11 SCIENTIFIC HIGHLIGHT OF THE MONTH

Self-Interaction Corrected Electronic Structure of Rare Earths

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Introduction

Solids containing rare earth (lanthanide) and actinide species are characterized by localized atomic-like f^n shells, with large magnetic moments of magnitudes grossly given by atomic Russell-Saunders coupling. The chemical bonding is provided predominantly by the non-f electrons. To describe the electronic structure of such systems from first principles, Skriver et al. introduced the two-fluid model [1] according to which an appropriate number, n, of f-electrons is accomodated in localized core-like f-states, while the remaining valence electrons are described by conventional Local-Spin-Density (LSD) band structure methods, in the subspace of Bloch states composed of s, p and d valence orbitals. In this way the systematics of the lattice structures occurring in lanthanide and actinide metals may be explained.[1] This approach is rather more successful than the straightforward application of LSD, which would describe all valence electrons, including the f's, as Bloch states. The partial occupation of narrow f-bands in this case leads to large cohesive contributions and much too small equilibrium lattice constants. Obviously, the LSD lacks the ability to describe the favourable formation of localized atomic-like f-shells. This is quite natural, since the LSD is derived from the free-electron gas.

The self-interaction corrected (SIC) LSD method constitutes an attempt to repair this deficiency of LSD theory. In the SIC-LSD approximation, the LSD total energy functional is corrected by the subtraction of the self-interaction of each occupied orbital. The occurrence of self-interaction is another deficiency of the LSD energy functional. The exact Kohn-Sham energy functional

is self-interaction free.[2] The self-interaction vanishes for Bloch states in the thermodynamic limit, but energetically more favourable states may be found, which benefit from the SIC. Such states are spatially localized on particular atomic positions and the SIC in Eq. (1) becomes equivalent to the energy gained by localization. The question whether localized or delocalized f-states are formed in rare earth systems becomes a question of the size of this localization energy versus the band formation energy. The relative size of these energy contributions may be altered with temperature and pressure. Hence, phase transitions involving changes in f-electron localization may take place as temperature and/or pressure is varied. In previous Newsletters [3] we discussed the successful use of the SIC-LSD to describe localization-delocalization transitions in Ce systems. In this Highlight we will present results obtained for the entire rare earth series for both the metals and the sulphides [6]. Moreover, we shall discuss briefly our results for a large number of Yb compounds [7], including Yb monopnictides, chalcogenides and intermetallics.

The self-interaction of an electron in orbital ψ_α is given by [2]

$$\delta_\alpha = U[n_\alpha] + E_{xc}^{LSD}[n_\alpha], \tag{1}$$

where U and E_{xc}^{LSD} are the Coulomb and exchange-correlation energies of the charge density n_α of orbital ψ_α. Thus the SIC-LSD energy functional is

$$E^{SIC-LSD} = E^{LSD} - \sum_\alpha^{occ.} \delta_\alpha. \tag{2}$$

The minimization of this functional within the LMTO method [4] has been described in Ref. [5]. In practice, a fixed number of localized states, n, on all atomic sites is chosen, and the functional minimized with this choice. Consequently, different scenarios (local minima) may be explored corresponding to different assumed valencies. In contrast to the two-fluid model, the present implementation includes those f-degrees of freedom not occupied by localized states in the space available for band states. Therefore, the total occupancy of f-electrons on a given atom will not be an integer, it is the number of *localized* f-electrons which is integral. This leads to a significant reduction of the fluctuation of f-electron number, compared to a full band description, as in LSD. However, the number fluctuation does not completely vanish, as it does in the two-fluid model. The relevance of this 'two kinds of f-electrons' picture was stressed by Gschneidner [8] on the basis of a detailed analysis of experimental data.

In cerium compunds [3] the relevant scenarios are those corresponding to either 1 or 0 localized f-states per Ce atom. The latter coincides with the LSD solution, since when no localized states occur, $E^{SIC-LSD}$ and E^{LSD} are identical. In cerium pnictides and chalcogenides the phase transitions occurring with applied pressure seem to be well described by these two scenarios. Of course other aspects of the physics of cerium compounds (heavy fermion behaviour etc.) is connected with quantum fluctuations between the f^0 and f^1 states, which are still not well described with a single Slater determinant representation as provided by both LSD and SIC-LSD.

