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To cite this version:

K. Syassen. PRESSURE-INDUCED 4f INSTABILITIES AND INSULATOR-METAL TRANSITIONS IN HEAVY RARE EARTH MATERIALS. Journal de Physique Colloques, 1984, 45 (C8), pp.C8-123-C8-139. <10.1051/jphyscol:1984824>. <jpa-00224324>

HAL Id: jpa-00224324
https://hal.archives-ouvertes.fr/jpa-00224324
Submitted on 1 Jan 1984

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PRESSURE-INDUCED 4f INSTABILITIES AND INSULATOR-METAL TRANSITIONS IN HEAVY RARE EARTH MATERIALS

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I - INTRODUCTION

Most of the rare earth (RE) atoms are divalent in the gas phase, but change their valence state to trivalent in the solid state. The valence change results from a gain in total energy due to the transfer of an electron from the 4f shell into a bonding state. In the middle (Sm and Eu) and at the end (Tm and Yb) of the RE series Hund's rule correlation energy is in some cases sufficient to either stabilize the divalent state or cause the occurrence of intermediate (non-integral) ionic valence states. The pressure variable plays an important role in creating the intermediate valence (IV) state or/and in the investigation of its many unusual features, as is well documented in several review articles and conference proceedings.

RE materials showing divalent or IV behavior are most easily recognized by their large molar volume (or the larger ionic size of the RE ion) as compared to similar compounds across the RE series. This is demonstrated in Fig. 1 for the RE metals and the RE monochalcogenides (including oxides). The anomalies near the middle and the end of the RE row, which correspond to divalent behavior, are immediately obvious. In particular the Sm and Tm chalcogenides have attracted considerable interest, because their valence state can be changed significantly by the application of moderate pressures (7 kbar in SmS, 50 kbar in TmTe), by chemical alloying, or by temperature. Eu and Yb metal and their monochalcogenides (MC's) are more stable against a pressure-induced valence transition, and considerably higher pressures are required in order to possibly induce a significant valence change. Thus, in following the scope of this conference, which emphasizes the high pressure regime, we will discuss valence related properties of Yb and its monochalcogenides, but also...
add some remarks regarding the corresponding Eu based materials. A further aspect of the high pressure regime, brought about by the occurrence of structural transitions in IV MC's, is the interplay between crystal structure and electronic structure in these materials.

The outline of the paper is as follows: First, a brief characterization of the IV state and of the overall features of the electronic structure of the RE materials of interest here is given. Second, the experimental and theoretical evidence supporting the (still controversial) occurrence of a pressure-induced valence change in Yb metal is summarized. Third, the optical response of IV YbS is discussed, which lends strong support to a localized mechanism of the valence instability in this material. This unusual behavior is in sharp contrast to the common picture of the electronic structure of other IV MC's. Finally, the effect of a B1-B2 structural transition (NaCl-type to CsCl-type) on the electronic structure of IV SmTe is compared to the situation in the alkaline earth compound SrTe.

II - INTERMEDIATE VALENCE AND ELECTRONIC STRUCTURE

An exhaustive presentation of the many facets of the valence fluctuation phenomenon is given in Refs. 1-10. Very briefly, the IV state can be thought of as a mixture of RE ions with two nearly degenerate ionic configurations $4f^{n+1}$ and $4f^{n}5d$. At any given site, charge fluctuations between the two configurations occur on a time scale known as the valence fluctuation time (typically $10^{-11}$ to $10^{-13}$ seconds). In the IV (or homogeneously mixed-valent) state all the RE ions occupy crystallographically equivalent sites. This has to be distinguished from such inhomogeneously mixed-valence compounds, where two distinct valence states occupy inequivalent lattice sites. Quantum mechanically the situation is described in terms of a hybridization of the two configurations. A common view is that the hybridization involves 5d itinerant states or "band electrons". The IV state is then described in terms of a band structure picture.
As indicated in Fig. 2, the $4f^{n+1}$ multi-electron level of a divalent RE metal is located below the Fermi level (Fig. 2a), while in the divalent RE-MC's the $4f^{n+1}$ level falls in the gap between valence band and 5d6s conduction band states (Figs. 2b and c). We emphasize that the meaning of these energy level schemes is to account for energy differences measured in optical excitation processes. Under pressure the conduction band broadens and the bottom of the 5d band is lowered relative to the 4f state, while s-like conduction band states are pushed up in energy. This behavior is suggested by more general trends in bandstructure under pressure. As a result, the optical 4f-5d excitation energy is reduced under pressure. The decrease of the optical f-d excitation energy is closely related (but not identical) to the decrease in the enthalpy difference between divalent and trivalent ground state. Within the given interpretation of our energy level scheme, the IV state corresponds to an overlap of the Fermi level with the localized $4f^{n+1}$ level, as indicated in Fig. 2d for a RE-telluride. In the IV state charge fluctuates between the $4f^{n+1}$ state and band states, and the bonding properties change considerably. The Fermi level remains pinned to the 4f level, as long as it is not exhausted by a complete transfer of one full electron into band states. In the IV state the 4f level is broadened with the width given by the inverse of the fluctuation time. We will refer to the situation described here as the "band picture" of the IV state.

