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Method for Calculating Valence Stability in Lanthanide Systems

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We demonstrate that from a state-of-the-art total energy method combined with information on atomic excitation energies, it is possible to calculate the energy difference between the divalent and trivalent states in lanthanide systems with an error less than 0.15 eV. This is shown by comparing theory with well documented experimental data for the lanthanide metals. In addition, we reproduce the intricate valence stability of selected Sm and Tm chalcogenides. Theory is thus shown to be able to address, without experimental input from the solid, important questions concerning intermediate valence. [S0031-9007(97)04680-2]

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During the last three decades much attention has been focused on f-electron materials with unusual physical and chemical properties, signaling so-called strongly correlated electron behavior. Examples are the intermediate valence compounds and alloys [1–3], which have properties nontypical of an integer occupation of the f shell, and the heavy fermion systems [3,4], with an extremely large electronic contribution to the specific heat and their sometimes unconventional superconducting behavior [5]. Experimental observations of these systems suggest that key ingredients in many cases are two energy configurations, f^n and f^{n+1}, close to being energy degenerate, in between which the system fluctuates [3,6]. These systems are addressed by means of many-body Hamiltonians, such as the Anderson [7], Hubbard [8], and Kondo [9] model Hamiltonians. A key question in any theoretical modeling of these systems is to determine first the different contending states the system fluctuates between, and second how close these states are in energy. Experimentally such data may be hard to extract. One may, for instance, get some information from the magnetic susceptibility, resistivity, lattice constants, and so on, but the conclusions drawn from such an investigation may not be unique. A theoretical tool, with which these questions could be answered, would therefore be most useful. The purpose of the present Letter is to demonstrate, using the lanthanide metals as testing ground, that such a tool, in fact, exists, is simple and fast to use, and gives accurate results. In principle, our method is also applicable to actinide systems. Here, however, we have chosen to concentrate on the di- trivalent stability of lanthanide systems and will explain our method explicitly in terms of the configurations relevant for that problem. Thus, we demonstrate that first principles theory together with information on atomic excitation and ionization energies can determine the relative stability of the pertinent energy configurations of any lanthanide system, e.g., the intermediate valence Sm chalcogenide compounds.

Straightforward use of the local spin density approximation to the exact density functional (or the more advanced generalized gradient corrected functionals), with or without the constraint of treating the $4f$ electrons as atomiclike, fails in reproducing the correct valence of all the systems studied here [10]. This demonstrates that the energy functional used is not sufficiently accurate for such a calculation and that other avenues need to be explored. This Letter represents such an effort and is an alternative to finding the exact density functional total energy expression.

Our method is based on the idea that the coupling energy within the $4f$ shell is essentially the same in the atom and in the solid, and that the difference between $4f$-$5d$–intershell couplings for the two configurations in the solid is negligible above the magnetic ordering temperature. We then calculate the paramagnetic ground state for the divalent and trivalent atoms, and for the divalent and trivalent solids. By expressing the total energy difference between the divalent and trivalent solids in terms of energy differences between the solid and the isovalent atom plus atomic correction energies related to the $4f$ shell, the total energy difference between the different valence configurations in the solid is calculated.

The relevant energies and energy differences involved are defined with the help of Fig. 1. In this figure, the divalent and trivalent configurations for a typical lanthanide are illustrated, both for the atomic state as well as for the condensed state. The full-drawn horizontal lines refer to the true ground state total energy of each configuration including the coupling energy within the $4f$ shell and between this shell and the $5d$ shell. The quantity to be determined is $E(\mathrm{II},\mathrm{III})$, the total energy difference between the divalent and trivalent bulk states. The dashed horizontal lines refer to the total energies when the coupling energies, $E_c(\mathrm{III})_{\mathrm{atom}}$, $E_c(\mathrm{III})_{\mathrm{bulk}}$, $E_c(\mathrm{II})_{\mathrm{atom}}$, and $E_c(\mathrm{II})_{\mathrm{bulk}}$, are not taken into account. This "decoupled" state is also called the grand barycenter of the configuration [11]. $E^*(\mathrm{II})$ and $E^*(\mathrm{III})$, which are the energy differences between the grand barycenter of the solid and the grand barycenter of the isovalent atom, are called the divalent and trivalent generalized cohesive energies, respectively. They can be accurately calculated using *ab initio* density functional theory band structure methods. In order to find