Applications

Most of the rare earth atoms are divalent. However, in the metallic state most of the elements become trivalent. In some materials the energy difference between the divalent and the trivalent state is small and by changing some external parameters a transition from one valence state to
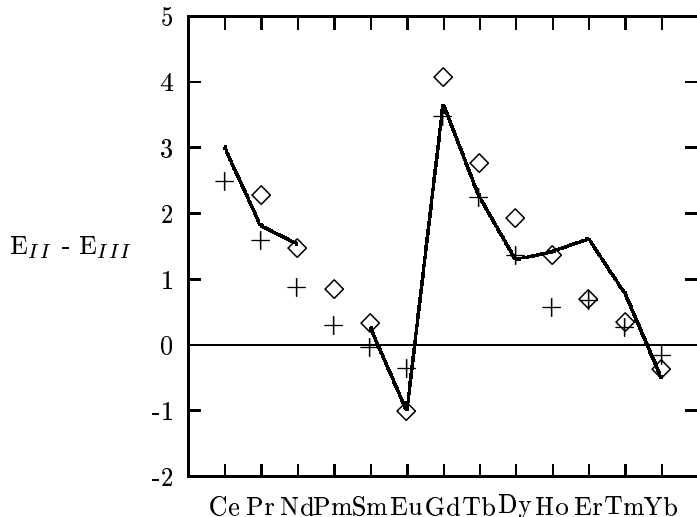
Figure 1: The energy difference (in eV) between the divalent and trivalent state of the rare earth materials. The solid line shows the 'experimental' values for the rare earth metals from Johansson [9]. The diamonds and the crosses are the calculated values for the rare earth metals and the rare earth sulphides, respectively. As the divalent-trivalent energy differences calculated *ab initio* were too negative, they were uniformly shifted by 43 mRy to agree with the observed valence transition pressure of 6 kbar in SmS [10]. This shift also fixes the energy differences for all the other rare earth materials. In particular, for EuS and YbS we find valence transitions occurring at 184 and 75 kbar, respectively, while experimentally, transitions occur at $\sim$ 160 and $\sim$ 100 kbars, respectively.[11]

the other occurs. Perhaps the most famous example of this is observed in SmS which exists in the divalent state as a black semiconductor with the rocksalt crystal structure. Under a pressure of about 6 kbars it undergoes a valence transition to the trivalent state. This involves a 15 % decrease in volume, although there is no change in crystal structure, and a transition to a golden metallic state. But the mechanism underlying this transition and the reason for the differing valence states are not well understood. The SIC-LSD calculations presented here allow us to determine both the valency and the lattice parameter as a function of atomic number. We find, that the delocalized band-like f-electrons are found only in the trivalent systems, and if their number exceeds a certain threshold it becomes energetically favourable for these electrons to localize, causing a transition to a divalent ground state.

