Pressure dependence of the absorption edge of some divalent rare-earth monochalcogenides

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By means of thermodynamic principles, the pressure dependence of the $4f \rightarrow 5d$ excitation energy is calculated for some divalent rare-earth chalcogenides. The agreement with experiment is rather satisfactory. Implications on the pure metals europium, ytterbium, and cerium are discussed. For the two former elements a valence transition is estimated to take place at a pressure of about 175 and 140 kbar, respectively. Also, ytterbium monoxide is briefly commented on.

I. INTRODUCTION

Although it was noted a rather long time ago[1] that certain rare-earth compounds show divalent character, in contrast to their trivalent metallic state (samarium and thulium), and that in other compounds and intermetallics the reverse situation sometimes is true (europium and ytterbium), it is not until quite recently that these matters have become widely studied. Even the now popular so-called "intermediate valence state"[2,3] was discussed quite a time ago by Gschneider.[1] However, it is only with the aid of the present available experimental techniques that a more detailed atomistic understanding seems to be under development. Especially intriguing properties of the intermediate valence state are the high electronic specific heat and in some cases the apparent absence of magnetic ordering.

High-pressure work on some of the divalent rare-earth monochalcogenides has shown that, if sufficiently compressed, they transform into the trivalent ionic configuration.[4] In a limited pressure range a mixed valence state has been demonstrated for some of these compounds. Whether an intermediate valence state always will accompany a valence change or not is not settled. In principle, a transition from a pure divalent configuration into a pure trivalent state is quite conceivable, but its occurrence has not been reported for any system yet.

The concept of the intermediate valence state does not seem to have been introduced for actinide compounds. No doubt, since the energy of the $5f$ state is very close to that of the $6d$ state, intermediate valences should be much more common in compounds of these elements than of the rare earths. In fact, this picture provides a very plausible explanation to the difficulties met in the assignment of an integral number of $5f$ electrons from magnetic-susceptibility measurements and at the same time may explain the abnormally high electronic specific heat found in many of these compounds.[5] Therefore, we feel that the most fruitful progress in the understanding of the intermediate valence state in the future will be developed for compounds of the actinide series of elements. Further, these systems may also provide useful insight to the physics of the formation of localized moments of $3d$ atoms in metallic hosts, since $5f$ electrons are in their behavior in many respects intermediate to $4f$ and $3d$ electrons.

In a recent paper[6] we studied the behavior of the pure elements europium and ytterbium under compression theoretically. It was shown that the enthalpy of the trivalent state becomes lower than that of the divalent metallic state above a certain critical pressure. In a later communication[7] this work was extended to include the intermediate valence state, treated as an alloy between divalent and trivalent atoms. It was found that the intermediate valence state may be stable over quite an appreciable range of pressures. The main underlying assumption of the theory was the nonbonding property of the $4f$ electrons, an assumption which nowadays seems to be commonly agreed upon. Therefore, in this treatment the mechanism driving the transition is the difference in binding properties of a divalent and trivalent metallic system. The presence of the $4f$ electrons is mainly recognized as a reservoir of electrons regulating the number of conduction electrons. The attained number of metallic electrons is determined by the corresponding binding property of the crystal.

Another recent approach to valence transformations also recognizes the importance of the lattice elasticity of the system.[8] In this model, however, the driving mechanism of the transition is assumed to be a movement of the $4f$ level under compression relative to the Fermi level. This movement is parametrized by a linear volume dependence resulting in a crossing of the two levels at a certain critical volume. This may turn out to give a qualitatively correct account of the true behavior

of a valence transformation, but in our opinion this picture obscures the basic mechanism for the transition. To us the important matters are that the higher valence state has stronger binding properties, and therefore, a lower equilibrium volume and a lower compressibility than the lower valence state. At low pressures the gain of binding energy obtained by promoting a localized $4f$ electron to the conduction band may not outweigh the energy lost in the promotion process. Under further compression, however, the enthalpy increase of the higher valence state is considerably less than for the lower valence state, and therefore it will eventually become the stable configuration. To what extent these basic features may be *simulated* by an effective movement of the $4f$ level relative to the Fermi energy then becomes a secondary question. However, as shown in the treatment by Hirst,[8] if this simulation can be considered as realistic quite an attractive approach to the intermediate valence state may be formulated.

