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Equilibrium properties of hcp titanium and zirconium

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The electronic and structural properties of hexagonal-close-packed titanium and zirconium are determined from self-consistent linearized augmented-plane-wave (LAPW) calculations within the framework of the local-density-functional approximation (LDA). The equilibrium lattice parameters, bulk moduli, Poisson's ratios, and cohesive energies are obtained from the total energies calculated as functions of the a and c lattice parameters. As found in other LDA calculations, the cohesive energies are overestimated compared to experiment, but otherwise generally good agreement with experiment is obtained. The uncertainty in the results due to the particular choice of the LDA exchange-correlation potential is also examined by performing parallel calculations using the Kohn-Sham-Gaspar $X\alpha$ ($\alpha=\frac{2}{3}$) exchange-only potential. We find that these calculations yield equilibrium volumes which differ by 6–8 % (with the $X\alpha$ results in better agreement with experiment) with proportional differences in other structural properties, which we take to be an indication of the intrinsic reliability of the LDA.

I. INTRODUCTION

In recent years the local-density-functional approximation (LDA) has, by its numerous successful applications, proved to be a powerful starting point for the calculation of structural and electronic properties of solids and surfaces. There have been relatively few LDA-based calculations of the ground-state properties of elements at the beginnings of the transition-metal series, however, perhaps because of the fact that these elements (Sc, Ti, Y, Zr, La, and Hf) crystallize in the hcp structure. Here, we report structural and electronic properties of hcp titanium and zirconium calculated within the LDA using a highly accurate self-consistent general-potential linearized augmented-plane-wave (LAPW) method. Most of the earlier calculations have focused on the band structures and densities of states of hcp titanium[1–7] and zirconium.[6–12] In order to assess the reliability of the LDA for these materials we carried out parallel calculations of ground-state properties of Ti and Zr using two different exchange-correlation potentials, namely the widely used Hedin-Lundqvist form (HL) (Ref. 13) and the exchange-only $X\alpha$ ($\alpha=\frac{2}{3}$) form (Ref. 14). We find that these different local approximations yield equilibrium volumes which differ from each other by about 6–8 % with corresponding differences in other structural properties. We take these differences to be an indication of the intrinsic reliability of the LDA in these metals.

II. METHOD OF CALCULATION

The LAPW method has been discussed in detail elsewhere,[15,16] its efficiency and the accuracy of the method being well established.[17,18] Here, we will only present a brief summary of the details of the calculation.

In the LAPW method space is partitioned into two regions: (1) nonoverlapping muffin-tin (MT) spheres centered on the atom sites, and (2) the remaining interstitial region. The potential and the charge density are shape unrestricted in both regions. The band states are treated in a scalar-relativistic[19] approximation, while the core states are treated fully relativistically in an atomiclike approximation. The total energy is evaluated within the LDA using a method developed by Weinert *et al.*,[20] which is easy to implement in the LAPW method and is very stable numerically.

The MT radius is chosen in order to have nearly touching spheres at the smallest lattice parameter; the MT radii used in the present calculations were 2.59 a.u. for titanium and 2.84 a.u. for zirconium. A basis set of about 110 LAPW's was used for both titanium and zirconium, corresponding to $R_{\mathrm{MT}}K_{\max}=8.0$. Inside the MT spheres, the LAPW basis functions were expanded up to $l=8$, as were the potentials and charge densities.

The Brillouin-zone summations were done using 40 special k points,[21] which results in the total energy converging to better than 0.5 mRy, for both titanium and zirconium. An artificial Fermi-Dirac distribution of width $kT=2$ mRy was used in performing Brillouin-zone summations. Self-consistency was considered achieved when the total energy was stable to within 0.01 mRy.

The densities of states (DOS's) were calculated using the tetrahedral method with 133 uniformly distributed k points in the irreducible Brillouin zone (corresponding to 1728 in the full zone), which results in 432 tetrahedra in the wedge.

