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Full-potential calculations using the generalized gradient approximation: Structural properties of transition metals

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The equilibrium volumes and bulk moduli of nonmagnetic 3*d*, 4*d*, and 5*d* transition metals have been calculated using a full-potential linear-muffin-tin-orbitals (FP-LMTO) method and the generalized gradient approximation (PW91) of Perdew and Wang [in *Electronic Structure of Solids 1991*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991), Vol. 11]. The gradient-corrected FP-LMTO results are found to be superior to the corresponding local-density approximation (LDA) results in all transition-metal series. Furthermore, the atomic-spheres approximation (ASA) is found to yield larger equilibrium volumes and smaller bulk moduli than the FP method. The inaccuracies introduced by the ASA are of the same magnitude as the gradient-corrections, suggesting that a FP treatment is important for gradient-corrected calculations. Excellent agreement with experiment is found for the c/a ratios of the hcp metals using both the LDA and the PW91, while for the fcc-bcc structural energy differences of 4*d* metals disagreement with semiempirical estimates remains.

The local-density approximation (LDA) to the density-functional theory[1,2] of Hohenberg, Kohn, and Sham has proven to be very useful for calculating the structural properties of solids. However, the LDA has some well-known deficiencies, e.g., it incorrectly predicts a nonmagnetic close-packed ground-state of iron[3] and it underestimates the equilibrium volumes and overestimates the bulk moduli in the 3*d* transition metal (TM) series.[4,5] The generalized-gradient approximations[6–8] (GGA's) attempt to correct these deficiencies by including corrections to the LDA exchange-correlation functional through the gradient of the charge density. The GGA (Ref. 9) proposed by Perdew and Wang (referred to as PW91 hereafter) was constructed to satisfy sum rules, bounds, and scaling relations for the exact exchange-correlation functional. This density-functional parametrization has been shown to give an improved description of the ground-state properties of many atomic, molecular, and solid systems (see Ref. 10 and references therein).

Recently, there has been a great interest in the effects of the GGA's on calculated structural properties of bulk transition metals.[11–20] An early success was the prediction of the correct (ferromagnetic bcc) ground-state structure of iron,[11] but it has to date remained unclear whether the GGA's give a consistent improvement of equilibrium volumes and bulk moduli of all TM's. Previous investigations[11–19] found the GGA's to improve the calculated structural properties of the 3*d* metals. However, in the 4*d* and 5*d* series, linear-muffin-tin-orbitals (LMTO) calculations[12,13,20] using the atomic-spheres approximation (ASA) yielded GGA results in worse agreement with experiment. It has been suggested[13–15] that the remaining discrepancy may be due to the use of the ASA. To our knowledge there has been no systematic study of the importance of a general-potential treatment for gradient corrected calculations.

In the present work we will show that general-potential PW91 calculations yield accurate equilibrium volumes and bulk moduli for all nonmagnetic TM's. Furthermore, the ASA will be shown to give systematically larger equilibrium volumes than a general-potential treatment, thus suggesting that the discrepancy between the earlier GGA results[12,13] and experimental data in the 4*d* and 5*d* series is mainly due to the use of the ASA.

We have performed *ab initio* total-energy calculations for two 3*d*, eight 4*d*, and six 5*d* TM's using a fast full-potential (FP) version of the LMTO method due to Methfessel.[21] A characteristic feature of this scheme is interpolation over the interstitial region using the values and slopes at the muffin-tin (MT) spheres. For instance, the charge density is calculated exactly inside the nonoverlapping MT spheres, yielding its values and slopes on the MT spheres. In the interstitial region it is represented by a linear combination of Hankel functions fitted to the same values and slopes on all MT spheres. Thereby the three-center integrals are reduced to two-center integrals and all the volume integrations can be performed analytically. This procedure has been shown[21] to have an error in the interstitial matrix elements of less than 3% for close-packed structures. The nonlinear exchange-correlation functional is treated in a similar manner. We evaluate all gradient terms numerically inside the MT spheres and expand the exchange-correlation energy and potential in spherical harmonics. However, in the interstitial region, the exchange-correlation energy and potential are not evaluated from the charge-density directly. Instead, they are obtained by interpolating between the MT spheres using a linear combination of Hankel functions chosen to match the values and slopes at the MT spheres for each angular-momentum component separately. This approach assumes that interpolation using the values and slopes on the MT spheres accurately represents smooth functions in the interstitial region of close-packed structures. Furthermore it eliminates the difficulties associated with discontinuities in the charge density derivatives[15] on the surfaces of the MT spheres and preserves the computational efficiency of the Methfessel method.

