PHYSICAL REVIEW B VOLUME 13, NUMBER 4 15 FEBRUARY 1976

Alloy theory of the intermediate valence state: Application to europium metal

Anders Rosengren
Institute of Theoretical Physics, University of Stockholm, S-113 46 Stockholm, Sweden

Börje Johansson
Department of Physics, FOA, He 2, S-104 50 Stockholm 80, Sweden

(Received 10 March 1975)

A microscopic theory for the intermediate valence state is given, containing no phenomenological parameters. The intermediate state is considered as an alloy of constituents of different integral valence and treated in the virtual-crystal approximation. The theory is applied to europium metal, resulting in a continuous change of valence, starting at 180 kbar and being completed at 350 kbar. The calculated pressured-volume relation resembles those found for some rare-earth monochalcogenides.

I. INTRODUCTION

Considerable interest has recently been devoted to the so-called intermediate valence state.[1–7] Although this state should be more common among compounds of the actinide elements, the studies and discussions of it have hitherto been limited to the rare earths and especially to the monochalcogenides of Sm, Eu, Tm, and Yb. Most of these systems must be compressed before a valence transition from divalent to trivalent metallic ions is induced. The transition thereby takes place gradually and stable nonintegral valences are observed for quite a wide range of pressures. Also, a discontinuous jump from one intermediate state to another has been reported.[1] The very existence of an intermediate valence state is already seen from the lattice constants in the sense that they attain values intermediate to those expected for pure divalent and trivalent compounds. From photoemission spectra the samarium ions in "chemically collapsed" phases of SmS are found to be in a state of mixed valence.[6] For some rare-earth intermetallics also, strong evidence for such a state has been reported.[7] As regards the possibility of valence transitions in the rare-earth metals themselves, the divalent metals europium and ytterbium are expected to become normal trivalent rare earths when sufficiently compressed.[8] Metallic cerium is commonly considered to be in a mixed-valence state in its dense α phase. However, this has been shown to be a highly unlikely interpretation.[8–10]

All experimental evidence obtained so far implies that the intermediate valence state is a *temporal* rather than a spatial mixture of ions of different valence.[2,4–6] That is, in the intermediate state the ions fluctuate between the two pure ionic configurations. Theoretically, the present understanding of this mixed-valence state is rather limited. Anderson and Chui[11] have considered it as an alloy of divalent and trivalent ions and argue that anharmonic strain effects may be responsible for its stability. Sicardi *et al.*[12] suggest that when the position of the $4f$ level is sufficiently close to the conduction band it attains a small but finite width (owing to resonant scattering) and accordingly may be occupied by a nonintegral number of electrons. Other authors[13,14] have stressed the importance of considering the lattice elasticity of the system, which in our opinion is the most realistic approach to the problem. However, in their present form these theories lean heavily on several parameters difficult to obtain from experiment.

II. THEORY AND METHOD OF CALCULATION

As has been stressed elsewhere,[8] the mechanism driving the valence transition is to be found in the difference in cohesive properties between the two configurations. In this paper we want to show that also the occurrence of stable intermediate valence states, although more subtle, may be explained in terms of bulk cohesive properties. The main assumption will be that the $4f$ shell in itself does not contribute to the binding of the solid. This is certainly most reasonable and means that the $4f$ electrons in this respect may be regarded as "core" electrons. The interesting circumstance is that the energy level of this core state for some of the rare-earth metals and compounds is situated relatively close to the Fermi level. If each atom excites one $4f$ electron to the conduction band, these electrons will then contribute substantially to the binding of the solid. If this gain in binding energy outweighs the energy loss in the excitation of the $4f$ electron, the higher valence state will be the favorable one—if not, the lower valence state is stable. Therefore the mixed-valence state should be expected only when the gain and loss of energy are about equal.

Assume we have a pseudopotential description available for both the pure divalent and trivalent

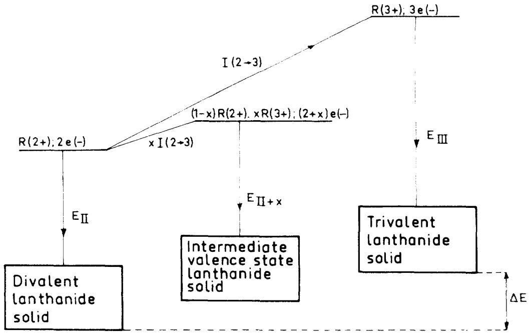

FIG. 1. Energy-level diagram for a lanthanide solid illustrating the binding energy E of the different valence states and their interrelation. The quantity ΔE stands for the energy difference between the divalent and trivalent solids. In the case of europium this difference is 1.02 eV. For SmTe we estimate ΔE to be about 0.3 eV.