A change from divalent to IV behavior in RE-MC's corresponds to a semiconductor to metal transition. Some of these IV "metals" exhibit several unusual features like, for example, the increase of the electrical resistance at low temperatures in "gold" SmS, which may be related to the presence of a small (7 meV wide) hybridization gap at the Fermi level. For our present discussion such more subtle features of the IV state will not be relevant, since we are concerned with IV behavior at normal temperature and at pressure conditions, which are not truly hydrostatic.
III - YTTERBIUM METAL

The energy balance for the occurrence of a valence change in Yb metal was first investigated by Johansson and Rosengren. Their model starts out from binding energy considerations, which suggest that at zero pressure the divalent state with electronic configuration $4f^{14}(6d6s)^2$ (in addition to the Xe core) is stable by about 0.5 eV/atom with respect to a hypothetical trivalent state $4f^{13}(5d6s)^2$. Similar energy differences have been derived by de Chatel and Boer starting from cohesive energies and the atomic $4f^{14}6s^2 - 4f^{13}5d6s^2$ excitation energy. A schematic diagram of their Born-Haber cycle is included in Fig. 3. Johansson and Rosengren use an empirical pseudopotential model to obtain the "repulsive" part of the potential curves for divalent and trivalent Yb as also shown in Fig. 3. The repulsive part obtained from an integration of the experimental pressure-volume (PV) relation of Lu, being a trivalent neighbor to Yb in the Periodic Table, is in close agreement with the theoretical prediction. We have added the attractive part using the empirical relation proposed in Ref. 22. In this way one arrives at $E_{\text{exc}} = 0.9$ eV/atom for the energy needed to excite divalent Yb to the trivalent state at fixed lattice spacing corresponding to divalent Yb at normal pressure. For comparison, photoemission studies yield an excitation threshold to the $4f^{13}5d$ configuration of about 1.2 eV. This is consistent with our value of $E_{\text{exc}}$ if one takes into account final state and/or lattice relaxation effects, which in photoemission increases the energy of the $4f^{13}5d$ state by about 0.2 to 0.3 eV (see, e.g., Ref. 24). Thus the approximate energy level diagram in Fig. 3 appears to be well supported by experimental data.

Fig. 3 - The ground state energies of divalent and trivalent Yb metal as a function of Wigner-Seitz radius. Energies are given relative to the divalent $(4f^{14}6s^2)$ free atom state. $\Delta H_{\text{coh}}(14)$ is the cohesive energy of divalent Yb. $\Delta H_{\text{coh}}(13)$ is the cohesive energy of hypothetical trivalent Yb. $\Delta E(14-13)$ is the energy required to excite a free Yb atom to the (spherically averaged) $4f^{13}5d6s^2$ configuration. These energy differences are taken from Ref. 20. See text for more details.
Fig. 4 - Pressure as a function of Wigner-Seitz radius for Yb. Solid line and closed circles represent recent experimental data of Ref. 26. The dashed line corresponds to pseudopotential calculations for divalent Yb. The dash-dotted line represents the results obtained by Skriver using the first principle LMTO-ASA method. The experimental PV relations of Ca and Lu are shown for comparison.

