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Effect of generalized gradient corrections on lanthanide cohesive properties

Anna Delin[a,*], Lars Fast[a], Olle Eriksson[a,b], Börje Johansson[a]

[a]*Department of Physics, Uppsala University, P.O. Box 530, S-75121 Uppsala, Sweden*
[b]*Center for Materials Science and Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87544, USA*

Abstract

We have calculated ab initio, using a full-potential linear muffin-tin orbital method, the equilibrium volumes, the bulk moduli, and the generalized cohesive energies for the entire lanthanide series and barium. Two different approximations to the density functional (DF) were compared: the local (spin) density approximation in the Hedin–Lundqvist parameterization (LDA) and the recently developed Perdew–Wang generalized gradient corrected functional, called the generalized gradient approximation (GGA). We find that GGA corrects most of the overbonding tendency of LDA. An interesting consequence of this is that, for the early lanthanides, the LDA results appear to agree better with experimental results than do the GGA results. In this case, we conclude that the 4f states probably have a significant impact on the equilibrium volumes of the early lanthanides. Both for the bulk moduli and for the generalized cohesive energies, we find that GGA generally, in comparison to LDA, gives results in closer agreement with experiment over the entire lanthanide series. © 1998 Elsevier Science S.A.

Keywords: Lanthanides; Cohesive properties; Density functional calculation; Generalized gradient approximation

1. Introduction

There has been a continuous development of approximations of the exchange-correlation functional since the first local density approximation (LDA) was proposed [1,2]. In the LDA, the exchange-correlation potential is obtained from a uniform electron gas. Any improvement upon the LDA has to take into account nonlocal information about the exchange-correlation potential. However, a straightforward gradient expansion (GEA) does not give better results than LDA. In fact, the overbonding tendency known from LDA becomes even worse with GEA [3]. Rather recently, Perdew and Wang [4] developed a generalized gradient approximation which, in contrast to GEA, obeys the sum rules of the exchange-correlation hole and satisfies many of the scaling relations for the exchange-correlation energy. These requirements, which are automatically fulfilled for LDA, seem to be an important ingredient in higher order density functionals. The Perdew–Wang functional, called GGA in the following, has proven very successful, and it has been tested and compared with other density functionals on a number of systems [5–12]. However, no systematic study of the differences between GGA and LDA has yet been performed for the lanthanide series. With the present paper, we intend to fill this gap by studying the equilibrium volumes, the bulk moduli and the generalized cohesive energies, defined below, of the lanthanide elements using the LDA in the Hedin–Lundqvist parameterization [13,14] and the GGA by Perdew and Wang [4].

As shown by Ozoliņš and coworkers [12], the atomic-spheres approximation (ASA) affects the cohesive properties by approximately the same amount as the corrections introduced through GGA [12]. Therefore, we test the functionals together with a full-potential method, so that our results will be free of errors originating from shape approximations, thus only reflecting the limitations of the tested functionals.

The cohesive properties of the lanthanides, using an ab initio approach, have previously been calculated by Duthie and Pettifor [15], Skriver [16], and Min et al. [17]. Cohesive energies of some lanthanides have also been calculated by Eriksson, Brooks and Johansson [18]. All these calculations were performed using the LDA and the ASA. More recently, Melsen et al. [19] calculated the cohesive energies for all lanthanides in the LDA, using a full-potential approach.

The rest of this paper is organized as follows. Below, we define the generalized cohesive energy, which is closely related to the cohesive energy, but varies smoothly across the lanthanides series. Then, in Section 2, we give some

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[*] Corresponding author. Fax: +46 184713524; e-mail: anna.delin@fysik.uu.se

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details of the numerical method used. The results of our calculations are presented and discussed in Section 3. Finally our conclusions are summarized in Section 4.

The cohesive energy E_{coh} is defined as the energy difference between the atomic and the bulk ground states. In contrast to the volume and bulk modulus, which vary rather smoothly as a function of atomic number for the trivalent lanthanide metals, the cohesive energy exhibits an irregular behavior. These irregularities can be removed, as will now be explained, by adding two atomic corrections to the cohesive energy.

