCl type. The volume discontinuity in SmTe near 110 kbar is due to a structural transition from the NaCl to the CsCl type. The pressure-volume behavior of Sm chalcogenides confirmed the notion of the promotion of a $4f$ electron into the $6s$ - $5d$ conduction band, proposed to explain the resistivity behavior under pressure. From a comparison of Figs. 3 and 7 it may be seen that the pressure-volume relationships of EuTe, EuSe, and EuS are totally different from those of their Sm counterparts. This can be rationalized on the basis of the differences in the parameters connected with the electronic band structure of the two sets of compounds, which we will discuss later in this paper. We will now turn to a consideration of the compressibilities of the divalent rare-earth monochalcogenides and compare them.

The solid lines in Figs. 3 and 6 represent the computer fit to the experimental data using the Birch equation of state, in the region of stability of the NaCl phases showing normal compression. The bulk moduli (B_0) obtained from these fits are listed in Table I. In the case of Eu chalcogenides the initial bulk moduli obtained by Levy and Wachter¹² from high-pressure single-crystal x-

ray-diffraction studies in the 1–4-kbar region and the adiabatic bulk moduli of Shapira and Reed¹³ are also given in the table for comparison. Our values are in reasonable agreement with the above determinations, considering the error bars in our and their data.

Anderson and Nafe¹⁴ have proposed an interesting empirical relationship between bulk modulus B_0 at atmospheric pressure and specific volume (per ion pair) V_0 of the form $B_0 \sim V_0^{-x}$. They find it to hold for a particular class of compounds, where the value of x depends on the class of compound. For alkali halides, fluorides, sulfides, and tellurides they find x to be 1 and for oxide compounds x is close to 4. A plot of $\ln B_0$ against the \ln of specific volume (M/ρ , where M is the molecular weight and ρ the density) for a number of tellurides, selenides, and sulfides exhibits a linear relationship.

The rare-earth chalcogenides represent an ideal series for a test of this relationship because of their close similarity. In Fig. 8 the logarithm of the experimental isothermal bulk moduli are plotted against the logarithm of the specific volumes computed from the crystallographic data. In the plot, some of the alkaline-earth chalcogenides, i.e., BaSe, BaTe, and CaTe, have also been included. Even EuO seems to fall in line with the tellurides, selenides, and sulfides. From this plot the bulk moduli of Yb chalcogenides can be predicted and in Table I these predicted values

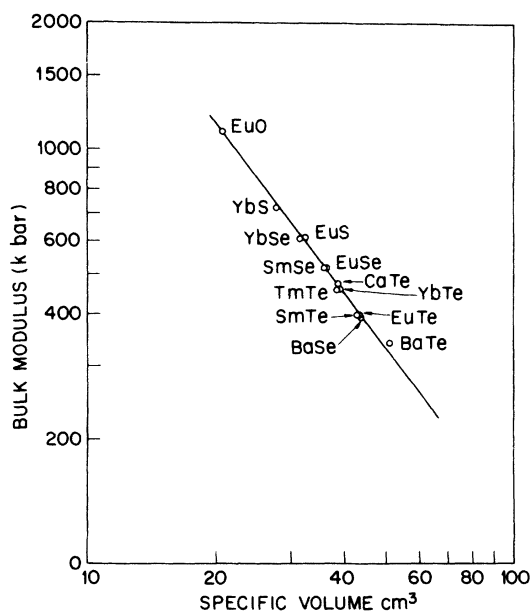


FIG. 8. Plot of the \ln of bulk modulus against the \ln of the specific volume (M/ρ) for divalent RE monochalcogenides and some alkaline-earth chalcogenides.

are compared with the experimental values. The agreement is good.

The bulk modulus for SmS that we quoted in an earlier publication² has recently been questioned by Kaldis and Wachter.¹⁵ These authors have determined the lattice parameter of SmS as a function of pressure in the 1–4-kbar region using single-crystal x-ray-diffraction techniques and quote a value of 476 ± 50 kbar for the bulk modulus of SmS.