Based on this energy level scheme and the corresponding enthalpy difference, a first order transition from the divalent to a fully trivalent state is predicted at about 130 kbar with a relative volume change of about 14%. A simplification in this picture is the neglect of quantum mixing between divalent and trivalent configurations of the Yb ions, which may turn the transition into a more gradual process, as is observed experimentally.

Experimental evidence for a pressure-induced valence change in Yb stems from PV studies and from x-ray absorption edge measurements. Fig. 4 shows the experimental pressure-radius relation for Yb at 300 K according to the most recent x-ray diffraction studies. Structural transitions from fcc to bcc and from bcc to hcp occur at 38 kbar and 260 kbar, respectively, with a small relative volume change of about 2.5%. The structural transitions are discussed in more detail elsewhere. Here, we will only consider the overall behavior of the pressure-radius relation with respect to divalent and trivalent references.

The experimental data for Yb are compared in Fig. 4 to calculated results obtained within the empirical pseudopotential approach and from the first principle linear muffin tin orbital method (LMTO-ASA) in combination with the atomic sphere approximation. In these calculations Yb is treated as purely divalent and a pressure-induced 6s to 5d electron transfer is, of course, taken into account. In addition, Fig. 4 also shows the experimental pressure-radius relation for Ca. A comparison between Yb and Ca appears reasonable, because they have a similar conduction band structure and ionic and atomic radii of Ca and divalent Yb at normal conditions are also very similar. The calculated results for divalent Yb agree reasonably well among each other and also with the experimental data for Ca, thus establishing an
approximate pressure-radius relation for ficticious divalent Yb under pressure. Comparison with experimental data then suggests that the compression of Yb is indeed strongly anomalous. An interpretation of the PV anomaly in terms of a participation of 4f electrons in chemical bonding appears to be not justified. Therefore, the PV relation provides strong support for a significant continuous valence change in Yb starting at pressures well below 100 kbar.

The compression curve of Lu (hcp phase is included in Fig. 4. The pressure-radius curves of Yb and Lu start to overlap at around 200 kbar. In the case of IV RE monochalco-
genides and intermetallics a lattice parameter scaling (Vegard's law or modifications of it, see Refs. 32 and 33) is frequently used to determine the valence. Such simple scaling procedures always yield a complete valence change to trivalent, if the experimental volume approaches the limiting value for the trivalent reference. Thus, one is tempted to claim a complete valence change to the trivalent state in Yb near 200 kbar. However, this conclusion is not consistent with results of \( L_{III} \)-edge absorption measurements.

The apparent discrepancy between volume and \( L_{III} \)-edge valence near 200 kbar may be resolved by taking into account the effect of quantum mixing between \( 4f^{n+1} \) and \( 4f^{n}d \) configurations of the rare earth ion. A phenomenological approach is proposed by Wohlleben and coworkers, who discuss the configuration mixing in the framework of statistical thermodynamics with application to Ce metal. In their model (see also Refs. 36 and 37) a volume-dependent mixing matrix element between the ionic \( 4f^{n+1} \) and \( 4f^{n}d \) configurations determines the valence fluctuation rate (or fluctuation temperature), which in turn plays an important role in calculating the mixing entropy term in the Gibbs free energy of a valence fluctuation system. As a result, the mixing entropy term yields a negative internal pressure contribution, which, at a given valence and external pressure, drives the volume towards smaller values as compared to the situation without quantum mixing. Furthermore, at a sufficiently high fluctuation temperature, the valence is pushed towards the entropy limit, which is close to 2.9 for Yb. This value is determined by the one- and eightfold degeneracy of the Hund's rule ground state of \( 4f^{14} (^{5}S_0) \) and \( 4f^{13} (^{4}F_{7/2}) \) configurations, respectively. The entropy mechanism is considerably more important in elemental Yb as compared to IV compounds or alloys, because the overlap between neighboring Yb atoms is much larger in the pure metal. Therefore, the approach to the trivalent reference volume near 20 GPa does not imply that Yb is in a fully trivalent state at this pressure. It would be conceivable that the entropy mechanism and the underlying configuration mixing results in a molar volume of IV Yb, which is smaller compared to the trivalent reference. At present it is premature to apply the statistical thermodynamics model to Yb in a quantitative manner, because, in addition to the PV relation, a more accurate determination of the valence under pressure is required in order to determine the volume dependence of the fluctuation temperature. These data may soon become available using improved techniques for x-ray absorption studies at high pressures.