III. RESULTS AND DISCUSSION

A. Equilibrium properties

In a cubic system the equilibrium lattice constant and bulk modulus can easily be obtained by calculating the total energy at a few values around the equilibrium lattice parameter, the lattice parameter and the bulk modulus being determined by a fit to the Murnaghan equation of state,[22]

$$E(V)=\frac{B_0 V}{B'_0}\left[\frac{(V_0/V)^{B'_0}}{B'_0-1}+1\right]+\text{const} , \qquad (1)$$

where B_0 and B'_0 are the bulk modulus and its pressure derivative at the equilibrium volume V_0. However, for hcp titanium and zirconium, things are not so straightforward; one must optimize both lattice parameters a and c. The above approach is thus not directly applicable to hcp systems. In order to obtain a physically meaningful (V_0,B_0,B'_0), one must find $E(V)$, the minimum total energy at fixed volume. The approach used was to first calculate the total energy as a function of the c/a ratio at a fixed volume V, and then fit $E(c/a)$ to a quadratic or a cubic form. The form used is given by

$$E(c/a)=\alpha(c/a)^3+\beta(c/a)^2+\gamma(c/a)+\delta , \qquad (2)$$

where α, β, γ, and δ are fitting parameters. For each volume V, total energies at a minimum of four distinct c/a ratios are required by Eq. (2). From the fit of $E(V)$, the minimum energy at volume V was obtained. The resulting $E(V)$ near the equilibrium volume was then used to extract (V_0,B_0,B'_0) from a fit to (1). A similar procedure was used in Ref. 23. In order to evaluate the lattice parameters, one must find the c/a ratio at the calculated equilibrium volume V_0. This was done using the total energy as a function of the c/a ratio at the equilibrium volume V_0 which was obtained as above, the c/a ratio corresponding to the minimum energy in (2) being the equilibrium c/a ratio. This calculation at V_0 provided additional data with which to check the accuracy of the Murnaghan fit. The fits turned out to be very stable for (V_0,B_0,B'_0). The rms fitting errors for both (1) and (2) were all of the order of 10^{-5} Ry. Tables I and II present $E(c/a)$ versus c/a at the calculated equilibrium volume V_0 for titanium and zirconium, respectively, using two different exchange-correlation potentials, the Hedin-Lundqvist and $X\alpha$ forms. We also tabulate the minimum energies $E(V)$ at fixed volumes V in Tables III and IV, which are plotted in Figs. 1 and 2 for

TABLE I. $E(c/a)$+const vs c/a at the calculated equilibrium volume for titanium. For the HL form, $V_0=109.21$ a.u., const=1703 Ry, and $E(V_0)=-1703.97798$ Ry. For the $X\alpha$ form, $V_0=116.65$ a.u., const=1700 Ry, and $E(V_0)=-1700.41153$ Ry.

HL		$X\alpha$	
c/a	$E(c/a)$	c/a	$E(c/a)$
1.540	−0.977 71	1.560	−0.411 36
1.570	−0.977 95	1.570	−0.411 49
1.585	−0.977 98	1.585	−0.411 53
1.600	−0.977 96	1.600	−0.411 52
1.634	−0.977 74	1.615	−0.411 48
		1.634	−0.411 43

TABLE II. $E(c/a)$+const vs c/a at the calculated equilibrium volume for zirconium. For the HL form, $V_0=147.85$ a.u., const=7190 Ry, and $E(V_0)=-7190.42068$ Ry. For the $X\alpha$ form, $V_0=158.92$ a.u., const=7183 Ry, and $E(V_0)=-7183.26556$ Ry.

HL		$X\alpha$	
c/a	$E(c/a)$	c/a	$E(c/a)$
1.580	−0.420 44	1.570	−0.265 38
1.600	−0.420 59	1.585	−0.265 49
1.620	−0.420 67	1.600	−0.265 55
1.630	−0.420 68	1.615	−0.265 55
1.640	−0.420 65	1.634	−0.265 46

