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Cohesive and electronic properties of transition metals: The generalized gradient approximation

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We present a comparison between the local-spin-density approximation and the generalized gradient approximation for the calculation of cohesive and electronic properties of transition metals. Atomic *s*-*d* promotion energies, equilibrium lattice constants, bulk moduli, magnetic moments, and cohesive energies have been determined for 3*d*, 4*d*, and 5*d* transition metals. Gradient corrections to the density functional seem to have very small effects on calculated atomic *s*-*d* promotion energies. In agreement with previous results, we find that the generalized gradient approximation yields equilibrium lattice parameters and bulk moduli that are very close to experimental values for the 3*d* transition metals, while the results in the 4*d* and 5*d* series are less accurate. Cohesive energies calculated with the local-spin-density approximation are found to be too high for all transition metals. The generalized gradient approximation lowers these values, which, however, leads to cohesive energies that are too low in many cases. We argue that a major part of the remaining discrepancy may be due to the muffin-tin-potential approximation.

I. INTRODUCTION

Much of the success of *ab initio* electron-structure calculations relies on the "density-functional theory" of Hohenberg, Kohn, and Sham.[1] This theory states that the general many-body problem for electrons in atoms, molecules, or solids can be formulated in terms of a single-particle equation. The difficulty lies in finding a single-electron potential $V(\mathbf{r})$ from the total electronic charge density $\rho(\mathbf{r})$. The approximation that has become most popular is the local-spin-density approximation (LSDA),[2,3] in which the potential at $\mathbf{r} = \mathbf{r}_0$ is a function only of the total electronic charge density at $\mathbf{r}_0$.

The LSDA may seem crude for systems with large variations in the electronic charge density as, e.g., in transition-metal (TM) compounds. Failures of the LSDA also occur for these systems. For example, the LSDA underestimates the atomic volumes of most transition metals in the 3*d* series,[4] it predicts the wrong ground-state lattice configuration for certain solids [e.g., Fe (Ref. 5)], and it overestimates the bonding strength (cohesive energy) of most transition metals and their compounds.[4,6–8] However, it has proven very difficult to find an alternative density functional that works better than the LSDA throughout the entire TM series.

The purpose of this work is to investigate the properties of the generalized gradient approximation (GGA) which may currently be the best candidate for replacing the LSDA. We have used a version of the GGA (Refs. 9 and 10) that treats both exchange and correlation effects without empirically adjusted parameters. The properties of earlier versions of the GGA (Refs. 11–13) have been studied previously, both in the atomic[14–16] and bulk[17–21] cases. However, it is not clear whether the GGA gives an overall improvement of calculated cohesive energies. This aspect is crucial when discussing the possible role of *ab initio* results in predictions of phase diagrams of solids. Absolute cohesive-energy values yielded in LSDA calculations are often too far from experimental data to be useful in phase-diagram modeling.[6,8] Although it is possible[8] to correct for known deficiencies in the theoretical approach, and thus to reduce the magnitude of the discrepancy between theory and experiment, the calculation of accurate cohesive energies remains an important challenge to solid-state theory.

The paper is organized as follows. In Sec. II we present results from atomic calculations using both the LSDA and the GGA. We focus there on those atomic properties which are relevant in cohesive-energy determinations. We proceed with results from spin-polarized linear-muffin-tin-orbital (LMTO) band-structure calculations in Sec. III and we use atomic and bulk total energies in Sec. IV to calculate the cohesive energies of 3*d*, 4*d*, and 5*d* transition metals. The paper ends with conclusions in Sec. V.