The temperature dependence of the high pressure electrical resistance of Yb does not show any evidence for anomalous scattering processes, which are usually observed in IV intermetallics. Based on their experimental results, Bireckhoven and Wittig conclude that Yb metal remains essentially divalent up to at least 270 kbar. The validity of this conclusion would, for instance, imply the complete failure of a first principle calculation to yield the pressure-volume relation of divalent Yb metal in reasonable agreement with experiment. This is difficult to imagine in view of recent successes of total energy calculations. Furthermore, the energy level
diagram presented in Fig. 3, which is supported by experimental data, would be seriously in error, at least with regard to the "repulsive parts". In our opinion, the considerable difference in electronic structure of IV Yb metal as compared to IV Yb-intermetallics has to be taken into account, before any conclusions about the degree of configuration mixing in Yb can be drawn from resistance measurements.

Recent renormalized atom calculations by Herbst and Wilkins are consistent with the onset of a 4f instability in Yb in the 100 kbar range. These calculations also suggest that a predominantly divalent state of Yb may become stable again at pressures in the order of 3 Mbar. Such a reversal of the valence change may be interpreted by analogy to the potential and kinetic energy considerations, which qualitatively explain the electron transfer from extended s-states into the higher angular momentum d-states in transition and RE metals under pressure (see, e.g., Refs. 11, 12, 42). The outer 5d electrons of Yb are excluded from the core region by orthogonality requirements. At large compression the increase of their one-electron kinetic energies will dominate over the change in potential energy. Thus, the 5d levels should rise in energy relative to the more localized 4f states. The predicted "reentrance pressure" of roughly 3 Mbar is surprisingly low. A possible consequence of this prediction is that Yb metal will never completely transform into a fully trivalent state. Furthermore, a similar argument may apply to many IV materials.

Eu is the other divalent RE metal being a candidate for a pressure-induced 4f instability. The experimental PV relation in the 300 kbar range suggests that the compression of Eu is also anomalously large, thus providing evidence for a major change in electronic structure involving 4f electrons. Eu metal may, however, be more stable against a pressure-induced 4f instability resulting in a smaller valence change as compared to Yb at the same pressure. This is indicated by the larger free enthalpy difference (~1 eV) between divalent and hypothetical trivalent configurations at normal pressure and also by the larger 4f\textsuperscript{n+1} - 4f\textsuperscript{n-1}d excitation energy (~1.5 eV) seen in photoemission.

IV - THE 4f INSTABILITY IN YbS

The only experimental evidence for pressure-induced valence transitions in Yb-MC's comes from x-ray diffraction data, which reveal the onset of continuous compression anomalies at pressures ranging from 80 kbar in YbO to 170 kbar in YbTe. Here we are concerned with the optical detection and characterization of the IV behavior in YbS, which leads to a very different picture of the IV state in this material (and other Yb-MC's) as compared to the Sm- and Tm-MC's. In order to clarify this difference, it is appropriate to summarize some optical properties of IV Sm and Tm compounds and the commonly accepted interpretation.

One of the most striking features of the valence change in SmS near 7 kbar is the color change from dark grey to golden yellow. As shown in Fig. 5, the collapsed "metallic" phase exhibits high reflectivity in the near-infrared and a pronounced reflectivity edge in the visible part of the optical spectrum. A very similar behavior is found for SmSe, SmTe (see also below), and TmTe in the pressure-induced IV phase and also in TmSe, which shows IV behavior at normal pressure. Moreover, the gross features of the optical response of these IV compounds is similar to that of GdS (see, e.g., Ref. 49), which is a trivalent RE material showing normal metallic behavior.