The relationship between the bulk moduli and the specific volume presented in Fig. 8 predicts 400, 520, and 600 kbar for SmTe, SmSe, and SmS, respectively. These are to be compared with our previous estimate of 400, 400, and 151 kbar for SmTe, SmSe, and SmS.² While the agreement for SmTe is excellent, our previous values for SmSe is somewhat lower and the discrepancy for SmS is large. We now believe that our previous estimate of the initial bulk modulus of SmS is low and the value of 476 ± 50 kbar obtained by Kaldis and Wachter is likely to be closer to the true value. Kaldis and Wachter have argued that the compressibility of SmS has to be the same as for EuS, since their valence states and the radii of the respective ions are the same. However, it should be recognized that the $4f$ - $5d$ energy separation in SmS, even according to them, is less than 0.1 eV,¹⁵ whereas it is 1.64 eV for EuS. SmS is just on the verge of making a valence transformation and this fact makes it different from EuS. Because of the small energy separation in SmS (over an order of magnitude smaller than EuS) there is bound to be an appreciable change in the valence state of the Sm ion at room temperature even at low pressures in SmS. Hence the initial compressibility of SmS may be expected to be higher than that of EuS. In fact, this appears to be true when the value of 474 kbar for B_0 of SmS obtained by Kaldis and Wachter is compared with 600 kbar predicted from the plot in Fig. 8. The abnormally low value of the bulk modulus of SmS that we reported earlier is the result of our having taken the volume change of compression at a pressure of 6.5 kbar and assuming that a straight line P - V relationship holds from zero pressure to this value. However, we believe that before the discontinuous transition there is a substantial change in the valence state of the Sm ions in SmS, leading to abnormal compression, and hence our earlier estimate of dV/dP is not correct.

B. P - V relationship and the $4f \rightarrow 5d$ electronic transition

The divalent rare-earth (RE) monochalcogenides are all semiconductors, because the RE ions in these are divalent, leading to exact charge compensation. Optical absorption studies^{16–24} have established that the localized $4f$ state in these materials lies in the energy gap between the valence band

derived from the anion p states and the conduction band derived from the RE $6s$ and $5d$ states. The optical-absorption features and electrical properties are dominated by the presence of the $4f$ level. Optical-absorption studies have shown that the $4f$ -level-conduction-band energy separation decreases systematically in going from the telluride to the oxide (see Table II). Since the valence transformation involves the delocalization of the $4f$ electron and its merging with the conduction band at some high pressure, the occurrence or nonoccurrence of the valence transformation in a certain range of pressure is determined by the magnitude of the $4f$ -conduction-band energy separation ΔE_g and the rate at which it decreases with pressure. The smaller is ΔE_g and the larger its pressure coefficient, the higher is the probability for a pressure-induced valence transformation. The $4f$ -level-conduction-band energy separation ΔE_g and the experimentally determined $d(\Delta E_g)/dP$ for the RE chalcogenides are presented in Table II. From these data and the bulk modulus B_0 , it is possible to estimate the relative volume at which ΔE_g would go to zero. This is done by converting the $d(\Delta E_g)/dP$ to the deformation potential Σ , $\Sigma = [d(\Delta E_g)/dP]B_0$ and then dividing the gap ΔE_g by Σ . The values thus obtained are shown in Table II. In Sm chalcogenides the electronic collapse occurs near these values (see Fig. 7). In the case of EuO the isostructural transition occurs near the predicted V/V_0 of 0.77, which we believe is strong evidence for the valence transformation. The rather rapid change in V/V_0 from about 0.82 to 0.77 within a narrow pressure interval strongly suggests that the transition may be first order. Further, the energy gap between the $4f$ level and the conduction-band edge should be about 0.2 eV at V/V_0 of 0.82, and the collapse of this large gap to zero within a small pressure interval has to involve a first-order transition because the $d(\Delta E_g)/dP$ for EuO is quite small. In EuTe, EuSe, and EuS the NaCl-CsCl transition takes place long before V/V_0 reaches the value for the closure of ΔE_g (see Table II) in their respective NaCl phases. Apparently the NaCl-CsCl transition competes with the electronic transition in all the Eu monochalcogenides and it is only in the case of EuO that the electronic transition precedes the former. This must mean that the free energy of the CsCl phase is lowered more rapidly with pressure in EuTe, EuSe, and EuS, forcing this transition.