II. ATOMIC CALCULATIONS

There are several reasons why it is difficult to find a density functional for calculating the electronic structure of atoms. One problem is to describe correctly the region far from the nucleus where the electronic potential is almost of Coulomb type. Another difficulty arises from the angular variations of exact atomic orbitals. The use of the LSDA and a spherically averaged potential accounts for neither of these effects, and it has been demonstrated[4] that such calculations yield the wrong ground-state electronic configuration for many atoms. For atoms in the transition-metal series, this failure is due to an overestimation of the bonding energy of *d* states compared to that of *s* states, an effect which is seen[22] as a difference between experimental and theoretical *s*-*d* promotion energies. This quantity is defined through

$$\Delta E = E[3d^{n-1}4s^1] - E[3d^{n-2}4s^2] \qquad (1)$$

for the $3d$ TM series and accordingly for the $4d$ and $5d$ series. Several attempts to reduce the discrepancy between theoretical and experimental ΔE have been made. Gunnarsson and Jones[23] stated that the addition of nonlocal terms to the density functional reduces the error, and a similar trend was observed by Boschan and Gollish[15] and Kutzler and Painter[16] using an earlier version of the GGA.[12,13]

In this work, we report on spin-polarized atomic calculations performed using the LSDA (Ref. 3) and the GGA (Refs. 9 and 10) on a spherically averaged charge density and with electronic configurations of maximum spin multiplicity. Our computer program has been described previously.[6] It was designed to resemble our code for band-structure calculations as closely as possible, which is the reason why it treats core electrons fully relativistically and valence electrons semirelativistically, i.e., neglecting the spin-orbit coupling.

Figure 1 shows our calculated ΔE values for the $3d$, $4d$, and $5d$ transition-metal atoms. The experimental curve was obtained by averaging[24,25] over multiplet energies from spectroscopic measurements[26] in order to simulate the energy of a spherical charge density. The spectroscopic information on Pd and Pt is incomplete, which explains the different behavior in experimental ΔE for these atoms. It is seen that the GGA does not significantly reduce the discrepancy between theoretical and experimental ΔE. The error reduction reported in Refs. 15 and 16 is probably explained by the fact that these authors worked with an earlier version of the GGA.[12,13] We conclude that the error in calculated *s*-*d* promotion energies is inherent in both the LSDA and the GGA. This view is supported by results from recent atomic calculations by Perdew *et al.*[10]

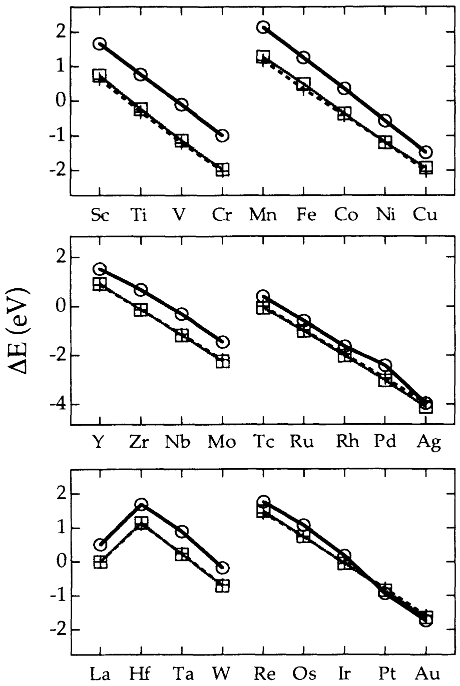

FIG. 1. *s*-*d* promotion energies (ΔE) for all $3d$, $4d$, and $5d$ transition-metal atoms. ΔE from LSDA calculations are marked with crosses, GGA results with empty squares, and experimental data with circles.

III. BULK CALCULATIONS

The effects of gradient corrections to the density functional in band-structure calculations have been investigated by several authors. In particular, earlier versions of the GGA were found[17–21] to give better agreement with experiment for the ground-state properties of certain materials (e.g., $3d$ transition metals) while a tendency for overcompensation of errors was found in other systems (e.g., $4d$ transition metals).

We have determined the total electronic energies for $3d$, $4d$ and $5d$ transition metals using the LMTO method.[27] Spin-polarized calculations were performed using both the LSDA in the parametrization of Gunnarsson and Lundqvist[3] and the recent GGA or Perdew.[9,10] The semirelativistic approximation was adopted and the lattice configuration was set to either fcc or bcc. The **k** mesh in the irreducible wedge of the Brillouin zone contained 505 points in the fcc case and 506 points in the bcc case. The basis set included *s*, *p*, *d*, and *f* functions for all systems. Equilibrium lattice constants (a_0) and bulk moduli (B) were obtained by fitting a Murnaghan equation of state to total energies calculated for 10–15 different lattice parameters for each element.