The high reflectivity in IV SmS, SmSe and TmSe has been attributed to a Drude-like behavior arising from a transfer of 4f electrons into one-electron conduction band states. It is in fact the optical response, which lends strong support to the "band picture" (see section II) of a valence transition in these materials. Within this picture, the position of the reflectivity edge is approximately given by the screened plasma frequency

\[ \omega_p = (ne^2/m*_{\infty})^{1/2} \] (1)
where $n$ is the density of band electrons and $m^*$ is their optical effective mass. The background dielectric constant $\varepsilon_\infty$ is primarily determined by valence to conduction band transitions (see Fig. 2), which have appreciable oscillator strength commencing in the photon energy range from 3 to 6 eV near normal pressure. The analysis of the optical response of IV SmS*9 and TmSe*9 suggests that the density of band electrons in these materials is roughly consistent with the fractional occupation of the $4f^{n5d}$ configuration, i.e., the d electron fully contributes to a free electron like response.

With the help of Fig. 5, we point out a technical detail. In the high pressure reflection spectra reported below the reflectivity (denoted $R_d$) is always measured at the sample-diamond interface (for more details see Ref. 54). The large refractive index of diamond ($n_m = 2.41$) is responsible for the fact that the reflectivity $R_d$ is in general lower as compared to measuring at the usual sample-vacuum interface. This is demonstrated in Fig. 5 which also shows the reflection spectrum of SmS for the sample-diamond interface as calculated from the dielectric function given in Ref. 49.

Optical reflection spectra of YbS at pressures between 6 and 390 kbar are shown in Fig. 6. In the semiconducting phase below about 80 kbar one observed two weak reflection bands separated by about 1.3 eV. These transitions correspond to excitations from the $4f^{14}$ ground state to an excitonic (or atomic-like) $4f^{13}5d(t_{2g})$ excited state, which is basically split into two components $^2F_7/2$ and $^2F_5/2$ due to spin-orbit interaction (1.24 eV in the free ion) of the $4f^{13}$ configuration (see also Refs. 56 and 57). A f-d Coulomb interaction or 5d electron spin-orbit splitting may introduce further splittings, which would account for the weak structure observed in the first reflection peak (see Fig. 6). Excitations of $4f^{n+1}$ into localized $4f^{n5d}$ states are always observed in semiconducting RE-MC's, but are not included in Fig. 2. The excitation threshold from $4f^{14}$ to 5d conduction band states in YbS is 1.27 eV at normal pressure, which is slightly less than the energy of the maximum of the first excitonic peak. With increasing pressure the crystal field acting on the d component $4f^{13}5d(t_{2g})$ increases and the excitation energy decreases at a rate of about 11 meV/kbar. This pressure dependence indicates the onset of IV behavior in the vicinity of 100 kbar.

In accordance with this extrapolation, the reflectivity starts to increase considerably above 100 kbar reaching saturation between 300 and 400 kbar. However, below 1 eV one finds a sharp reflectivity edge, which becomes more pronounced and shifts to
higher energy with increasing pressure. It is this behavior, which is completely different from the IV Sm and Tm MC's.

The reflectivity of YbO under pressure qualitatively shows a similar behavior in the semiconducting phase as well as in the pressure range corresponding to the existence of a IV phase. Obviously, the pronounced near-infrared reflectivity minimum in IV YbO und YbS is characteristic for the Yb ion. A crystal structure effect can be excluded, because the NaCl phase in YbO and YbS has been shown to be stable up to at least 350 and 250 kbar, respectively, and, furthermore, the crystal structure systematics in monochalcogenides under pressure suggests a transition to the most likely CsCl structure to occur at pressures above 400 kbar.

In order to facilitate the interpretation of the optical reflection spectra of YbS, Drude-Lorentz type expressions were fitted to the experimental spectra. As an example, Fig. 7 shows an optical conductivity spectrum (real part $\sigma_1$) of YbS at 390 kbar, as obtained from the fitting procedure. (The optical conductivity $\sigma_1(\omega)$ is proportional to $\omega \varepsilon_2(\omega)$ with $\varepsilon_2(\omega)$ being the imaginary (absorptive) part of the dielectric function.) For the analysis we have assumed that the reflectivity of IV YbS below the present experimental energy range increases again towards high values, due to either metallic behavior or other strong low energy excitations (see dotted line in Fig. 7). Furthermore, the background dielectric constant $\varepsilon_\infty$ was chosen to be 4.5, which is slightly larger compared to the corresponding values of alkaline earth sulphides at normal pressure. Although the absolute values of $\sigma_1$ are somewhat uncertain due to these assumptions, the spectral shape of the conductivity spectrum is not
Fig. 7 - Optical conductivity (real part) of YbS at 390 kbar. The dotted line is the corresponding reflection spectrum with the assumed extrapolation below 0.5 eV.

affected. Thus, a dominant feature in the optical response of IV YbS is a pronounced narrow absorption peak in the near-infrared, which exhibits a blue-shift with increasing pressure.