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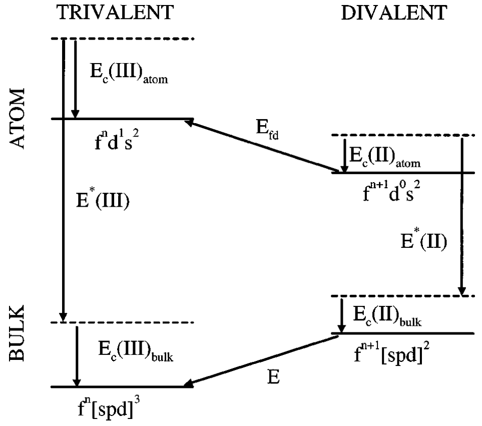

FIG. 1. Definition of the promotion energy E_{fd}, the coupling energies E_c, the generalized cohesive energies E^*, and the di-trivalent energy difference $E(\mathrm{II}, \mathrm{III})$. On the left (right), we have the energy levels for the trivalent (divalent) atom and bulk. The full-drawn horizontal lines refer to the total energies, including coupling energies within the $4f$ shell and between this shell and the $5d$ shell. The horizontal dashed lines refer to the total energies when the coupling energies E_c are not taken into account.

TABLE I. The atomic correction energies E_{fd} and ΔE_c relevant for the divalent/trivalent energy balance.

Element	E_{fd} (eV)	ΔE_c (eV)
Ce	−0.59	0.23
Pr	0.55	0.29
Nd	0.84	0.35
Sm	1.92	0.52
Eu	3.11	0.49
Gd	−1.32	0.37
Tb	0.04	0.45
Dy	0.94	0.51
Ho	1.04	0.26
Er	0.89	0.27
Tm	1.63	0.43
Yb	2.88	0.48

$E(\mathrm{II}, \mathrm{III})$, we now need to consider the coupling energies in the different cases, and how to connect the divalent atom with the trivalent atom. The $4f$-shell intracoupling energies are virtually the same in the atom and the isovalent solid, and therefore cancel out in the energy difference. This is not the case for the intershell couplings, i.e., the couplings between the $4f$ shell and other open electron shells. Such couplings exist in all cases except for the divalent atom, where there is no open electron shell except the $4f$ shell. In the solids, above the magnetic ordering temperature T_c, there will be a slight coupling to the (almost) paramagnetic (spd) band due to the open $4f$ shell in the core. The main difference between the divalent and trivalent solids in this respect is that one more $4f$ electron is active coupling to the valence band. The difference in energy between this coupling in the trivalent and divalent solids is minute, and is therefore neglected in the present calculation. Much larger is the $4f$-$5d$ intershell coupling in the trivalent atom. The total residual of the intershell coupling energies is called ΔE_c and consists thus to a very good approximation of only the $4f$-$5d$ intershell coupling in the trivalent atom. In order to energetically connect the trivalent configuration with the divalent configuration, we need to know the energy difference between the divalent and trivalent atoms. They differ only in that one $4f$ electron has been promoted into the $5d$ shell. This energy is therefore called the $4f \rightarrow 5d$ promotion energy E_{fd}. The values of the atomic correction energies ΔE_c and E_{fd} used here are taken from Ref. [11]. For clarity, we display these numbers in Table I. Now, we have all energies necessary to determine $E(\mathrm{II}, \mathrm{III})$.

The bulk calculations were performed using the full-potential linear muffin-tin orbital method developed by Wills [12]. In this *ab initio* band structure method, the Kohn-Sham equations [13] are solved without shape approximation of the potential, wave functions, or charge density. Space is divided into nonoverlapping muffin-tin spheres surrounding each atomic site, and an interstitial region. A basis function in the interstitial is expressed as a Bloch sum of Hankel and/or Neumann functions which in turn is represented as a Fourier series. Inside the muffin-tin spheres [14] the basis functions are Bloch sums of radial functions times spherical harmonics. All calculations were done in the fcc structure. This approximation of the structure was seen to give a negligible change in the calculated generalized cohesive energies. We used the pseudocore $5p$ wave, and the valence $6s$, $6p$, $5d$, and $5f$ waves, and sampled the reciprocal space with 84 **k** points in the irreducible $1/48$ of the Brillouin zone [15].

The electron core was treated fully relativistically, but the valence states were described scalar relativistically; i.e., the spin-orbit interaction was neglected. The justification for omitting the valence spin-orbit term is that the valence band in the present case is much broader than the spin-orbit splitting, making the error introduced by omitting this term negligible.