For bcc and fcc metals two LMTO envelopes of Hankel functions with kinetic energies −0.01 Ry and −1.0 Ry were used. The basis set consisted of s, p, d, f orbitals from the first and s, p, d orbitals from the second envelope. For hcp metals, an additional envelope with energy −2.3 Ry was included, using a $3s3p3d1f$ basis. Hankel functions with energies −1.0 Ry and −3.0 Ry were used for the interstitial fit and nonspherical terms were expanded in spherical harmonics up to $l_{\max} = 6$. The extended $4p$ states of $4d$ metals were treated as a semicore by performing a separate diagonalization at each iteration. The scalar relativistic approximation was adopted for both core and valence electrons. We used $\mathbf{k}$ meshes containing 670, 330, and 266 special points in the irreducible wedge of the Brillouin zone of the fcc, bcc, and hcp structures, respectively.

Equilibrium volumes V_0 and bulk moduli B were obtained by fitting Murnaghan's equation of state to the calculated total energies. For hcp metals, a third-order polynomial was fitted to total energies calculated at several c/a ratios in order to obtain the equilibrium c/a ratios.

The FP-LMTO calculations using the LDA of Ceperley and Alder[22,23] and the PW91 will be referred to as FP-LDA and FP-PW91, respectively. The results from the FP-LDA and FP-PW91 calculations are reported in Table I. The errors in V_0 and B with respect to experimental data are shown in Figs. 1 and 2, respectively. For comparison we also show the errors in previously reported[13] LMTO-ASA results, which will be referred to as ASA-LDA and ASA-PW91. Table II summarizes the root-mean-square errors in the calculated V_0 and B.

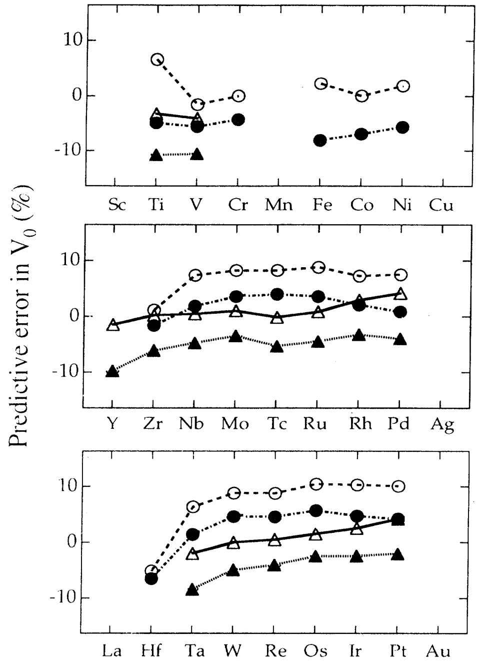

FIG. 1. Errors in calculated equilibrium volumes V_0 with respect to experimental data. FP-LDA values are marked with filled triangles, FP-PW91 with open triangles, ASA-LDA (from Ref. 13) with filled circles, and ASA-PW91 (from Ref. 13) with open circles.

Figures 1 and 2 show that the FP-LDA calculations underestimate V_0 and overestimate B, in agreement with Ref. 5. The well-established effect of the gradient corrections to increase V_0 and decrease B is confirmed by our FP calculations and brings the FP-PW91 results in good agreement with experiment in all TM series. The increase in V_0 can be explained[10] by noting that the functional of Perdew and Wang favors charge-density inhomogeneities, which are known to increase upon lattice expansion. The change in B is generally correlated to the change in V_0, due to the softening of the lattice as it expands. Although the FP-PW91 results are significantly better than those of the FP-LDA, it should be noted that there is a trend to underestimate V_0 in the beginning of the series and to

TABLE I. Calculated and experimental equilibrium volumes V_0, bulk moduli B, and c/a ratios for $3d$, $4d$, and $5d$ transition metals. Blank spaces are left in the c/a columns for elements that are not stable in the hcp structure. Experimental data for V_0, B, and c/a are taken from Refs. 24, 26, and 25, respectively.

	V_0 (a.u.)			B (GPa)			c/a		
	LDA	PW91	Expt.	LDA	PW91	Expt.	LDA	PW91	Expt.
Ti(hcp)	106.3	115.2	119.1	114	108	105	1.589	1.589	1.588
V(bcc)	84.56	90.66	94.56	212	184	157			
Y(hcp)	201.1	219.6	222.9	45.6	39.0	36.6	1.567	1.529	1.571
Zr(hcp)	147.4	157.5	157.1	106	91.2	95	1.613	1.603	1.593
Nb(bcc)	115.7	122.1	121.5	189	167	170			
Mo(bcc)	101.6	106.4	105.3	297	259	264			
Tc(hcp)	91.11	96.10	96.26	330	280	281	1.604	1.606	1.605
Ru(hcp)	87.45	92.34	91.57	360	302	311	1.584	1.586	1.583
Rh(fcc)	89.86	95.66	92.92	313	257	267			
Pd(fcc)	95.27	103.4	99.27	226	171	188			
Ta(bcc)	111.8	119.7	122.1	187	175	193			
W(bcc)	101.6	106.9	106.9	305	271	310			
Re(hcp)	95.31	99.78	99.30	427	355	365	1.620	1.620	1.615
Os(hcp)	92.08	95.79	94.37	430	390	410	1.588	1.587	1.579
Ir(fcc)	93.31	98.06	95.66	400	356	355			
Pt(fcc)	99.67	105.9	101.7	306	263	283			