Since the valence transformation involves the delocalization of one $4f$ electron per molecule into the conduction state, a semiconductor-to-metal transition follows. The high-pressure phase of EuO may therefore be expected to have a carrier density of 3.74×10^{22} electrons/cm³ (calculated from the lattice parameter of 4.743 Å at 310 kbar

TABLE II. *4f*-conduction-band-edge separations, and their pressure and volume derivatives for Eu and Yb monochalcogenides.

Substance	Energy separation <i>4f</i> -cond. -band edge (eV)	$\frac{d(\Delta E_g)}{dP}$ (meV/kbar)	Deformation potential Σ (eV)	V/V_0 for $\Delta E_g \rightarrow 0$	Phase transition (kbar)	ΔV of Transition at NaCl-CsCl
EuTe	$\sim 2.0^a$	-12.0^b	-4.8	0.58	NaCl-CsCl ~ 110	-11.6%
EuSe	~ 1.7	-8.4^b	-4.37	0.59	NaCl-CsCl ~ 145	-12.8%
EuS	$\sim 1.64^a$	-7.9^b	-4.82	0.66	NaCl-CsCl ~ 215	-12.5%
EuO	$\sim 1.12^a$	-4.4^b	-4.84	0.77	Electronic collapse ~ 300 NaCl-CsCl ~ 400	-6.5%
YbTe	$\sim 1.80^c$	-11 ± 1^c	-5.06	0.65	Electronic collapse 150-200	...
YbSe	$\sim 1.50^c$	-10 ± 1^b	-6.1	0.75	Electronic collapse 150-200	...
YbS	$\sim 1.0^c$	-6 ± 1^c	-4.32	0.77	Electronic collapse 150-200	...
SmTe	0.70^d	-11.9^d	-4.7	0.85	Electronic collapse contin. 1-60 NaCl-CsCl 110	-9.1%
SmSe	0.50^d	-11.0^d	-5.7	0.92	Electronic collapse contin. 1-50	
SmS	0.065^e	-10.0^f	-4.7	0.98-0.99	Electronic collapse discont. 6.5	

^aReference 23.^bReference 25.^cReference 22.^dReference 1.^eReference 15.^fA. Jayaraman (unpublished).

and assuming that one *4f* electron per EuO is delocalized). We have not measured the conductivity of EuO as a function of pressure but have made visual observations of the reflectivity characteristics in the diamond anvil apparatus. The high-pressure phase of EuO exhibits a *silvery luster*. This we believe is strong evidence for the metallic nature of the high-pressure phase for the following reason. For a system with $N = 3.74 \times 10^{22}$ electrons/cm³ the plasma frequency ω_p [$\omega_p = (4\pi Ne^2/m^*)^{1/2}$] would be 10.4×10^{15} if 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 visible spectrum to be totally reflected making the material appear silvery. Our qualitative observations on EuTe, EuSe, and EuS with the diamond-anvil apparatus reveal

no striking changes in the reflectivity to 300 kbar. If any valence change had taken place in the Eu ion, striking changes in the reflectivity are inevitable; in analogy with the high-pressure phases of SmTe, SmSe, and SmS, deep purple, metallic copper, and bright gold²⁶ color would have resulted for the EuTe, EuSe, and EuS, respectively. Neither in their NaCl phase nor in the CsCl phase is any drastic change in reflectivity observable and hence we conclude that no change in the valence state of the Eu ion occurs in EuTe, EuSe, and EuS in the pressure ranges studied.