In the present paper we will apply our ideas to some of the rare-earth monochalcogenides. The property we will be concerned with is the pressure dependence of the absorption edge. Some implications for the pure elements cerium, europium, and ytterbium will also be discussed as well as for the ytterbium-monoxide compound. Thus, in Sec. II we briefly comment on some of the general aspects of an excitation of a $4f$ electron. In Sec. III we consider the pressure dependence of the absorption edge and in Sec. IV we extend this treatment to some rare-earth elements. The final section contains a discussion.

II. ELECTRONIC EXCITATION IN A $4f$ SYSTEM

The common verbal description of a valence change with pressure seems to be that the energy of the f^n state raises relative to the Fermi energy. When it crosses the Fermi level, it starts to empty part of its electron content into the conduction band. When sufficiently compressed the occupation number again becomes integral and a pure f^{n-1} ionic configuration is found stable. This is certainly an appealing description and we are not going to directly oppose this view, but only add that it must be applied with a considerable care. This is so since a $4f$ state, being a localized state, does not directly belong to an energy-band diagram. The reason for this is that when a f electron is excited, it leaves behind itself a quite localized "hole," and therefore the excited state is not describable within the usual energy band scheme. Thus, the excited state is not at all present in the energy band diagram. Such a precaution in the interpretation was made by Herbst *et al.*[9] in their

calculations of the $4f$ excitations for the pure rare-earth metals. In order to account for important relaxation processes these authors considered the excitation as a local process, where the excited electron stays within its original atomic cell. Within this cell it is assumed that the atom attains a fully relaxed configuration relative to the new "higher valence" core, which in itself also is assumed to be fully relaxed. The rest of the solid is considered as totally intact in the excitation process. Therefore, in practice this picture means that *one* atomic site changes its valence state—from the ground-state $4f^n$ configuration into the "ground state" of the $4f^{n-1}$ ionic configuration. The so calculated excitation energies were found to be in quite good agreement with experiment. However, it should be noted that in these calculations some atomic data were incorporated empirically in order to account for important $4f$-$4f$ electron correlations. More recently, the present author[10] has shown that their results can be derived from simple cohesive energy arguments combined with data of the free atomic excitation energy $4f^n5d^m6s^2 \rightarrow 4f^{n-1}5d^{m+1}6s^2$, again employing the local picture of the excitation process in the solid.

III. PRESSURE DEPENDENCE OF THE ABSORPTION EDGE

Recently, data on the pressure dependence of the $4f \rightarrow 5d$ excitation in some of the rare earth monochalcogenides have become available.[11, 12] For these systems, due to lack of cohesive energy data, we have not yet been able to apply the simple cohesive energy picture of the excitation as outlined in Sec. II. However, it turns out that it is still possible to estimate the pressure dependence of the excitation energy. We write the cohesive energy (with negative sign) per formula unit for the divalent state as E_{II} and for the trivalent one as E_{III}, where both are measured relative to a common energy level. Since at zero pressure the divalent state is stable, the energy difference

$$E_{III} - E_{II} = \Delta E \tag{1}$$

is positive and could according to the interpretation given above be related to the excitation energy of a $4f$ electron into the conduction band. As a function of compression the energy content per formula unit changes as

$$H_{II} = E_{II}(V) + PV,$$
$$H_{III} = E_{III}(V) + PV, \tag{2}$$

where H_{II} and H_{III} are the enthalpies of the divalent and trivalent configurations, respectively. With pressure P, the energy difference between the two states is given by $H_{III} - H_{II}$. This energy difference $\Delta E(P)$, is again interpreted as the en-

ergy necessary to excite a $4f$ electron into the conduction band state in the solid at a fixed pressure P. Here we are interested in $d\Delta E(P)/dP$ at small pressures. Expanding an enthalpy function, $H(P) = E(V) + PV$, for small values of P we obtain

$$H(P) = E(V_0)$$
$$+ \frac{1}{2}\left(\frac{d^2E}{dV^2}\right)_{V=V_0} (V-V_0)^2 + PV_0 + P(V-V_0)$$
$$+ \text{higher-order terms}, \tag{3}$$

where V_0 is the equilibrium volume. To first order in pressure the enthalpy is therefore given by