In Fig. 8 the optical transition energies of YbS (maxima of \( e_2(\omega) \)) are plotted as a function of pressure. Results for the IV phase are given as negative energies. By representing the data in this way, an explanation of the unusual absorption feature in IV YbS becomes immediately obvious. After the "crossover" between the two 4f configurations near 100 kbar, a correlated (or localized) \( 4f^{13}5d \) state becomes the ground state of the system. In this picture, the strong absorption peak in the IV phase corresponds to optical excitations from the localized \( 4f^{13}5d \) ground state to the \( 4f^{14} \) state, which now is the excited state. This description only gives the very basic features of our interpretation. The actual situation is certainly more complicated. First, hybridization between \( 4f^{14} \) and \( 4f^{13}5d \) (indicated by dotted lines in Fig. 8) is possible according to a mechanism proposed by Kaplan and Mahanti and also discussed in Refs. 62-64. Thus, the valence change is a gradual transition with the \( 4f^{14} \) ground state acquiring more and more \( 4f^{13}5d \) character and, simultaneously, with the excited state becoming of predominant \( 4f^{14} \) character. The relative admixture of the two configurations in the ground state determines the valence state. Second, since d conduction band states overlap the localized ground state, some of the electrons of \( 4f^{13}5d \) go into band states. Thus, the system becomes "metallic", which then justifies our above extrapolation of the experimental reflectivity below 0.5 eV photon energy. A schematic picture of the situation near the Fermi level is given in Fig. 9, which also demonstrates the difference between the localized picture and the "band picture" of the IV state in RE MC's. It seems that the optical response of the IV Yb-MC's provides the first clear experimental evidence for a localized mechanism of a 4f instability in Re-MC's.

The localized mechanism of the valence transition in Yb-MC's requires a strong Coulomb interaction for the formation of the localized \( 4f^{13}5d \) configuration. Intuitively, it may be plausible that an almost filled 4f shell has a strong tendency to bind an extra 5d electron in order to form a spin singlet state. However, it remains to be investigated in more detail, why a predominantly localized ground state is formed in IV Yb-MC's, but not in the corresponding Sm and Tm compounds. It should
Fig. 8 - Optical transition energies in YbS as a function of pressure.

Fig. 9 - Schematic representation of the difference between (a) "band picture" and (b) localized picture of the IV state in rare earth monochalcogenides.
be mentioned, however, that weak local correlation effects have very recently been postulated in the interpretation of experimental results related to the valence instability in the TmSe-TmTe alloy system. Furthermore, Kaplan et al. argue that a localized model would even be consistent with the optical response of "gold" SmS. An interesting question now is, how large a screening by band electrons is tolerable for the stability of a localized ground state. In other words, is a localized mechanism to some extent relevant to IV Yb-intermetallics or even in Yb metal?

A comparison with Eu-MC's is difficult, because EuO appears to be the only compound in this group, which undergoes a significant valence change in the pressure range of 400 kbar. Optical reflection measurements and x-ray diffraction data reveal a continuous onset of the 4f-instability starting at the unexpectedly low pressure of 130 kbar, which is in marked contrast to the previously reported transition at about 300 kbar. Essentially based on the validity of the "band picture" for IV EuO, the low transition pressure was tentatively interpreted in terms of an interplay between ferromagnetic ordering, exchange splitting of the conduction band, and the onset of the 4f instability. The new results for Yb-MC's suggest to also consider the possibility of a predominantly localized mechanism of the valence instability in EuO. This might affect the interpretation of the unusual behavior of EuO near 130 kbar. Although the optical data are possibly consistent with a more localized ground state in IV EuO, the evidence is not as strong compared to the situation in Yb-MC's.