We used the Hedin-Lundqvist parametrization of the local density functional [16], and for the generalized gradient corrected functional we used the form recently developed by Perdew and Wang [17].

Figure 2 shows the valence stability for the lanthanides with atomic number 58 to 71, Pm excepted. The experimental points are taken from Ref. [11]. From this figure we see that the valence state is correctly predicted for all elements both with the local density approximation (LDA) and the generalized gradient approximation (GGA), but the GGA results are, as expected, much closer to the experimental points. Thus, all studied elements are calculated to be trivalent except Eu and Yb, which are divalent. The GGA calculations reproduce the experimental data with an error less than 0.15 eV, and our present calculations are far more accurate than all previous calculations of the

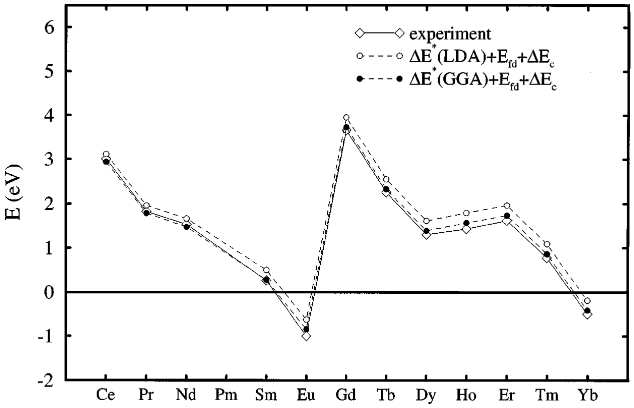

FIG. 2. Di- trivalent energy difference $E(\mathrm{II}, \mathrm{III})$ at zero pressure for the elements 58 to 70, Pm excepted. Calculated results are shown for two different approximations to the density functional, LDA and GGA. The experimental points are taken from Ref. [11].

valence stability of the lanthanides made; see, for example, Refs. [18] and [19].

Our accurate determination of the di- trivalent energy difference for the elemental lanthanides suggests that a meaningful energy balance investigation of the highly interesting intermediate valence systems is within reach. As an example, we have calculated the di- trivalent energy difference for selected Sm and Tm chalcogenides as a function of pressure. These systems have received a truly vast amount of experimental and theoretical attention due to their interesting intermediate valence behavior [1–3,20–25].

Experimentally, the Sm chalcogenides SmS, SmSe, and SmTe are semiconductors at ambient pressure. Jayaraman [21] demonstrated that these systems undergo a pressure-induced semiconductor to metal transition (SMT), accompanied by a valence change of the Sm ions. SmS exhibits a SMT together with a volume collapse at 0.65 GPa. SmSe and SmTe show no volume collapse. Here, the SMT is smooth, and the metallic regime is reached at 4.5 and 5.5 GPa, respectively. For the corresponding Tm chalcogenides, the situation is somewhat different. Both TmS and TmSe are metallic at ambient pressure and have lattice parameters close to a trivalent value, whereas TmTe is a semiconductor, with a SMT at 2 GPa [21,24].

Our calculated energy balances for SmS, SmSe, SmTe, and the corresponding Tm compounds are listed in Table II. Since these systems are semiconductors in the divalent state, the discussion regarding the $4f$-$5d$ intershell coupling energies in the solid changes somewhat. In a paramagnetic semiconductor, this coupling will be zero, so the cancellation between the trivalent and divalent solid does not occur. Nevertheless, the contribution from the intershell coupling in the solid, which actually is possible to calculate and therefore poses no principal problem, should still be negligible.

Starting with the Sm chalcogenides, we see that the correct valence is predicted for all three systems since $E(\mathrm{II}, \mathrm{III})$ in the second column of the table is negative for all three compounds. The number in parentheses (-0.01 eV) is the difference between the GGA calculation and the experimental result in Fig. 2. We will use this number when estimating the sensitivity and systematic error in the calculated divalent to trivalent transition pressure. Since $E(\mathrm{II}, \mathrm{III})$ decreases with increasing atomic number of the ligand (S, Se, Te), we note that the divalent configuration becomes more stable the heavier the ligand is. It now becomes of interest to determine when the enthalpy difference between the two configurations is zero, i.e., to derive the theoretical pressure $P_{\mathrm{II\text{-}III}}$ at which the divalent f^6 configuration will transform to the trivalent f^5 configuration, neglecting the possibility of a mixture of the two phases. In the third column of Table II the calculated divalent to trivalent transition pressure is listed, while the fourth column shows the experimental semiconductor to metal transition pressure. We note first of all that the observed transition pressures are very small and pose a great challenge to reproduce. The two pressures in Table II cannot be compared directly since the experimental high pressure phase involves an intermediate valence