In the lanthanide series we have considered configurations f^n and f^{n+1} of the lanthanide atom with n chosen so as to represent trivalent and divalent rare earth atoms, respectively.[6] Here we define valency as the number of electrons per atom available for band formation. In Fig. 1 we show the energy difference between these two valency configurations as a function of the lanthanide elements. The figure shows results for both the pure metals and for rare earth sulphides, and the numbers are compared to the experimental estimates. [9] For both the elemental metals and the sulphides the trends are the same, and also the same for the first and second half of the series. In the beginning the trivalent state is very much favoured over the divalent state, but the latter becomes progressively more favourable as we proceed through the
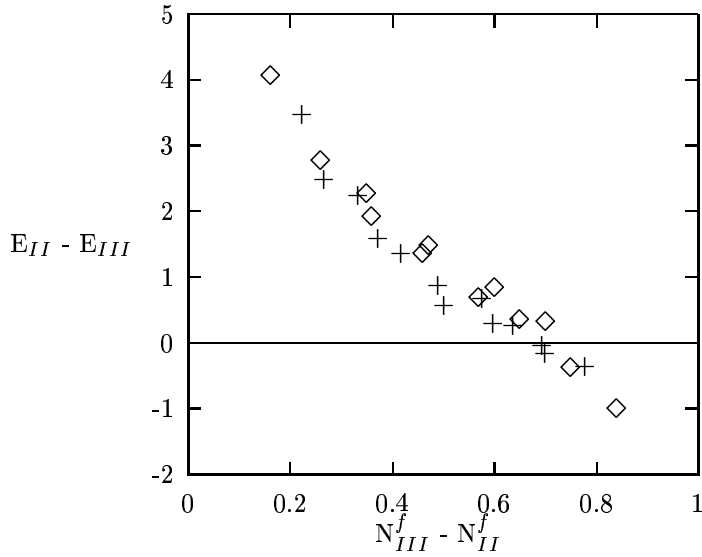
Figure 2: The energy difference (in eV) between the divalent and trivalent state of the rare earths and their sulphides plotted as a function of the difference in the number of band-like f-electrons. Each point in this figure represents one rare-earth element (diamonds) or one rare earth sulphide (crosses). The fact that the metals and the sulphides fall on the same line strongly suggests that it is the number of delocalized f-electrons that determines the valence. When the difference becomes ~ 0.7 or more, the divalent state is more stable.
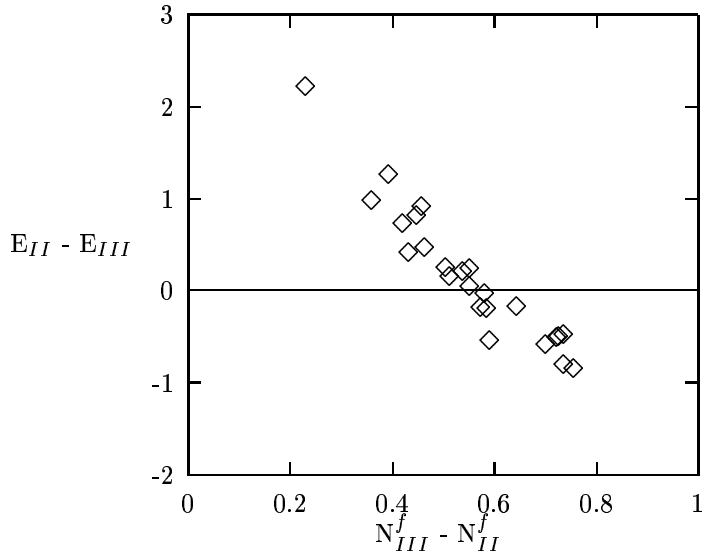

Figure 3: The energy difference (in eV) between the divalent and trivalent configurations of Yb compounds versus the total f occupancy difference between the trivalent and divalent configurations, as given by the SIC-LSD approach. The data points correspond to YbCd, YbZn, YbPd, YbRh, YbRu, YbIr, YbAg, YbAu, YbAl$_3$, YbPd$_3$, Yb$_3$Pd, YbIn, YbTe, YbSe, YbS, Yb, YbSb, YbBi, YbBiPt, YbN, YbP, YbAs, YbO, YbAl$_2$.

series. Around Sm the two valencies are nearly degenerate, and for Eu and EuS the divalent state has lowest energy. In the second half of the series, when the minority spins of the f-shell are being filled the same things happen: for Gd the trivalent configuration is strongly favoured but towards the end the two valencies are again nearly degenerate, with the divalent state favoured in Yb and YbS. The results are seen to reproduce the experimental estimates quite well. These trends are caused by the position of the f-resonance for the majority (minority) spin band in the first (second) half of the lanthanide series. When the atomic number Z of the rare earth atom is increased, the f-resonance moves down a bit with respect to the $6s$-$5d$ conduction states. Consequently, progressively larger f-hybridization into the conduction bands occurs. In Fig. 2 we correlate the number of f-electrons in the conduction bands in the trivalent configuration with the divalent-trivalent energy difference. A neat linear relationship is observed. When ~ 0.7 or more f-electrons are accomodated in the conduction states, it becomes energetically more favourable to occupy one additional f-electron in a localized state, i. e. to switch to the divalent configuration.