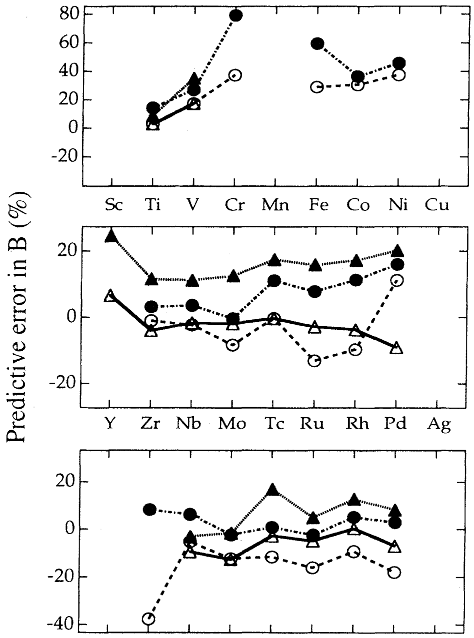

FIG. 2. Errors in calculated bulk moduli B with respect to experimental data. Note the different scales in the three panels. For explanations, see Fig. 1.

overestimate V_0 at the end of the series.

It has been noted[27] by Hathaway, Jansen, and Freeman that overlapping atomic spheres (as in the ASA) tend to increase the equilibrium volume, concealing the disagreement of the LDA with experiment. This is confirmed by our ASA calculations, which yield systematically larger V_0 and smaller B than the FP method. The ASA increases the equilibrium volumes and decreases the bulk moduli by approximately the same amount as the gradient corrections. This suggests that the poor agreement with experiment in the ASA-PW91 results for $4d$ and $5d$ metals is due to the use of the ASA, and the relatively good accuracy of the ASA-LDA calculations is due to an error cancellation between the LDA and the ASA. We conclude that a full potential treatment is important for gradient corrected calculations.

The calculated c/a ratios of hcp metals (see Table I) are in excellent agreement with experiment using both the FP-LDA and FP-PW91 approaches. The results are in accord with those for Ti in Ref. 5 and for Os in Ref. 28.

Figure 3 displays calculated structural energy differences, $E(\mathrm{fcc}) - E(\mathrm{bcc})$, in the $4d$ TM series, together with semiempirical estimates obtained from analyses of phase diagrams.[29,30] It is seen that neither the PW91 nor the FP treatment significantly affects this quantity. It has been shown[31] that these energy differences are well described by the differences in band energies of the fcc and bcc structures. As the gradient corrections to the energy bands are negligible,[12,32] it is not surprising that $E(\mathrm{fcc}) - E(\mathrm{bcc})$ is almost unaffected. Thus, the disagreement between *ab initio* results and semiempirical estimates for this quantity remains.

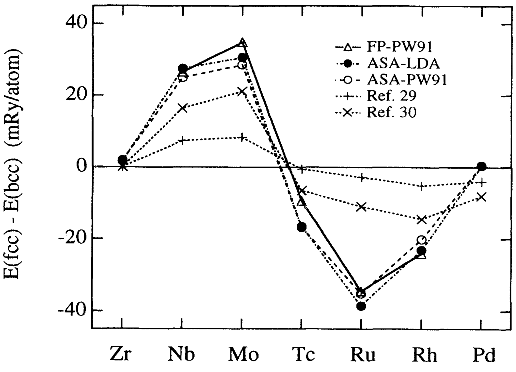

FIG. 3. Calculated structural energy differences, $E(\mathrm{fcc}) - E(\mathrm{bcc})$, for $4d$ transition metals, using the FP-PW91, ASA-LDA, and ASA-PW91 methods. Also shown are semiempirical estimates taken from Refs. 29 and 30.

In conclusion, it has been shown that for full-potential calculations the PW91 gradient corrections improve calculated equilibrium volumes and bulk moduli in all transition metal series. The ASA has been shown to affect the structural properties by approximately the same amount as the gradient corrections. It is therefore suggested that a general-potential method for electronic structure calculations is necessary for a fair comparison of results obtained using different density functionals. Furthermore, it would be of considerable interest to perform fully relativistic calculations in the $5d$ series, where the spin-orbit interaction may influence the results.

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TABLE II. Root-mean-square (rms) errors in calculated V_0 and B for $3d$, $4d$, and $5d$ metals from Figs. 1 and 2. The ASA-LDA and ASA-PW91 values are taken from Ref. 13.

	rms error in V_0 (%)				rms error in B (%)			
	ASA-LDA	ASA-PW91	FP-LDA	FP-PW91	ASA-LDA	ASA-PW91	FP-LDA	FP-PW91
$3d$	6.1	3.0	11	3.7	49	28	26	12
$4d$	2.8	7.4	5.9	1.9	9.1	8.2	17	4.6
$5d$	4.7	8.7	4.6	2.2	4.7	18	9.6	7.4
Total	4.6	7.0	6.3	2.3	27	20	16	7.1

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