V - B1-B2 TRANSITION IN SmTe AND COMPARISON TO SrTe

High pressure x-ray investigations suggest the occurrence of a continuous valence change in SmTe at pressures below 100 kbar. From a lattice parameter scaling a mean valence of roughly 2.7 at 100 kbar can be derived. High pressure reflection spectra of SmTe are shown in Fig. 10. The two sharp peaks below 2 eV observed in the semiconducting phase (Fig. 10a) can be attributed to 4f6 - 4f55d(t2g) transitions. The doublet originates from the 6H1 and 6Fj terms of the 4f5 configuration. The third peak near 3 eV cannot be interpreted as a similar atomic transition. We tentatively assign this peak to an excitonic structure associated with zone center valence to conduction band (p to d) transitions. This assignment is suggested by a comparison to the high pressure optical response of SrTe, which, with regard to the valence-conduction band structure, should be very similar to SmTe.

The first strong absorption feature in SrTe at normal pressure occurs at 3.75 eV. This excitonic transition is clearly observed in high pressure reflection spectra as shown in Fig. 11. Below 120 kbar, one finds two sharp structures near 3 eV, which are separated by about 0.65 eV. Both peaks undergo a red-shift with increasing pressure, which suggest the interpretation as excitonic p to d transitions. The 0.65 eV separation is due to spin-orbit splitting of the valence band. The fact that the corresponding peak in SmTe occurs at about 0.8 eV lower energy as compared to SrTe arises from the larger nuclear charge of Sm, which pulls the states down relative to the top of the valence band. For comparison, the first excitonic peak in BaTe is shifted by 0.65 eV to lower energy relative to SrTe. We note, that a number of band structure calculations for alkaline and RE MC's predict an indirect band gap for these materials in the NaCl phase, i.e., the top of the valence band is at the zone center and the bottom of the conduction band at the zone edge (X-point). Thus, weak valence-conduction band excitations are expected below the first excitonic peak. Experimentally, the excitation threshold for these band to band transitions seems to be unknown.

The continuous evolution to a Drude-like metallic reflectivity in SmTe (Fig. 10b) with saturation near 100 kbar supports the occurrence of a major valence change in this pressure range. The pressure required to initiate the electronic transition (-40 kbar) is consistent with an f-d band gap of 0.62 eV at normal pressure. The spectral characteristics of the reflectivity of SmTe near 100 kbar are qualitatively similar to the optical response of SmS. The reflectivity edge is observed at lower energy in SmTe, mainly because the p to d transitions occur at lower energy in SmTe. Thus the screened plasma frequency (Eq. 1) is reduced.
Fig. 10 - Optical reflection spectra of SmTe at high pressures. (a) semiconducting phase; (b) IV phase with NaCl structure; (c) IV phase below (120 kbar) and above (147 and 220 kbar) the NaCl-CsCl structural transition.

At about 130 kbar, the reflectivity edge in SmTe is suddenly pushed back by about 0.7 eV into the near-infrared and then remains almost stable up to 220 kbar (Fig. 10c). This discontinuous change in reflectivity can be related to a structural B1-B2 transition occurring at 130 kbar with a relative volume change of 9%. At this structural transition the p-d gap becomes direct or close to direct according to several recent band structure calculations for SmTe and related compounds. A corresponding observation can be made in SrTe, which undergoes a B1-B2 transition at 120 kbar. The reflection spectra of SrTe in the B2 phase (also shown in Fig. 11) clearly exhibit a near-infrared reflectivity edge, which may be interpreted as a signature of direct band to band transitions. For comparison, from absorption
measurements we find the absorption edge at 150 kbar to be close to 1.1 eV. Thus, the discontinuous red-shift of the reflectivity edge in SmTe at the B1-B2 transition appears to partly arise from a conversion of the p-d band gap from indirect to direct and the associated spectral redistribution of the oscillator strength. This does not necessarily imply a major decrease of the minimum p-d (direct or indirect) band separation at the B1-B2 transition.