Yb compounds, similarly to Ce compounds, exhibit valence fluctuations, in this case between trivalent (f^{13}) and divalent (f^{14}) configurations. We have investigated a large number (24 systems) of Yb compounds [7] and again find that the valence stability depends on the degree of hybridization of the last f-electron into the conduction band in the trivalent Yb compounds. This is illustrated in Fig. 3. When the number of band f electrons in the trivalent configuration exceeds a value ~ 0.7, the divalent Yb configuration is favoured.

The Yb compounds considered here can be divided into three groups, according to the energy difference between the divalent and trivalent Yb configurations. The group of strongly trivalent compounds comprises YbN, YbP, YbAs, YbRu, YbRh, YbIr, YbAl$_3$ and YbPd$_3$. For this group the trivalent configuration is favourable over the divalent configuration by more than 20 mRy per Yb atom. In addition, the calculated equilibrium volumes for the trivalent configuration agree well with experimental volumes (within an average 3.4 % deviation). In comparison, the calculated equilibrium volumes for the divalent Yb configurations are an average 14 % too large. The second group consists of the strongly divalent Yb compounds, encompassing YbO, Yb, YbS, YbSe, YbTe, Yb$_3$Pd and YbIn. Here the divalent Yb configuration is favoured over the trivalent by more than 20 mRy. The calculated volumes for the divalent configuration agree within an average 2 % deviation with the experimental volumes, whereas the equilibrium volumes for the trivalent state are lower by 12 % on the average.

The remaining compounds are characterized by having the energy of the divalent and trivalent configurations equal within 20 mRy. Hence effects of valency fluctuations may start to be impor- tant. We have found, however, that the weakly divalent compounds, the intermetallics YbCd, YbZn, YbAg and YbAu, are in fact well described by the divalent configuration, as evidenced by the agreement between the calculated and experimental volumes (general agreement within 3 %). Hence, for these compounds there seems to be no need for additional cohesive contribution stemming from valence fluctuations. Interesting behaviour is to be expected when pressure is applied to these materials, since the trivalent state will then become more favourable. We are, however, not aware of any pressure experiments done on any of these Yb intermetallics. Finally, the compounds YbPd, YbSb, YbBi, YbBiPt and YbAl$_2$ are weakly trivalent, i.e. according to the calculations the trivalent state is favoured by less than 20 mRy. Among these, YbBiPt and

$YbAl_2$ are known heavy-fermion compounds, and YbPd is believed to be mixed valent system, with approximately equal proportions of Yb^{2+} and Yb^{3+} ions. Hence, for compounds in this group the valence fluctuation phenomena are most significant.

We conclude that the SIC-LSD does provide a reliable scheme for calculating the valence stability in Yb compounds, maybe with an error of the order of 10-20 mRy. Given the complexity of the phenomena studied, such an error is quite reasonable and acceptable.

Conclusions

The SIC-LSD method represents a rather simple implementation of the two-fluid model of Skriver et al., however, with an important extension of allowing for f-hybridization into the conduction bands. As a consequence two kinds of f- electrons are present in rare earth systems, as argued earlier by Gschneidner [8]. The method describes successfully the equilibrium lattice constants of rare earth metals and sulphides, where the LSD generally leads to much too small lattice parameters. However, several questions remain, since the method can only treat ideal f^n shells with n integral. Valence fluctuations and the gradual delocalization of the f manifold is therefore still outside the scope of the method, and if significant energy contributions are associated with such effects, this will have to be considered separately. In addition, one may question whether the self-interaction correction (1) represents the appropriate localization energy. It obviously has the correct order of magnitude, otherwise the valence transitions in cerium compounds and the trends of Fig. 1 would not come out correctly. On the other hand, the calibration needed in Fig. 1, or the ~ 10 mRy overestimation of the stability of the Yb^{3+} configurations over Yb^{2+} configurations, may be due to an error in the appropriate localization energy. Also, other aspects of the atomic coupling energies, like the orbital polarization energy [12], may be important to consider.

Acknowledgements

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