configurations of the system, providing a mean to describe the variation of cohesive properties with pressure for the two pure valence states involved. Turning to the possibility of an intermediate valence state, it is quite natural to treat this system as an alloy between divalent and trivalent atomic constituents. The theory we will employ for describing this state is the so-called virtual-crystal approximation.[15–17] In the usual applications of this theory a complete disorder is assumed for the positions of the two alloy component atoms. In a "true" alloy (with a spatial mixture of atoms) there is nevertheless often some short-range order. However, in the present case of a mixed-valence state with a temporal mixture between the two ionic states, the assumption of complete randomness of the alloying atoms should be more realistic. Furthermore, and most important, *with the present approach to the intermediate valence state no phenomenological parameters are introduced.*

In the virtual-crystal approximation the binding energy is given by[15,16]

$$E = E_0 + E_{es} + E_{bs}^{(1)} + E_{bs}^{(2)} + xI_{2\to3}. \qquad (1)$$

Here E_0 depends only on atomic volume and composition, and E_{es} is the electrostatic energy. The so called band-structure energy is given by $E_{bs}^{(1)}$ and $E_{bs}^{(2)}$. The first three terms in Eq. (1) represent scattering of electrons in an ideal lattice where the metallic-ion pseudopotential is characterized by the average $w(q) = (1-x)\, v_{II} + x v_{III}$, v_{II} and v_{III} being the form factors of the divalent and trivalent ions, respectively, and x being the average concentration of the trivalent component. The term $E_{bs}^{(2)}$ is the so called "difference energy," and for a disordered alloy this term includes a factor $x(1-x)$ and depends on the difference between the pseudopotentials describing the two pure states.[16–18]

Finally since we are going to compare energies, the binding energy for the different concentrations x must refer to a common energy level (Fig. 1). This is accomplished by the last term in Eq. (1), where $I_{2\to3}$ is the ionization energy of the doubly ionized lanthanide ion.

In a recent paper we derived semiempirical pseudopotentials for the rare-earch metals and a fairly realistic representation of their equation of state was obtained.[8] Here we now choose europium as an *illustrating example* of the outlined mixed-valence theory. The employed pseudopotential is the Krasko-Gurskii model potential[19]

$$v(q) = (4\pi Z/\Omega\, q^2)\,[(2a-1)(qr_c)^2 - 1]/[(qr_c)^2 + 1]^2 , \qquad (2)$$

where Z is the ionic charge, Ω is the atomic volume and the parameters a and r_c specify the element in question. In Table I we give the employed parameters, and also the calculated binding energy and compressibility, and compare them with experimental values. As seen, the chosen potential accounts quite well for these bulk properties.

TABLE I. Pseudopotential parameters for divalent and trivalent europium. The chosen values give an energy minimum at the correct lattice parameter. The parameter r_s is the usual electron gas parameter. For $q=0$ in the potential r_c is replaced by r_c'. This causes a discontinuity in the pseudopotential and a smoothening is accomplished by the parameter C as described in Ref. 20. Some calculated properties are compared with experiment.

	r_s (a.u.)	a (a.u.)	r_c (a.u.)	r_c' (a.u.)	C	Binding energy (Ry/ion) calc.	Binding energy (Ry/ion) exp.	Compressibility (10^{-6} cm^2/kg) calc.	Compressibility (10^{-6} cm^2/kg) exp.
Eu(+2)	3.38[a]	3.0	0.510	0.566	0.3	1.417	1.378[a]	7.32	8.29[a]
Eu(+3)[b]	2.61[a]	5.0	0.340	0.470	0.3	3.191	3.138[a]	3.43	3.35[c]

[a] Reference 8.

[b] The parameters have been changed in comparison to those of Ref. 8 to improve the value of the binding energy.

[c] This value is the experimental value for samarium (Ref. 8).