Most of the lanthanides have a trivalent ground state in the condensed phase, i.e., the electronic configuration (Xe)$4f^{n+1}[5d6p6s]^3$, and a divalent atomic configuration, i.e., (Xe)$4f^n5d^06p^06s^2$. Thus, promotion of a 4f electron to the 5d band takes place during condensation. The atomic energy associated with this valence change is called the promotion energy $E_{f\to d}$, and it varies substantially from one element to another. Note that $E_{f\to d}$ is the energy difference between the divalent and trivalent atom. The irregular behavior of $E_{f\to d}$ as a function of atomic number explains to a large extent the irregularities in E_{coh} [20,21].

Even after the addition of $E_{f\to d}$ to E_{coh}, some irregularities remain. It has been shown [20,21], that these are in fact due to the 5d–4f intershell coupling energy of the trivalent atom. This energy will be called $\Delta E_{\mathrm{coupling}}$ in the following.

With the two corrections $E_{f\to d}$ and $\Delta E_{\mathrm{coupling}}$ we construct, for the trivalent lanthanide metals, a smoothly varying function given by

$$E^* = E_{\mathrm{coh}} + E_{f\to d} + \Delta E_{\mathrm{coupling}} \qquad (1)$$

E^* is called the generalized cohesive energy, and its theoretical value is easily calculated as the difference between the total energy of the spin-degenerate trivalent atomic and bulk ground states. For obvious reasons, both $E_{f\to d}$ and $\Delta E_{\mathrm{coupling}}$ are zero for Ba, Eu, and Yb.

2. Details of the calculations

In our present calculation we used the full-potential linear muffin-tin-orbital method (FPLMTO) [22–26]. In this method, the Kohn–Sham equations are solved for a general potential without any shape approximation.

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 or/and Neumann functions which in turn is represented as a Fourier series. Inside the muffin-tin spheres the basis functions are Bloch sums of radial functions times spherical harmonics. In the present calculation, the expansion in spherical harmonics is taken up to $l=8$.

We used the pseudo-core 5p wave, and the valence 6s, 6p, 5d and nf waves, where $n=4$ for Ba and La and $n=5$ in all other cases, i.e., Ce–Lu. We sampled the reciprocal space with around 2000 k-points in the full Brillouin zone, using special k-point sampling methods [27,28].

The electron core, to which the 4f electrons belong, 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, so that the influence of the spin–orbit splitting on the chemical bonding is very small, and thus it is expected that the error introduced by omitting this term be negligible [15,29,30].

For the elements Ba, Ce and Eu–Lu, the calculations were performed assuming the crystal structure found at ambient conditions. The calculations for La, Pr, Nd, Pm, and Sm were performed assuming the hcp structure. The equilibrium volumes and bulk moduli were extracted from the calculated energy/volume data points by fitting them to the universal equation of state [31,32]. In the calculation of the bulk moduli, the c/a ratio was kept constant at the experimental value.

3. Results and discussion

Our LDA and GGA results for the volumes of the lanthanides are shown in Fig. 1, together with the experimental volumes [33]. We see that for all elements having either an empty or full 4f shell, i.e., Ba, La, Yb, and Lu, the GGA results are in excellent agreement with experiment, whereas the LDA results underestimate the volumes by approximately 15%. Then, for the early elements from Ce up to Pm, the LDA volumes appear to agree better with experiment than do the GGA volumes.