Our LSDA and GGA results for a_0 and B are summarized in Table I. Experimental lattice parameters are from Ref. 28. Measured bulk moduli are from Ref. 29. We see that the GGA gives a systematic increase in the lattice parameter while it yields lower bulk moduli than the LSDA. Whereas the GGA reduces the discrepancy between theoretical and experimental results in the $3d$ series, it gives lattice parameters that are too high and bulk moduli that are too low in the $4d$ and $5d$ series. Our results are in fairly close agreement with those of Ref. 19. This indicates that the modification of the correlation part in the density functional of the recent GGA (Refs. 9 and 10) leads to small changes in calculated a_0 and B. We have also verified that changes in band energies are negligible.

It is interesting to know whether the errors in a_0 and B calculated with the GGA are due to incompletenesses in the density-functional parametrization, or if they are mainly caused by other approximations in our calculations, e.g., the muffin-tin-potential approximation. Recent full-potential calculations on Fe(bcc) (Ref. 21) yielded a negligible difference in a_0 and a small increase in B compared with LMTO results. However, studies of the cohesive energy have indicated that the effect of the muffin-tin-potential approximation is significant in the $4d$ and $5d$ transition-metal series (cf. Sec. IV). It is therefore possible that a full-potential treatment

TABLE I. Calculated and experimental equilibrium lattice constants and bulk moduli for 3*d*, 4*d*, and 5*d* transition metals. Experimental lattice constants are from Ref. 28. Blank spaces are left for those elements that are not stable in the bcc or fcc structures. Experimental bulk moduli are from Ref. 29.

	Ti	V	Cr	Mn	Fe	Co	Ni
	fcc	bcc	bcc	fcc	bcc	fcc	fcc
a_0^{LSDA} (a.u.)	7.68	5.63	5.37	6.59	5.27	6.54	6.53
a_0^{GGA} (a.u.)	7.98	5.71	5.45	6.83	5.46	6.70	6.70
a_0^{expt} (a.u.)		5.74	5.45		5.42	6.70	6.66
B^{LSDA} (GPa)	120	199	287	314	266	255	268
B^{GGA} (GPa)	108	184	220	281	215	244	253
B^{expt} (GPa)	105	157	160	131	167	187	184
	Zr	Nb	Mo	Tc	Ru	Rh	Pd
	fcc	bcc	bcc	fcc	fcc	fcc	fcc
a_0^{LSDA} (a.u.)	8.52	6.28	6.02	7.37	7.24	7.24	7.37
a_0^{GGA} (a.u.)	8.60	6.39	6.11	7.47	7.36	7.36	7.53
a_0^{expt} (a.u.)		6.24	5.95			7.19	7.35
B^{LSDA} (GPa)	98	176	263	312	335	297	218
B^{GGA} (GPa)	94	166	242	280	270	241	209
B^{expt} (GPa)	95	170	264	281	311	267	188
	Hf	Ta	W	Re	Os	Ir	Pt
	fcc	bcc	bcc	fcc	fcc	fcc	fcc
a_0^{LSDA} (a.u.)	8.27	6.28	6.07	7.46	7.36	7.37	7.51
a_0^{GGA} (a.u.)	8.31	6.38	6.15	7.56	7.47	7.50	7.65
a_0^{expt} (a.u.)		6.25	5.98			7.26	7.41
B^{LSDA} (GPa)	118	205	303	368	400	373	291
B^{GGA} (GPa)	68	183	272	323	344	322	232
B^{expt} (GPa)	109	193	310	365	410	355	283

may reduce the errors in a_0 and B calculated with the GGA.