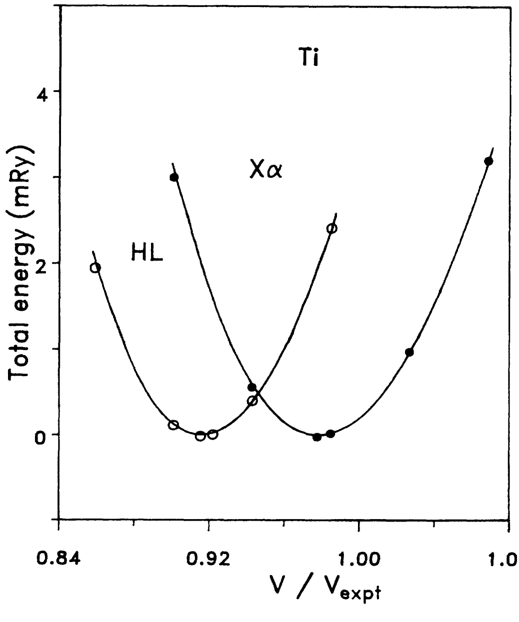

FIG. 1. Calculated $E(V)-E(V_0)$ vs V of titanium with the HL and $X\alpha$ forms; the solid line is a Murnaghan equation-of-state fit. $E(V_0)=-1703.97798$ Ry for the HL forms and $E(V_0)=-1700.41153$ Ry for the $X\alpha$ form.

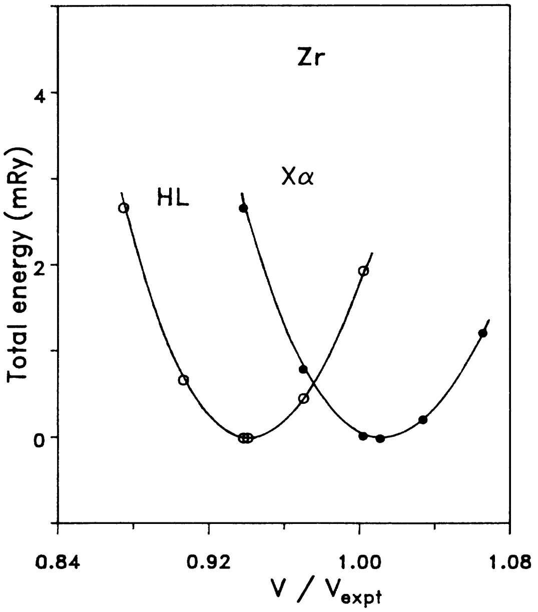

FIG. 2. Calculated $E(V)-E(V_0)$ vs V of zirconium with the HL and $X\alpha$ forms; the solid line is a Murnaghan equation-of-state fit. $E(V_0)=-7190.42068$ Ry for the HL form and $E(V_0)=-7183.26556$ Ry for the $X\alpha$ form.

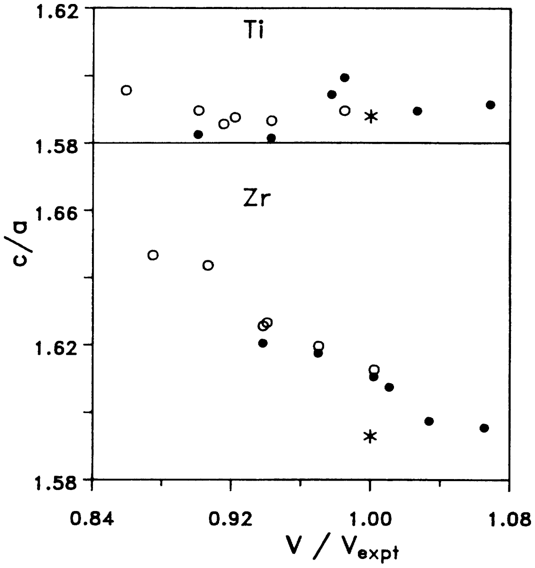

FIG. 3. c/a ratio corresponding to the minimum energy at certain volumes vs volume for titanium and zirconium. Open circles represent the HL results, while solid circles represent the $X\alpha$ results, and stars represent the experimental c/a ratio at experimental volumes.

titanium and zirconium, respectively, along with the Murnaghan equation-of-state fits.

We find that the structural parameters of both Ti and Zr are rather sensitive to the particular form of the exchange-correlation potential used. It is found that the HL exchange-correlation potential significantly underestimates the equilibrium volumes of both titanium and zirconium, while the simpler $X\alpha$ form yields very good ground-state properties for these two elements. We will return to this issue later.