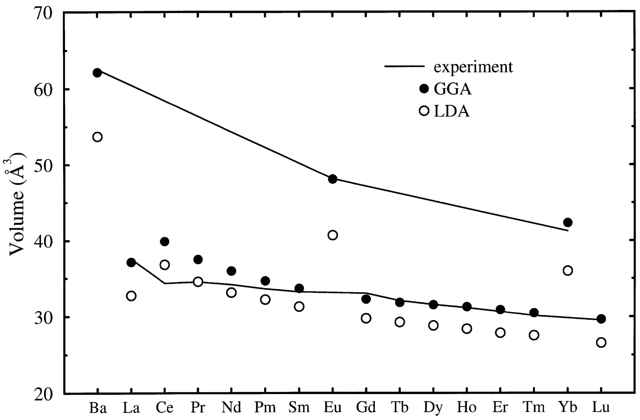

Fig. 1. Experimental volumes at ambient temperature (taken from Ref. [33]) and calculated volumes using LDA and GGA. Ba and Eu is calculated in the bcc structure, Ce and Yb in the fcc structure. All other elements are calculated in the hcp structure assuming the experimental c/a ratio.

For the later lanthanides, the GGA calculations again give excellent agreement with the experimental volumes. The error introduced by the approximate crystal structure used in the calculations for the early lanthanides (hcp instead of dhcp and Sm-type) was seen from test calculations to be very small.

For all elements studied here, GGA gives an upward shift in the equilibrium volume relative to LDA. The relative increase is largest for the divalent elements, where it is between 15% and 20%. For the trivalent elements, the shift is somewhat less, around 10% on average.

Maybe more interesting than the absolute values of the volumes, is the way in which the volumes decrease as the series is traversed. Clearly, the calculations overestimate the lanthanide contraction for the early elements. This trend is the same both for LDA and GGA. The result of this erroneous trend is that LDA appears to give better results for the early elements. This, however, is a result of cancellation of errors and tells us that the error in the standard model of the lanthanides is about as large as the overbonding tendency of LDA, but with the opposite sign. Thus, the standard model of the lanthanides seems to be unsatisfactory for the early elements in the series.

Fig. 2 shows experimental and calculated bulk moduli, comparing the two functionals. The experimental bulk moduli in Fig. 2 are calculated as the mean of the isothermal bulk moduli B_T, found in Ref. [34], for each element, with error bars indicating the maximum and minimum quoted values of B_T. The bulk modulus for Ba is taken from Kittel [35] and lacks error bars. Comparing our 0 K calculations with experimental data measured at ambient temperature will introduce a systematic error due to thermal expansion. However, this error is of the order of only a few percent, and probably less than the error caused by magnetic ordering in the low temperature experimental data. Furthermore, the error in the bulk modulus caused by using an approximate crystal structure for the early elements is negligible.

The first thing to note in Fig. 2 is that LDA overestimates the bulk modulus in all cases except Ba. However, the nice result for Ba is due to cancellation of errors since, at the same time, LDA underestimates the equilibrium volume by approximately 15%. The average LDA-overestimate of the bulk modulus, Ba excepted, is around 30% compared to the mean experimental values. This is qualitatively consistent with the result that LDA underestimates the volumes (Ce and Pr excepted) since a decrease in B is generally correlated to a increase in V, due to the softening of the lattice as it expands. The GGA results agree much better with experiment. In fact, for the elements beyond Sm, the agreement is excellent. Also, the agreement is very good for the elements having a closed 4f (sub)shell. For the early elements, GGA overestimates the bulk modulus. Naively, one would have expected the opposite, since GGA overestimates the volumes for these elements. This indicates again that the standard model of the lanthanides breaks down for the early lanthanides. A most interesting trend in the bulk modulus also emerges from the GGA results. This trend looks like a third order polynomial, as opposed to the trend in the LDA results.