$$H(P) = E(V_0) + PV_0. \tag{4}$$

Thus, we may write the enthalpies of the divalent and trivalent states to first order in P as

$$H_{II}(P) = E_{II}(V_{II}) + PV_{II}$$
$$H_{III}(P) = E_{III}(V_{III}) + PV_{III}, \tag{5}$$

where V_{II} and V_{III} are the equilibrium volumes of the formula unit cells for the divalent and trivalent configuration, respectively. From these expansions we then derive the simple formula

$$\lim_{P\to 0} \frac{d\Delta E(P)}{dP} = (V_{III} - V_{II}). \tag{6}$$

The equilibrium volume for the trivalent state is obtained by interpolation in the lattice constant of neighboring trivalent rare-earth monochalcogenides.[1,13] From the formula in Eq. (6) we are thus in a position to calculate the initial decrease of the energy gap with pressure. In Table I we compare the experimental results with our calculated values. First of all, we note that the calculated values are of the right order of magnitude. Secondly, the agreement is by no means perfect but the derived values show the right tendencies for different chalcogenic compounds (compare the differences between the pressure coefficients of excitation energies of the series EuTe, EuSe, EuS, and EuO). In comparison with more detailed theoretical calculations[14] the agreement is most satisfying. Certainly, the given picture of the excitation process as confined to one formula unit cell with a rigid surrounding is a rather drastic simplification as it neglects all the relaxation movements of neighboring atoms. However, since the calculated values are not too far away from the experimental values, the given picture seems to contain a substantial part of the real nature of the excitation.

Some additional comments may be in order for the EuTe, EuSe, and EuS compounds. For these systems the expected valence transition at high

TABLE I. Comparison between experimental and theoretical values of pressure dependence of the lowest-lying $4f \to 5d$ absorption band in some rare-earth monochalcogenides (units of meV/kbar).

EuTe	-12.0[a]	-8.0	YbTe	-11 ± 1[b]	-7.0
EuSe	-8.4[a]	-6.4	YbSe	-10 ± 1[b]	-4.9
EuS	-7.9[a]	-5.9	YbS	-6 ± 1[b]	-3.9
EuO	-4.4[a]	-2.3			

[a] Reference 12.
[b] Reference 11.

pressure has not yet been experimentally verified. Still, a quite drastic phase transformation under pressure has been observed for these compounds resulting in a considerable volume reduction.[4] Instead of being a valence transition it involves a crystallographic change from the NaCl into the CsCl structure, the rare earth ions maintaining their divalent configuration.[4] Thus there are in these systems four different competing states; divalent and trivalent NaCl structure as well as divalent and trivalent CsCl structure. Apparently, in the present compounds it so happens that the divalent CsCl structure becomes favorable before the valence change is induced. No doubt, a valence transition will sooner or later take place with further increase of pressure. Then it becomes a question whether the trivalent state will be of NaCl or CsCl structure. For several reasons we favor the latter possibility, the main one being that in EuO the isostructural valence transition precedes the NaCl-CsCl transition and thus the high-pressure phase is a trivalent CsCl structure. As regards the absorption edge it seems quite clear that in the excitation process of *one* $4f$ electron within the NaCl structure there will be no interference from the CsCl structure, since this phase can only be induced by a rearrangement of a fairly large number of atoms. Therefore, the values listed in Table I are appropriate also for the present europium monochalcogenides. At high pressure, however, we would in these compounds expect a discontinuity in both the magnitude and pressure coefficient of the absorption edge in connection with the NaCl-CsCl transition.

IV. IMPLICATIONS FOR Eu, Yb, Ce, AND YbO

The formula in Eq. (6) may also be applied to pure europium and ytterbium which both are divalent metals at normal conditions. Thereby, we obtain a value of -9.4 and -7.3 meV/kbar for the quantity $d\Delta E(P)/dP$, respectively. The pressure dependence of the promotion energy of an f elec-

tron into the conduction band is not experimentally known for these elements. However, it seems reasonable to assume that our calculated values are off by about the same amount as in chalcogenides and we estimate a pressure dependence of about −12 and −10 meV/kbar, respectively. At equilibrium conditions the excitation energy has been reported to be 2.1 eV for europium and 1.4 eV for ytterbium.[15] From the monochalcogenides it has been found that the *experimentally* determined excitation energy is essentially linear in pressure[12]. Assuming that this circumstance holds also for the pure elements we would estimate that a valence transition should take place at about 175 and 140 kbar for europium and ytterbium, respectively. These estimated critical pressures are in quite good agreement with other theoretical estimates of this transition.[6]