Magnetic moments (M) for Fe(bcc), Co(fcc), and Ni(fcc) have been calculated at the experimental lattice parameters and are shown in Table II. We get larger magnetic moments with the GGA than with the LSDA and thus values which are further from experimental data for Fe and Ni, but in better agreement with experiment for Co. The difference between LSDA and GGA results is even greater than that reported in Ref. 19, which indicates that the modified correlation part of the recent GGA (Refs. 9 and 10) is important for magnetic properties. However, full-potential calculations[20,21] have shown that the GGA is sensitive to the muffin-tin-potential approximation in spin-polarized calculations, and a major part of the discrepancy between theoretical and experimental M values is probably due to this approximation in our calculations.

TABLE II. Magnetic moments for Fe(bcc), Co(fcc), and Ni(fcc). Calculated values were determined at experimental lattice spacings. Experimental data are from Ref. 34.

		Magnetic moment (μ_B)
Fe	LSDA	2.28
	GGA	2.44
	Expt.	2.22
Co	LSDA	1.62
	GGA	1.68
	Expt.	1.75
Ni	LSDA	0.62
	GGA	0.67
	Expt.	0.62

IV. COHESIVE ENERGIES

Cohesive energies can be obtained from *ab initio* total-energy calculations as the difference between bulk and atomic total energies through

$$E_{\mathrm{coh}} = E(\mathrm{atom}) - E(\mathrm{solid}). \qquad (2)$$

However, using spectroscopic data,[26] it is easy to correct the atomic energies[24,25] for the fact that we use a spherical charge distribution. Similarly, atomic ground-state energies can be estimated from calculated total energies corresponding to different electronic configurations (e.g., $4s3d^{n-1}$ or $4s^2 3d^{n-2}$). Following Ref. 30, we write

$$E_{\mathrm{coh}} = [E(\mathrm{atom}) - \Delta] - E(\mathrm{solid}), \qquad (3)$$

where Δ contains the experimental correction.

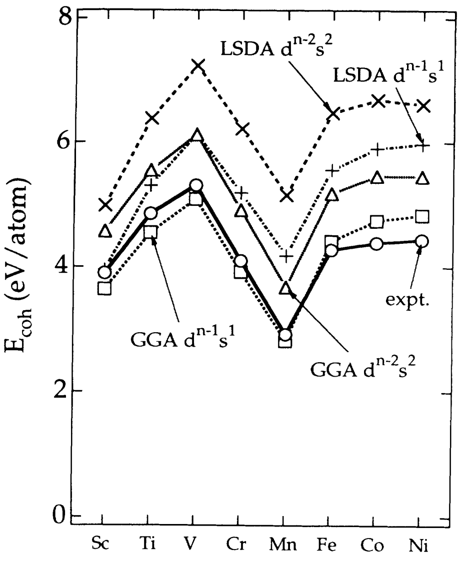

FIG. 2. Cohesive energies of 3d transition metals. Data points marked with diagonal crosses refer to E_{coh} values determined with the LSDA and based on the atomic electronic configuration $d^{n-2}s^2$. Vertical crosses show LSDA, $d^{n-1}s^1$ values, while triangles and squares represent GGA results for $d^{n-2}s^2$ and $d^{n-1}s^1$ atomic electronic configurations, respectively. Circles connected with a solid line show experimental E_{coh} from Ref. 31.

Figures 2, 3, and 4 show cohesive energies for 3d, 4d, and 5d transition metals, respectively. Our LSDA and GGA E_{coh} values are compared with experimental data from Ref. 31. The fact that we have restricted ourselves to the bcc and fcc structures is expected to give very small changes in E_{coh} for elements with different ground-state lattice configurations (e.g., hcp). This view is supported by recent calculations on the transition metals in the 3d series.[32]