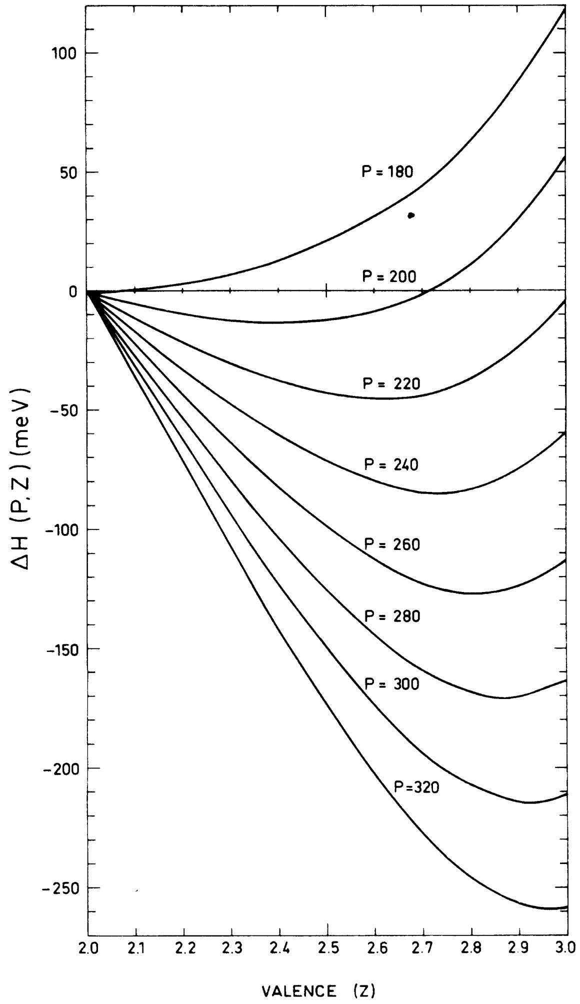

FIG. 2. Calculated enthalpy difference between the mixed-valence state and the pure divalent state of europium as a function of valence for different pressures P (kbar).

Owing to the close similarity among the rare-earth metals reliable interpolations may be performed between the elements to derive otherwise inaccessible experimental information,[21] e.g., the binding energy of hypothetical trivalent europium. From this quantity the energy difference between divalent and trivalent metallic europium is found to be 1.02 eV (cf. Fig. 1).[8] To calculate a realistic critical pressure for the valence transition, it is important that our calculations give this energy difference at zero pressure. As can be seen in Table I, the calculated binding energies are not perfect, and therefore we modify the ionization energy $I_{2\to3}$ to a value of 25.16 eV (experimental value[22] 24.92 eV) in order to keep the zero-pressure energy margin between the two valence states at the "experimental value".

For the dielectric screening function we use the Singwi-Sjölander-Tosi-Land form,[23] and for the correlation energy the expression derived by Pines and Nozières.[24] All of the calculations are performed for a bcc lattice structure.

III. RESULTS

To investigate the behavior of europium under pressure, we calculate the enthalpy for different values of x (Fig. 2). When the pressure exceeds 180 kbar, the lowest enthalpy is found for a nonzero value of x. As the pressure is increased the value of x minimizing the enthalpy is also found to increase. Finally, for pressures larger than 350 kbar the pure trivalent configuration is energetically the most stable one. In Fig. 3 we depict the intermediate valence as a function of pressure. The calculated pressure range for persistence of an intermediate valence is quite appreciable. The rather rapid increase of Z with pressure probably means that rather slight changes in the parameters describing the pure configura-

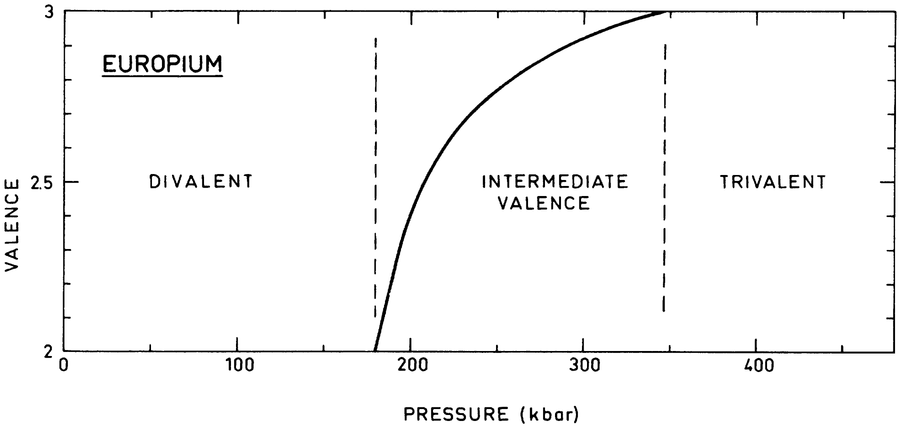

FIG. 3. Calculated intermediate valence as a function of pressure for europium metal.