Finally, the generalized cohesive energies are presented in Fig. 3. Here, also GGA gives overall better results than LDA. The agreement between GGA and experimental results for the elements with closed 4f (sub)shell is less satisfactory than for the volumes and bulk moduli. For Eu and Yb, the experimental points are placed almost intermediate in between the calculated LDA and GGA points, and for La both LDA and GGA overestimate the generalized cohesive energy, which is a unique situation. In contrast to the situation in La, the agreement between GGA and experiment is truly excellent for Ba, which is reassuring since the same basis set is used both for Ba and La (4f instead of 5f). LDA overestimates E^* by about 0.5 eV for the trivalent elements and 0.2 eV for the divalent. With GGA the agreement is excellent for the early

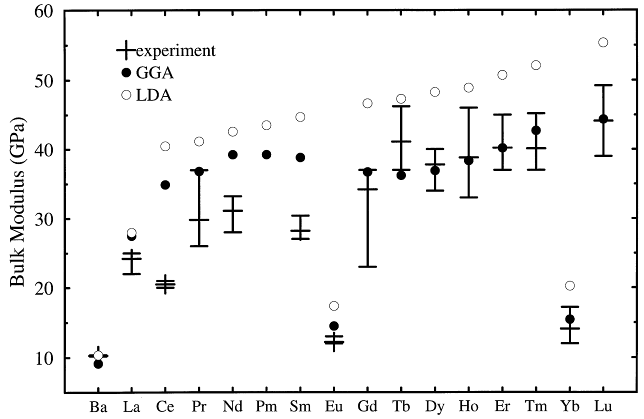

Fig. 2. Experimental bulk moduli at ambient temperature (taken from Ref. [34]) and calculated bulk moduli for both LDA and GGA. Ba and Eu are calculated in the bcc structure, Ce and Yb in the fcc structure. All other elements are calculated in the hcp structure assuming a c/a ratio fixed at its experimental equilibrium value.

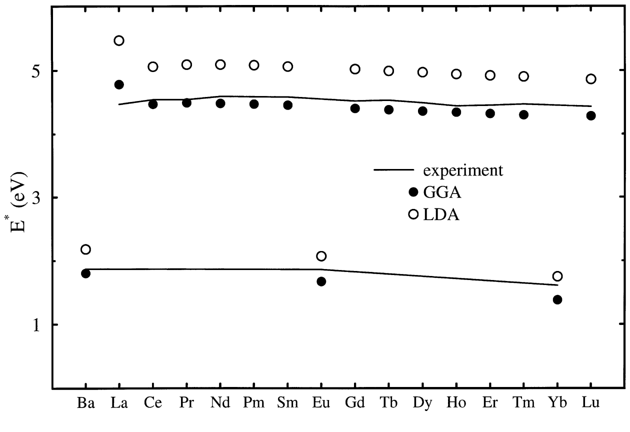

Fig. 3. Calculated generalized cohesive energies compared with experimental values taken from Ref. [20,21].

trivalent metals, La excepted, with discrepancies less than 0.1 eV. For the divalent and for the heavier trivalent elements, GGA underestimates E^* by about 0.2 eV. The trend in the experimental values for the generalized cohesive energies is very smooth, and this trend is excellently reproduced by both the LDA and the GGA from Ce and onwards.

4. Conclusions

In conclusion, our calculations show that in general for the elements studied here, GGA gives better volumes, bulk moduli, and cohesive energies than LDA. In fact, for the late lanthanides, the agreement is excellent for all properties studied. The reason why GGA gives better results is due to the fact that the nonlocality of exchange and correlation, which must become increasingly important for larger density variations, is better taken into account with this functional than with LDA. The effect is that GGA favors nonspherical densities more than LDA, and this results in larger lattice constants, since expansion increases the inhomogeneity. A larger lattice parameter, in turn, will lower both the bulk modulus and the cohesive energy, which is also what happens in our calculations.

The combination of GGA and a full-potential method resolves that the standard model of the lanthanides, in which the 4f electrons are isolated from the valence states, is unsatisfactory for the earlier elements in the lanthanide series. This is clear from the trend in the experimental volumes, which for the early lanthanides is much flatter than the theoretical trend.

Furthermore, LDA and GGA give different trends in the bulk modulus. The LDA trend is rather straight, whereas the GGA trend, which actually seems to be supported by the experimental points, resembles a third order polynomial with a local maximum at Nd and a local minimum in Tb.

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