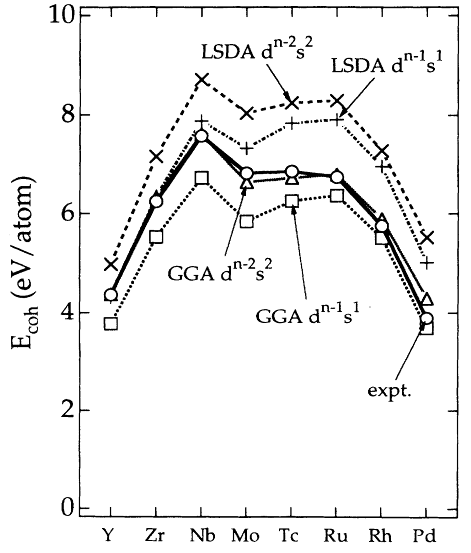

FIG. 3. Cohesive energies of 4d transition metals. For explanations, see Fig. 2.

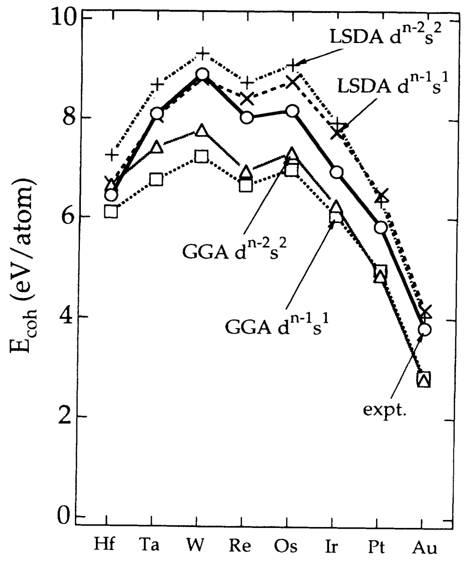

FIG. 4. Cohesive energies of 5d transition metals. For explanations, see Fig. 2.

It is seen that the GGA yields lower E_{coh} values than the LSDA for all elements studied in this work. This is a clear improvement for the 3d elements[17] for which our GGA curves lie very close to the experimental one. In the 4d and 5d series, the GGA produces cohesive energies below the experimental curve, and the correspondence with experiment is not significantly better than what is obtained with the LSDA. However, it has been shown[30,33] that a full-potential treatment of the electronic structure of transition metals increases calculated cohesive energies, especially in the middle of the TM series. The correction is larger in the 5d series[33] than in the 4d series.[30] It is therefore possible that errors due to the muffin-tin-potential approximation can account for a large part of the remaining discrepancy between theoretical and experimental E_{coh} values. The close agreement between experimental cohesive energies and our E_{coh} values calculated with the LSDA in the 5d series is thus explained by a cancellation between errors due to the muffin-tin-potential approximation and those due to the omission of gradient corrections.

V. CONCLUSIONS

We have investigated in this paper the properties of the generalized gradient approximation (GGA) in calculations of the electronic structure of transition-metal atoms and solids. In atomic calculations, it is a well-known problem that the local-spin-density approximation (LSDA) overestimates the bonding energy of d states compared with that of s states. The GGA gives no noticeable change in calculated atomic s-d promotion energies, and we conclude that gradient corrections of this type have a negligible influence on relative s and d stabilities. The GGA yields equilibrium lattice parameters and bulk moduli that are close to experimental data for the 3d transition metals. However, in the 4d and 5d series, the LSDA still produces theoretical lattice parameters and bulk moduli that are in better agreement with experiment. Magnetic moments for ferromagnetic Fe(bcc), Co(fcc), and Ni(fcc) are clearly increased by the GGA, but this can largely be attributed to the omission of nonspherical terms in our calculations.[21]

An important result in this work concerns the effect of gradient corrections on calculated cohesive energies ($E_{\rm coh}$). The GGA yields lower $E_{\rm coh}$ values than the LSDA for all transition metals which is an improvement in the 3d series. The cohesive energies in the 4d and 5d series from GGA calculations are smaller than the experimental values, but in light of recent full-potential calculations,[30,33] we suggest that a large part of the remaining discrepancy between theoretical and experimental $E_{\rm coh}$ may be due to the muffin-tin-potential approximation.

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