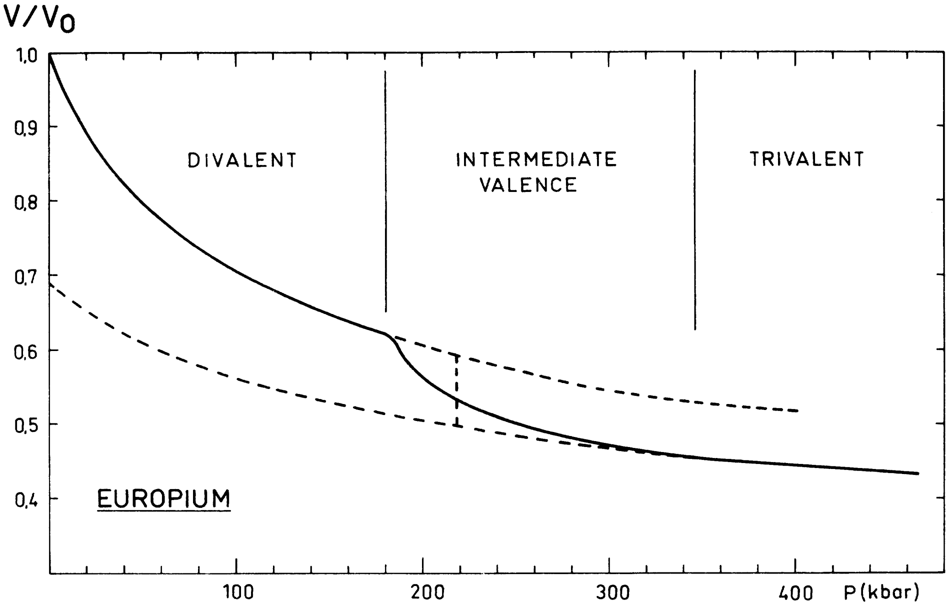

FIG. 4. Calculated reduced volume as a function of pressure for europium. The dashed curves give the corresponding relation in the case where only pure divalent and trivalent europium is considered.

tions may turn the present *continuous* change of valence *discontinuous*. If only the pure states are compared, we find that the divalent state is unstable against the trivalent one at around 220 kbar (Fig. 2).

In Fig. 4 we illustrate the obtained pressure-volume relation. The rather peculiar rapid volume decrease around 190 kbar is certainly very similar to that obtained for the rare-earth monochalcogenides.[1] As regards comparison with experiment, pressure-volume relations for the critical high-pressure region of interest are available only from shock-wave data. However, they are too few and somewhat too scattered to provide a meaningful comparison. Also, and even more important, the calculated compressibilities are not perfect, which they would almost have to be if a comparison with experiment were to be conclusive. Still, it is interesting to notice that a certain discontinuity, indicative of a phase transition, was found in shock-wave experiments corresponding to a temperature of 1810 °K and a pressure of 190 kbar.[25] From measurements of resistance versus pressure under static conditions a temperature-dependent anomaly was found in the pressure region 150–200 kbar.[26]

IV. DISCUSSION

The main purpose of this paper is to demonstrate that not only the valence transition in itself is driven by the difference in cohesive properties between the divalent and trivalent states,[8] but also that the very existence of the intermediate valence can be derived from cohesive properties. We have also been able to show that the model outlined in this paper is capable of describing several properties critical for an intermediate valence system, e.g., the variation of valence with pressure and the sudden softening of a material in the critical pressure range.

As an illustration of the theory we have chosen metallic europium. As regards the true behavior of this metal we have tacitly avoided one complication which doubtless will be of some importance. This concerns the fact that trivalent europium will not be a bcc metal at room temperature. Instead, it will attain either a dhcp (double hcp) or fcc structure.[8] Whether this crystal structure also can be favorable for valences somewhat lower than 3 is certainly beyond our judgment. Still, the main behavior of europium under pressure will be dominated by the valence change rather than by a crystal-structure transformation.

The divalent rare-earth metal ytterbium is also expected to become trivalent at high pressures. For this metal the valence transition should occur at somewhat lower pressures than for europium. Earlier calculations[8] indicated that the critical pressure region is to be found around 130 kbar. As in europium the transition in ytterbium will be accompanied by a crystal transformation, since in this case either a hcp or a samarium type structure is expected for the high-pressure trivalent state.[8] From shock-wave data[25] a discontinuity, indicative of a phase transition, was found at a temperature of 1230 °K and a pressure of 130 kbar.

An independent estimate of the critical pressure for a valence change in europium and ytterbium has been given elsewhere.[9] This semiempirical method is based on the variation with pressure of the position of the $4f$ level relative to the Fermi level. Interestingly enough the transition pressures thus found agree quite well with those discussed in the present paper.