The reflection spectra of SmTe in the CsCl structure can not provide an unambiguous information on the valence-conduction band gap. Here we again refer to SrTe. If we assume that the 0.8 eV difference in the energy of the first excitonic peak in the NaCl phase also applies to the p-d band separations of SmTe and SrTe in the CsCl phase, then, given a band gap of 1.1 eV in SrTe at 150 kbar, SmTe should be extremely close to a valence-conduction band overlap at this pressure. A consequence is the onset of p-d interband transitions at energies well below 1 eV. In other words, the lower reflectivity of SmTe (B2) in the infrared is at least partly due to interband absorption.

The question arises, what happens to the valence state of SmTe at the B1-B2 transition. The change in crystal field splitting acting on d states (reversal of t_2g and e_g) is expected to affect the relative energies of 4f and 5d states and the 5d density of states near the bottom of the conduction band. A more detailed analysis of the optical response of SmTe can not give a conclusive answer. In this context we mention results of optical reflectivity measurements of EuS at high pressures. EuS is a semiconductor at normal conditions with a 4f-5d optical gap of about 1.7 eV. The optical response indicates that EuS starts to become intermediate-valent just below the B1-B2 transition at 200 kbar. At the B1-B2 transition the 4f-5d gap increases again by about 0.2 eV resulting in a reversal of the valence change. These observations suggest that the valence state of EuS depends on structural properties and that a partial reversal of the pressure-induced valence change may also occur in SmTe at the structural B1-B2 transitions.

A decrease of the mean valence at the B1-B2 transition may be a more general feature in RE-MC's. Further evidence for this comes from a comparison of relative volume
changes at B1-B2 transitions. This volume change is at least 10.5% in all alkaline earth and divalent RE-MC's investigated so far, but also in trivalent compounds like, e.g., PrTe. The only known examples with a smaller volume change seem to be EuO (only 6.5% at the 400 kbar transition) and SmTe (9% at 130 kbar), which supports the partial reversal in SmTe and possibly an almost complete reversal in EuO. LIII-edge measurements in, e.g., SmTe under pressure could provide a broader experimental basis for this particular aspect of IV behavior in RE-MC's at very high pressures.

The compound EuTe is the least favourable case for a pressure-induced valence change, because it combines the largest 4f-5d excitation threshold at normal pressure with a B1-B2 structural transition near 100 kbar. Considering in addition the possible relevance of the "reentrance phenomenon" predicted for IV RE metals (see section III), it appears conceivable that EuTe will not become "metallic" under pressure due to a 4f instability. A more likely mechanism for a semiconductor-metal transition in EuTe is a valence-conduction band overlap. For example, we estimate the closure of the p-d gap in SrTe to occur at roughly 500 kbar. The corresponding transition in EuTe should occur at even lower pressures in analogy to our above arguments applied to SmTe. For comparison, recent optical absorption and electrical resistance measurements suggests a valence-conduction band overlap in BaTe near 200 bkar.

VI - SUMMARY AND CONCLUSIONS

The three different aspects of the effect of very high pressure on the electronic structure in heavy RE materials presented here may be summarized as follows:
(i) The energies relevant to the determination of the relative stability of divalent vs trivalent state in Yb metal are discussed and related experimental results are summarized. The application of new experimental probes like, e.g., position annihilation at high pressures is expected to provide further insight into the Yb problem.
(ii) The optical response of IV Yb-monochalcogenides and its interpretation in terms of a predominantly localized mechanism of the valence change is in marked contrast to the behavior of corresponding Sm- and Tm-compounds. This result may be taken as another clear evidence for the fact that the valence fluctuation phenomenon has quite different aspects depending on the specific RE ion or 4fn+1 configuration involved in the process.
(iii) The comparison of the high pressure optical response of SmTe and SrTe demonstrates that optical investigations of alkaline earth MC's under pressure are extremely helpful to clarify the valence-conduction band structure in the RE-MC's, where p to d transitions are obscured due to the presence of f states or band electrons. A partial reversal of a pressure-induced valence change at the B1-B2 transition may be a general phenomenon in the RE-MC's.

ACKNOWLEDGEMENTS

The author thanks K. Takemura, H. Tups, H. Winzen and H.G. Zimmer for their contribution to the experimental part of this work and for many discussions. We gratefully acknowledge H. Bach (Bochum), K. Fischer (Jülich), and J.M. Leger (Bellevue) for their generous supply of samples. We are indebted to H.L. Skriver for making available unpublished results of total energy calculations.

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