Equilibrium properties of zinc

D. Singh and D. A. Papaconstantopoulos
Naval Research Laboratory, Washington, D.C. 20375-5000

Total-energy and electronic-structure calculations have been performed for elemental zinc in the fcc, bcc, and hcp structures, using the general-potential linearized-augmented-plane-wave method within the local-density approximation. Calculated static structural properties for the hcp structure in good agreement with experimental data as well as the correct ordering of phases are obtained. In order to assess the importance of non-muffin-tin contributions to the potential, calculations have also been performed using a muffin-tin-approximation augmented-plane-wave code. It is found that, while the close-packed fcc phase can be rather well described using a muffin-tin potential, the bcc phase is not as well described in this approximation.

I. INTRODUCTION

In this manuscript we report the results of local-density-approximation (LDA) -based total-energy and electronic-structure calculations for zinc. These calculations were performed for the equilibrium hcp structure as well as the fcc and bcc structures, using the general-potential linearized-augmented-plane-wave (LAPW) method. In addition, a series of parallel calculations have been performed in order to test the sensitivity of the results to the particular choice of exchange-correlation (XC) functional and the effect of muffin-tin approximation. The motivation for this study is twofold.

The first motivation derives from a desire to obtain an understanding of certain structural properties of zinc in terms of its electronic structure. In particular, in this study we explore the relationship between the fairly distorted $(c/a = 1.828)$ hcp structure of zinc and its electronic structure.

The second motivation for this study results from the fact that an extensive series of calculations has been performed on the Cu-Zn alloy system by Johnson and co-workers, who used a muffin-tin Korringa-Kohn-Rostoker—coherent-potential-approximation (KKR-CPA) approach.[1] This series of calculations was performed both because of the physical interest in this particular alloy system and also in order to demonstrate the capability of their approach. In order to fully describe this alloy system an understanding of the end points and their phase stability is essential.[2] However, to our knowledge no *ab initio* LDA-based total-energy study has been performed for zinc in its equilibrium hcp structure. Further, while calculations have been performed for the fcc structure,[3] these were not performed using a general-potential approach, and thus the errors introduced by the muffin-tin approximation (which is also used in the KKR-CPA method referred to above) have not been quantified. In addition, the calculations of Ref. 3 did not include relativistic effects which are included in the present study. Therefore it seems that a study of bulk zinc and the applicability of the muffin-tin approximation to this system is needed.

II. METHOD OF CALCULATION

Since the general-potential LAPW method has been discussed in detail elsewhere, only those aspects particular to the present study are discussed here. A more general discussion of the method and its accuracy may be found in Ref. 4. In the LAPW method space is partitioned into two regions, nonoverlapping atom-centered muffin-tin spheres, and the remaining interstitial volume. Since the expansions of the charge density and potential are unrestricted in both regions this partition does not result in any shape approximations. However, in order to maintain the efficiency of the method, it is advantageous to choose the sphere radii, R_{MT}, as large as possible, subject to the constraint of nonoverlapping spheres. In the present study a zinc-sphere radius of 2.20 a.u. was used, with a basis-set cutoff corresponding to $R_{MT}K_{max} = 9.0$. Inside the spheres the LAPW basis functions were expanded up to $l = 8$, as were the charge densities and potentials. All the electrons were treated variationally, the core electrons fully relativistically in an atomiclike approximation, and the valence electrons in a scalar relativistic approximation.

The Brillouin-zone summations were performed using the special k-point method with the Fermi surface broadened using a Fermi-Dirac distribution of width $k_B T = 1$ mRy. For the total-energy calculations, sets of 60, 112, and 352 special k points[5] in the irreducible wedge of the Brillouin zone were used for the fcc, bcc, and hcp structures, respectively. Convergence tests were performed using as many as 408 k points for the fcc structure and 1632 for the bcc structure, as well as basis-set cutoffs up to $R_{MT}K_{max} = 9.75$. These tests indicated that the calculated total energies are converged to approximately 1 mRy with respect to these parameters.

For the fcc and bcc phases total energies were calculated for a range of lattice parameters around the equilibrium values (3.59–4.02 Å and 2.86–3.28 Å for the fcc and bcc structures, respectively). These total energies were then fitted to the Murnaghan[6] equation of state in order to determine the static structural properties. For the hcp structure, total energies were calculated for 25 different

TABLE I. Static structural properties of fcc, bcc, and hcp zinc, calculated using the general-potential LAPW method with the Wigner exchange-correlation functional. a and c are the calculated equilibrium lattice parameters, B the bulk modulus, B' its pressure derivative, and ΔE the energy of the minimum relative to the hcp minimum. Expt. denotes experimental data for the hcp structure from Ref. 12.