TABLE II. Energy balance $E(\mathrm{II}, \mathrm{III})$ for the Sm and Tm chalcogenides at zero pressure. A negative value for $E(\mathrm{II}, \mathrm{III})$ means that the divalent phase is stable. The numbers in parentheses after $E(\mathrm{II}, \mathrm{III})$ give the energy difference between the experimental value and our calculated value for the pure metal (Sm and Tm). $P_{\mathrm{II\text{-}III}}$ is the calculated transition pressure from the divalent to the trivalent state with error estimation calculated by increasing the atomic correction energies until the experimental and calculated $E(\mathrm{II}, \mathrm{III})$ for the element coincide. P_{SMT} is the experimental semiconductor to metal transition pressure.

System	E(II, III) (eV)	$P_{\mathrm{II\text{-}III}}$ (GPa)	P_{SMT} (GPa)
SmS	-0.015 (-0.01)	0.28 (+0.21)	0.65[a]
SmSe	-0.18 (-0.01)	4.0 (+0.2)	4.5[a]
SmTe	-0.42 (-0.01)	6.9 (+0.2)	5.5[a]
TmS	0.54 (-0.08)	-8.4 (+1.1)	metal at $P = 0$[b]
TmSe	0.23 (-0.08)	-3.5 (+0.9)	metal at $P = 0$[c]
TmTe	0.0097 (-0.08)	-0.14 (+1.1)	2[a,d]

[a] Ref. [21]; [b] Ref. [22]; [c] Ref. [23]; [d] Ref. [24].

state rather than the pure configurations assumed in the theoretical calculation. However, it is obvious that our prediction regarding the increased divalent stability for heavier ligand is confirmed, since P_{SMT} increases with the ligand atomic number. Also, the absolute numbers of our calculated $P_{\text{II-III}}$ compare well with P_{SMT}, suggesting that most of the physics determining P_{SMT} is, in fact, accounted for in our idealized $P_{\text{II-III}}$. The number in parentheses after $P_{\text{II-III}}$ is the calculated change in transition pressure when $E(\mathrm{II}, \mathrm{III})$ is adjusted to coincide with the experimental value. The change in $P_{\text{II-III}}$ is seen to be around 0.2 GPa for all three Sm chalcogenides.

Finally, turning to the last three systems in Table II, we see that the correct valence is predicted for TmS and TmSe; i.e., both are calculated to be trivalent and thus metallic at ambient pressure. This is still true after taking the systematic error of 0.08 eV in the valence stability of the pure metal into account. Since these two systems are trivalent at ambient pressure, $P_{\text{II-III}}$ is negative; see column three. TmTe is also calculated to be just about metallic at ambient pressure, with a very small energy difference, less than 0.01 eV between the divalent and trivalent configurations. If the systematic error for the pure metal is taken into account, however, TmTe is calculated to be divalent. Experimentally, TmTe is found to be a semiconductor at ambient pressure.

In conclusion, we have described a general method for calculating valence stability of lanthanide systems, and demonstrated its validity for the lanthanide elements and on several intermediate valent compounds. By recognizing that presently, density functional calculations cannot reproduce all coupling energies of atomiclike open electron shells, we have instead utilized the fact that many of these coupling energies cancel between the atom and the solid, and that the remaining ones can be taken from atomic data. This data may be either experimental, or, when highly accurate *ab initio* results from atomic calculations become available, e.g., configuration interaction results, they may be determined on a purely theoretical level. The error in our calculated valence stability is in most cases less than 0.1 eV, and in all cases less than 0.15 eV. However, the relative error of our calculations is smaller, and the trends in Fig. 2 are valid beyond 0.1 eV. Also, in situations where a mixed valence state develops, many-body effects will influence the total energy by 50–100 meV, which is on the same level as the uncertainty of our calculations. Combined with many-body model Hamiltonians, our method is therefore able to provide important information about mixed valence and heavy fermion systems. It is also a method that is suitable as a means to identify new materials exhibiting valence mixing. Recently, it has been pointed out that such a search might be most useful in the present attempts to derive new materials showing exceptional thermoelectric power [26].

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