The concept of valence change has also very commonly been connected to the γ-α transition in cerium, which at room temperature takes place at about 7 kbar. However, from simple cohesive energy arguments this interpretation has been shown to be unrealistic.[16] From the formula in Eq. (6) we calculate a decrease of about 5 meV/kbar of the excitation of the $4f$ electron into the conduction band. Again, we adjust this value to about 6–7 meV/kbar from the experience of the chalcogenides. At equilibrium conditions (room temperature) the measured excitation energy of the $4f$ electron was originally reported to be 1.8 eV.[17] From this value we find that the corresponding transition pressure is several magnitudes too large. This negative result for cerium implies that a quite different mechanism is responsible for the electronic transition in cerium, and its recent interpretation as a Mott transition within the $4f$ shell seems to be more appropriate.[16] Recently, the excitation energy of 1.8 eV has been revised and a value of 0.9 eV is reported.[18] However, even this new value gives an unreasonably high transition pressure. Further, from measurements on rare earth antimonides[19] concerning the position of the $4f$ level it was found that the excitation energies are shifted by a remarkably constant value from the values for the pure rare earth metals. From this consistency and the reported value in cerium-antimonide the earlier value of 1.8 eV in pure cerium seems to be more appropriate. In any case, the present experimental situation concerning the position of the $4f$ level in cerium is such that it is situated much further below the Fermi level than 0.05−0.1 eV, which is the value required in the promotion model of the γ-α transition.

Finally, we want to comment on ytterbium monoxide. For this compound there are very few data

available. However, from free atomic spectroscopy properties we can estimate the $4f \rightarrow 5d$ excitation energy to be about 0.25 eV lower than that in europium monoxide,[4] i.e., at equilibrium 1.12−0.25 ≈ 0.85 eV. From the tendency of the pressure coefficient to be lower in the ytterbium compounds than in the europium compounds, we estimate a decrease of about 3−3.5 meV/kbar for the $4f \rightarrow 5d$ excitation energy. Therefore, we expect a valence transition in YbO at a pressure around 250−300 kbar.

V. DISCUSSION

As emphasized in Sec. I, the driving mechanism of the valence transition is that the enthalpy difference between the two states becomes smaller with pressure, until it changes sign and a transition takes place. *Thus, it is the difference in cohesive properties between a divalent and trivalent configuration which drives the transition.* Since the $4f$ state is localized it does not in itself contribute to the binding of the compound. Therefore, in principle, it is not so much a possible movement of the $4f$ level relative to the other states which induces the transition. What we mean with this is that if a conventional band calculation is performed for a *fixed* valence state at different volumes, there is no *a priori* reason to expect that the $4f$ level will coincide with the Fermi level at the critical volume for a valence change. On the other hand, with the given interpretation of the excitation process of a localized $4f$ electron into the conduction band (Sec. II), it is quite natural that the *experimentally* measured position of the $4f$ level *appears* to cross the Fermi level at the transition. Therefore, the following comments should be added to the usual verbal description of the valence change. In the first place it seems physically more reasonable to say that the Fermi level comes down to the $4f$ level rather than the other way around. In the second place, the usual energy band scheme should not at all be used in this connection, and if so only as a tentative guide. Instead we have to await a better theoretical treatment of an excitation of a localized electron into the conduction band, where important relaxation effects are incorporated. The nature of the excitation should be quite similar to an impurity site in the solid (and probably it could also be described as a rather localized exciton). The picture presented in this paper seems undoubtedly to be a step in the right direction, but it is still far from anything like a good quantitative and rigorous treatment of the excitation process. Some drawbacks can be

noted immediately. First of all, the present picture can only give a transition from a pure divalent state into a pure trivalent state. Secondly, the energy decrease of the excitation process seems from experiment to be linear with pressure,[12] which it would not be if the present picture was applied to finite pressures (the enthalpy difference is then no longer quite linear in pressure).

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