Structure	a Å	c (Å)	B (GPa)	B'	ΔE (mRy/atom)
bcc	3.07		83.7	5.1	6.5
fcc	3.85		95.3	4.2	1.2
hcp	2.607	4.937	77.8		0
Expt. (0 K)	2.660	4.863	80		0
Expt. (300 K)	2.665	4.947	75		0

sets of cell volumes and c/a ratios. These included cell volumes from 26.1 to 32.2 Å^3 and c/a ratios from 1.637 and 2.215. These were then fitted to a polynomial form that included all terms up to third-order plus a fourth-order term composed of the square of the product of cell volume and c/a ratio.

III. RESULTS AND DISCUSSION

The static properties of fcc, bcc, and hcp zinc as calculated using the general-potential LAPW method with the Wigner[7] XC functional and the convergence parameters discussed above are summarized in Table I. As may be noted from the table, the agreement between the present results for the hcp phase and experimental data is quite good. The calculated cell volume is about 2.5% smaller than the experimental value, while the calculated c/a ratio is 3.6% larger. The fits to the Murnaghan equation of

state for the cubic structures and the fitted energy at the optimum c/a ratio as a function of volume for the hcp structure are shown in Fig. 1. The calculated variation of the optimum c/a ratio with volume is shown in Fig. 2. As the volume is reduced, the c/a ratio decreases in the direction of the ideal value of 1.633. This is consistent with the fact that at small volumes the dominant contribution to the total energy is expected to be an isotropic repulsion (which favors close packing) arising from the overlap of the ion cores.

The calculated electronic densities of states (DOS) for the three structures with lattice parameters near the calculated equilibrium values are shown in Fig. 3. The zinc d bands lie approximately 8 eV below the Fermi energy E_F and are approximately 1.9 eV in width for all three structures These d bands overlap and hybridize with the lowest s-like band whose minima lie at -11.0, -11.3, and -10.8 eV relative to the Fermi energy at the Γ point for the bcc, fcc, and hcp structures, respectively. This is
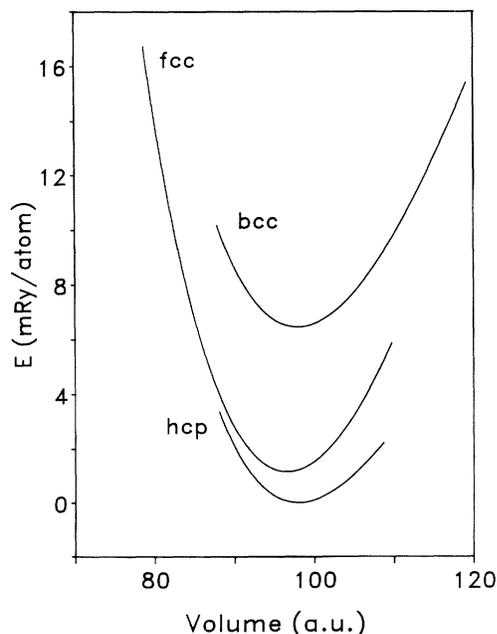

FIG. 1. Total energy (relative to the hcp minimum) as a function of atomic volume for fcc, bcc, and hcp zinc. The curves are fits (see text) to the calculated total energies and are shown over the volume ranges for which total-energy calculations were performed.
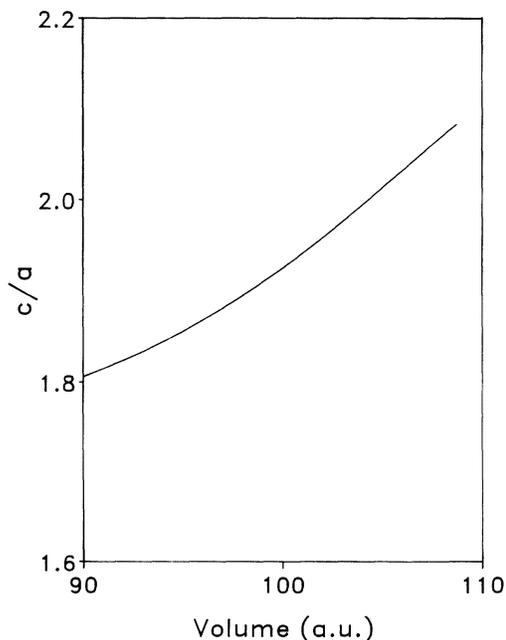