In the case of the Yb monochalcogenides the compression curves give strong evidence for the occurrence of electronic transitions. For Yb monochalcogenides, the energy gaps²⁰⁻²² ΔE_g , the pressure coefficients²² of this gap, the deformation potentials

calculated, and the estimated V/V_0 at which the $4f$ -conduction band gap ΔE_f should vanish are presented in Table II. From the V/V_0 data it is clear that the electronic transition may be expected in these near V/V_0 of 0.75. The experimental compression curves for the Yb monochalcogenides show an anomalous P - V relationship in the 150–200-kbar region which is close to V/V_0 of 0.75. The curves exhibit normal behavior (compressibility decreasing with pressure) up to about 150 kbar and then the compressibility increases with increasing pressure up to 200 kbar. Beyond 200 kbar the compression curves turn over and seem to exhibit normal behavior again. We have considered in our earlier paper² the manner in which a valence change would influence the compression curve if $4f$ electrons are delocalized and promoted to the $6s$ - $5d$ conduction-band states. From the compression curves of Yb chalcogenides it appears that the electronic collapse due to a change in the valence state of Yb from 2^+ towards 3^+ takes place continuously with pressure in all the Yb chalcogenides, for it seems to be spread over a range of pressure. The present P - V measurements are not fine enough to distinguish between a continuous or discontinuous transition with certainty. Resistivity measurements under pressure could provide more conclusive evidence on this aspect.

We have also obtained other strong qualitative evidence for the occurrence of the valence transformation in Yb chalcogenides. Since the valence change would involve the promotion of a $4f$ electron into the conduction band, striking changes in the optical reflectivity are to be expected, in analogy with the behavior of the Sm monochalcogenides. Our qualitative observations on the reflectivity change with pressure in the diamond-anvil camera show that above 200 kbar YbTe, YbSe, and YbS, all of which are usually black in color, turn deeply purple, copperish, and golden yellow in color, respectively. Such changes are the characteristic colors exhibited by the electronically collapsed high-pressure phases of SmTe, SmSe, and SmS.

VI. SUMMARY AND CONCLUSIONS

Pressure-volume studies have been very crucial in understanding and establishing pressure-induced

phase transitions in RE monochalcogenides. We have shown from pressure-volume relationships that the Sm monochalcogenides, the Yb monochalcogenides, EuO, and TmTe all undergo a pressure-induced change in their valence state from 2^+ towards the 3^+ state. Observations on the optical-reflectivity change have provided additional strong support for the valence transformation. In SmS this transition is discontinuous and strongly first-order. In EuO this electronic transition appears to be discontinuous and hence first order. In SmTe, SmSe, and Yb monochalcogenides the transition appears to be continuous. However, the P - V relationships obtained in this study are not fine enough to conclude whether the transition is abrupt or continuous in the latter. The Eu monochalcogenides, with the exception of EuO, do not seem to undergo any valence change in the pressure range investigated. They all, however, show the NaCl-to-CsCl transition. The magnitude of the volume changes accompanying this transition is comparable to the ΔV associated with the NaCl-CsCl transition in SmTe and PrTe,² which suggests that the Eu ions in the CsCl phase of EuTe, EuSe, and EuS have not undergone any appreciable change in their valence state. It would, therefore, be worthwhile to extend x-ray studies to higher-pressure ranges in the case of EuTe, EuSe, and EuS, since they should ultimately undergo a change in valence under pressure. In this connection it may be of interest to study them using shock-wave techniques to obtain their P - V relationships which would clearly reveal any valence transformation, if it occurs. In the Yb and Eu chalcogenides the pressure variation of resistivity should also be studied to corroborate the results of P - V studies and to determine the precise manner in which the $4f$ -electron delocalization occurs.

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