In this connection some highly relevant experiments[27,28] on very small particles of rare-earth elements should be mentioned. In the cases of europium and ytterbium it was found that the interatomic distance showed a discontinuity as a function of decreasing grain size. This discontinuity was more pronounced in ytterbium than in europium. Undoubtedly, this behavior must stem from a valence change. From the measured interatomic distances it can be concluded that the transition is to an intermediate valence state. When the grain size decreases the relative number of atoms at the surface increases. Therefore the surface tension increases in importance and can be looked upon as a pressure effect. Some attempts were made[27,28] to translate the found behavior to macroscopic samples, and critical pressures somewhat less than 50 kbar were deduced for the transition. This deviation from our calculations may partly stem from the fairly inaccurate method of translating grain size to pressure and partly from the fact that the physical situation for small particles is not quite comparable to macroscopic samples. Thus the energy difference ΔE between the divalent and trivalent states may depend on the grain size, making a direct comparison to macroscopic samples less meaningful.

As a final conclusion we state that the valence transitions of both europium and ytterbium should take place in a pressure region easily attainable with presently available static-high-pressure experimental equipment.

---

[1] A. Jayaraman, A. K. Singh, A. Chatterjee, and S. Usha Devi, Phys. Rev. B 9, 2513 (1974).

[2] D. K. Wohlleben and B. R. Coles, *Magnetism*, edited by H. Suhl (Academic, New York, 1973), Vol. V.

[3] L. L. Hirst, Phys. Kondens. Mater. 11, 255 (1970).

[4] E. R. Bauminger, I. Felner, D. Levron, I. Nowik, and S. Ofer, Phys. Rev. Lett. 33, 890 (1974).

[5] M. Campagna, E. Bucher, G. K. Wertheim, D. W. E. Buchanan, and L. D. Longinotti, Phys. Rev. Lett. 32, 885 (1974).

[6] M. Campagna, E. Bucher, G. K. Wertheim, D. W. F. Buchanan, and L. D. Longinotti, Phys. Rev. Lett. 33, 165 (1974).

[7] E. E. Havinga, K. H. J. Buschow, and H. J. van Daal, Solid State Commun. 13, 621 (1973).

[8] B. Johansson and A. Rosengren, Phys. Rev. B 11, 2836 (1975).

[9] B. Johansson, Phys. Rev. B 12, 3253 (1975).

[10] B. Johansson, Philos. Mag. 30, 469 (1974).

[11] P. W. Anderson and S. T. Chui, Phys. Rev. B 9, 3229 (1974).

[12] J. R. Iglesias Sicardi, A. K. Bhattacharjee, R. Jullien, and B. Coqblin, Solid State Commun. 16, 499 (1975).

[13] L. L. Hirst, J. Phys. Chem. Solids 35, 1285 (1974).

[14] H. S. Wio, B. Alascio, and A. López, Solid State Commun. 15, 1933 (1974).

[15] W. A. Harrison, *Pseudopotentials in the Theory of Methods* (Benjamin, New York, 1966).

[16] V. Heine and D. Weaire, Solid State Phys. 24, 249 (1970).

[17] G. L. Krasko and Z. A. Gurskii, Fiz. Tverd. Tela 14, 321 (1972) [Sov. Phys.-Solid State 14, 269 (1972)].

[18] Sometimes this term is left out in calculations made within the virtual-crystal approximation. In the present calculation this term is included.

[19] Z. A. G. Curskii and G. L. Krasko, Fiz. Tverd. Tela 11, 3016 (1969) [Sov. Phys.-Solid State 11, 2447 (1970)].

[20] A. Rosengren and B. Johansson, J. Phys. F 5, 629 (1975).

[21] B. Johansson and A. Rosengren, Phys. Rev. B 11, 1367 (1975).

[22] J. Sugar and N. Spector, J. Opt. Soc. Am 64, 1484 (1974).

[23] K. S. Singwi, A. Sjölander, M. P. Tosi, and R. H. Land, Phys. Rev. B 1, 1044 (1970).

[24] D. Pines and P. Nozières, *The Theory of Quantum Liquids* (Benjamin, New York, 1968), Vol. I.

[25] W. H. Gust and E. B. Royce, Phys. Rev. B 8, 3595 (1973).

[26] R. A. Stager and H. G. Drickamer, Phys. Rev. 133, A830 (1964).

[27] F. Vergand, Philos. Mag. 31, 537 (1975).

[28] C. Bonnelle and F. Vergand, J. Phys. Chem. Solids 36, 575 (1975).