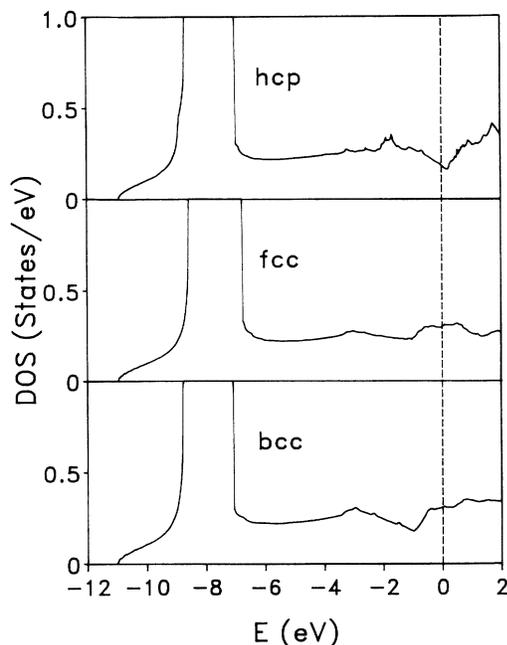FIG. 2. Variation of the c/a ratio as a function of atomic volume for hcp zinc.

FIG. 3. Electronic DOS for bcc, fcc, and hcp zinc. The DOS shown were at lattice parameters, $a=3.069$ Å for the bcc structure, $a=3.810$ Å for the fcc structure, and $a=2.619$ Å and $c=4.820$ Å for the hcp structure.

in agreement with the more recent LDA-based band-structure calculations for zinc,[3,8,9] but is in disagreement with some of the early work (see Ref. 8 for a review) which suggested that the d bands lie below the valence bands. Apart from the above and a small rounded peak near E_F, the fcc DOS is quite featureless. The bcc DOS is quite similar to the fcc except for a shift in weight from the region at -1 eV to the region around -3 eV. In particular, the DOS near E_F is very close to that of the fcc structure. The values at E_F are 0.305 and 0.308 states/eV for the fcc and bcc structures, respectively. This compares well with the value calculated for the fcc structure by Moruzzi, Janak, and Williams[3] in the muffin-tin approximation of 0.30 states/eV. The fact that the states which split in going from the fcc to the bcc structure lie entirely below E_F implies that the splitting is not effective in stabilizing the bcc structure and apparently this is why zinc does not occur in the bcc structure. On the other hand, there are large changes in the DOS near E_F in going from the fcc to the hcp structure. The DOS at E_F is reduced by 40% to 0.182 states/eV by a gaplike feature about 4 eV wide. This is in good agreement with the value of 0.178 states/eV obtained by Papaconstantopoulos,[9] who used a muffin-tin approximation. An examination of the DOS reveals that approximately 0.05 electrons are affected by this gapping and that the average eigenvalue change for these electrons is about 1.4 eV. Thus the contribution to the energy difference between the fcc and hcp structures from the change in the eigenvalue sum due to this gapping is about 5 mRy as compared to the calculated total-energy difference of 1.2 mRy. Therefore, it seems likely that this

splitting is responsible for the stabilization of the hcp phase. The deviation in the c/a ratio from the ideal value of 1.633 can also be understood in these terms. While the calculated DOS at the ideal c/a ratio shows related, though somewhat smaller, structure, in this case it is centered at -0.5 eV and thus lies almost entirely below E_F. The DOS at E_F at the ideal c/a ratio is 3.4 states/eV which is even larger than that calculated for the fcc structure. The important changes occur around the L point in the Brillouin zone. (Our band structure is quite similar to those reported in Refs. 7 and 8 and accordingly is not shown.) At the ideal c/a ratio the first and second non-d valence bands at L (the bands are doubly degenerate at this point) occur at -2.4 and -0.3 eV, whereas for a c/a ratio of 1.84 they lie at -2.1 and $+0.2$ eV. Perhaps not surprisingly in view of the above, the calculated total energy at the ideal c/a ratio is about 2 mRy/atom higher than when the c/a ratio is relaxed, i.e., close to the energy for the fcc structure.

Since the d bands in zinc are well below E_F and at least in the DOS appear to change little on going from one structure to another, it is natural to ask whether they play a significant role in the bonding or, from the opposite point of view, whether they are essentially inert. In order to answer this question, we have performed a total-energy calculation with the d states effectively removed. This was done by treating these states in an atomic approximation (i.e., as core states), and placing the d linearization parameter approximately 1.3 Ry above the Fermi energy, thereby preventing these states from appearing in the valence window. This effectively suppresses the contributions to the band structure and total energy from hybridization or overlap with the d states. This calculation gave a lattice parameter 2.6% larger and a bulk modulus 20% smaller than those produced by a parallel calculation in which the d states were treated as band states. This shows that the zinc d states do play a role in the bonding of metallic zinc and should not be treated as inert in electronic-structure calculations. This is consistent with the observation of Daniuk et al.[8] who, based on an analysis of the band structure of zinc, concluded that there is a strong d-like repulsion which significantly perturbs electronic states near E_F.

The results of LDA-based total-energy calculations typically display some degree of sensitivity to the particular choice of XC functional, with the extent of this sensitivity varying from material to material. A large sensitivity to the particular functional used may be taken as an indication that care is required in interpreting the results of total-energy calculations for the material in question. In order to assess the degree of sensitivity for zinc, parallel calculations were performed using both the Wigner[7] and Hedin-Lundqvist[10] (HL) functionals for the bcc and fcc structures. These calculations were performed using somewhat under-converged Brillouin-zone samples of 20 and 55 uniformly distributed k points in the irreducible wedge for the fcc and bcc structures, respectively. Accordingly, the results of these calculations should not be interpreted as converged LDA results, but rather should be used only in comparing the two XC functionals. The results of these calculations are summa-

TABLE II. Static structural properties of fcc and bcc zinc, calculated using the Hedin-Lundqvist (HL) and Wigner exchange-correlation functionals and using a muffin-tin APW method. Here ΔE is the energy difference between the bcc and fcc minima.

Method	a-fcc (Å)	B-fcc (GPa)	a-bcc (Å)	B-bcc (GPa)	ΔE (mRy/atom)
LAPW (Wigner)	3.87	88.9	3.07	83.2	7.1
LAPW (HL)	3.82	94.6	3.03	94.5	7.1
APW (HL)	3.83	92.3	3.04	77.3	9.2

rized in Table II where the calculated static properties for the bcc and fcc phases, as given by Murnaghan equation-of-state fits to the calculated total energies, are presented along with the results of muffin-tin APW calculations which are discussed below. The fits are shown in Fig. 4. The main difference is that the HL XC functional yields an equilibrium lattice parameter 1.3% smaller than the Wigner functional for both structures, along with a larger bulk modulus (6% and 14% for the fcc and bcc phases, respectively). It is noteworthy that the energy difference between the fcc and bcc structures is predicted to be the same to within 0.1 mRy/atom for both XC functionals.

As mentioned, in view of the recent work on the Cu-Zn alloy system, it is of considerable interest to examine the applicability of the muffin-tin approximation to zinc. Ac-
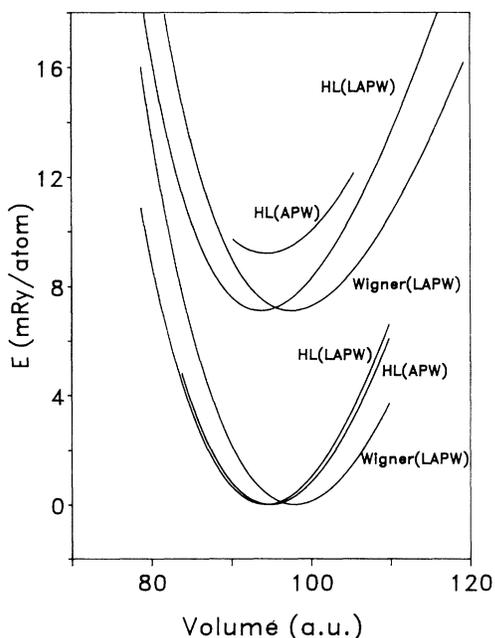

FIG. 4. Murnaghan fits to calculated total energies for fcc and bcc zinc using restricted Brillouin-zone samplings (see text). The zeros have been adjusted so that the fcc energy minimum occurs at 0. The notation LAPW refers to calculations performed using the general-potential LAPW method, APW to calculations performed using a muffin-tin-approximation APW code, and HL and Wigner to calculations performed using the Hedin-Lundqvist and Wigner exchange-correlation functionals, respectively.

cordingly, calculations parallel to those used in order to test the sensitivity to the choice of XC functional were performed using a self-consistent muffin-tin APW approach.[11] The results of these calculations are given in Table II and Fig. 4 For the fcc structure both the lattice parameter and bulk modulus are in quite good agreement with the results of the general-potential calculations, indicating that the muffin-tin approximation provides a good description of this close-packed phase. On the other hand, a somewhat worse agreement between the two calculations is obtained for the more open bcc structure. In addition the bcc-fcc energy difference is predicted to be more than 2 mRy/atom larger using the muffin-tin approximation. In view of the good agreement for the lattice parameter and bulk modulus of the fcc phase we believe that most of this error can be ascribed to the inaccuracy of the muffin-tin approximation for the bcc phase. This is consistent with the sign of the error. In most cases imposing the muffin-tin approximation may be expected to result in an increase in the total energy. This is due to the fact that the total energy contains density potential integrals. These preferentially weight the regions where the potential is lowest since the charge density tends to be larger in these regions. On the other hand, in a muffin-tin calculation the potential (and charge density) is averaged before this integration and so this preferential weighting is suppressed. To summarize, our calculations indicate that the muffin-tin approximation is quite reasonable for fcc zinc and thus in all likelihood is reasonable for the study of the close-packed Cu-Zn alloy system, but is not as reliable for treating the bcc structure.

In order to verify that the differences calculated using the parallel LAPW and muffin-tin APW calculations were in fact due to the muffin-tin approximation, tests were performed in order to verify that the convergence with respect to the Brillouin-zone samples was the same for both methods. Accordingly, parallel calculations were carried out at the equilibrium lattice parameters of 3.03 and 3.82 Å for the bcc and fcc structures, respectively. These calculations were performed using samplings of 14 and 55 uniformly distributed k points for the bcc structure and 20 and 89 k points for the fcc structure. In addition, well-converged calculations using 240 and 408 special k points were carried out for the bcc and fcc structures, respectively, using the LAPW method. For the bcc structure the LAPW calculation with 14 k points yielded a total energy 9.73 mRy higher than the calculation with a 55-k-point sampling. This is very close to the

difference of 9.64 mRy obtained using the muffin-tin APW method and thus demonstrates that the convergence with respect to Brillouin-zone sampling of the APW and LAPW calculations is essentially identical for the bcc structure. Moreover, the 240-k-point LAPW calculation yielded an energy only 0.28 mRy higher than the 55-k-point calculation, indicating that the 55-k-point sampling is quite good for bcc zinc and that the results obtained using this sampling are close to convergence. For the fcc structure, the LAPW calculation with an 89-k-point sampling yielded an energy 2.67 mRy above the result using 20 k points and 0.27 mRy above the 408 special k-point set. This indicates that the 20-k-point sampling was somewhat underconverged. The muffin-tin APW calculations yielded 2.80 mRy for the difference between the 89- and 20-k-point sets, thereby demonstrating that the convergence of the two methods with respect to Brillouin-zone sampling was essentially identical for the fcc structure as well. Thus it may be concluded that the differences being studied using the sets of parallel calculations were in fact due to the muffin-tin approximation, and are not an artifact of the Brillouin-zone samplings. We note that the muffin-tin APW and the LAPW band structures are quite similar. It is not, therefore, surprising that the convergence of the two methods with respect to the Brillouin-zone sampling is also very similar.

IV. CONCLUSIONS

Static and electronic properties of bcc, fcc, and hcp zinc have been calculated using the general-potential LAPW method. For the hcp phase good agreement with experimental data is obtained for the static properties. Moreover, the correct ordering of phases is obtained, and can be understood in terms of the calculated DOS. The stabilization of the distorted hcp structure is attributed to a dip in the DOS at E_F in that structure which arises from electronic states around the L point. Parallel calculations using a muffin-tin APW method indicate that the muffin-tin approximation for zinc is quite good for close-packed structures. While it is found to be less reliable for the more open bcc structure, it does yield the correct ordering of the fcc and bcc structures.

ACKNOWLEDGMENTS

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