The calculated $E(c/a)$ (Tables I and II) at the equilibrium volume clearly reveals that these curves are very flat, which makes it difficult to predict the exact c/a ratio. We estimate the error in the predicted c/a ratios to be about 1–2 %. Both the experimental and our calculated values of c/a are less than the ideal value of $\sqrt{8/3}$ (1.6333) for titanium and zirconium. In Tables III and IV, we also list minimum energies $E(V)$ and the corresponding c/a ratios at various volumes. The c/a ratio versus volume is plotted in Fig. 3. For Ti, the c/a ratio is weakly volume dependent. The considerable scatter in the calculated c/a ratios around an equilibrium value of 1.588 for Ti reflects the very small energy changes associated with this distortion. By contrast, the c/a ratio for Zr is considerably more volume dependent and increases with decreasing volumes. Similar behavior was found for Ru in Ref. 23.

Having calculated the c/a ratios, it is straightforward to find the lattice parameters a and c from the equilibrium volume obtained from the Murnaghan fit (1) as well as other equilibrium properties such as the Poisson ratio and the cohesive energy. These are reported in Tables V and VI. The experimental lattice parameters were taken from Ref. 24. In order to obtain the cohesive energies, the total energies of the isolated atoms were calculated using the same exchange-correlation potential as in the

TABLE III. Minimum $E(V)$+const (Ry) as determined from Eq. (1) vs volume V (a.u.) and the corresponding c/a ratio for titanium. For the HL form, const=1703 Ry. For the $X\alpha$ form, const=1700 Ry.

	HL			$X\alpha$	
V	E_0	c/a	V	E_0	c/a
102.50	−0.976 02	1.596	107.50	−0.408 51	1.583
107.50	−0.977 85	1.590	112.50	−0.410 95	1.582
109.21	−0.977 98	1.586	116.65	−0.411 53	1.595
110.00	−0.977 96	1.588	117.50	−0.411 48	1.600
112.50	−0.977 56	1.587	122.50	−0.410 53	1.590
117.50	−0.975 55	1.590	127.50	−0.408 30	1.592

TABLE IV. Minimum $E(V)$+const (Ry) as determined from Eq. (1) vs volume V (a.u.) and the corresponding c/a ratio for zirconium. For the HL form, const=7190 Ry. For the $X\alpha$ form, const=7183 Ry.

	HL			$X\alpha$	
V	E_0	c/a	V	E_0	c/a
137.50	−0.418 01	1.647	147.50	−0.262 89	1.621
142.50	−0.420 01	1.644	152.50	−0.264 76	1.618
147.50	−0.420 68	1.626	157.50	−0.265 53	1.611
147.85	−0.420 68	1.627	158.92	−0.265 56	1.608
152.50	−0.420 22	1.620	162.50	−0.265 34	1.598
157.50	−0.418 74	1.613	167.50	−0.264 34	1.596

bulk calculation but including spin polarization. The difference between E_{atom} and $E(V_0)$ yields the cohesive energy, where $E(V_0)$ is the total energy at equilibrium volume V_0 as determined from (2). The spin-polarized ground-state configurations are Ti($3d^34s^1$) and Zr($4d^35s^1$).[25] We calculated the cohesive energies using both the HL and $X\alpha$ exchange-correlation potentials. The calculated atomic energies E_{atom} are −1703.5061 Ry for titanium and −7189.8768 Ry for zirconium using the von Barth–Hedin exchange-correlation potential, which reduces to the HL form in the paramagnetic limit. $E(V_0)$ can be found in Tables I and II. The cohesive energies thus obtained are about 32% larger than the experimental value[26] for titanium and 18% larger for zirconium. When the $X\alpha$ exchange-correlation potential was used, we find that $E_{\text{atom}} = -1700.0290$ Ry for titanium and −7182.8214 Ry for zirconium. Thus, the cohesive energies are in better agreement, being about 7% larger than the experimental value for titanium and 3% less than the experimental value for zirconium. It is well known that the local-density approximation tends to overestimate cohesive energies, the error coming from the atomic calculation. This is the case for the HL result, errors of similar size for titanium were also observed by Moruzzi *et al.*,[25] who calculated the electronic properties using a close-packed fcc lattice, which is very similar to the hcp structure. For zirconium, the calculated value in Ref. 25 was 6.75 eV, in somewhat better agreement with experiment than the present results. An $X\alpha$ calculation by Hattox *et al.*[27] for vanadium also underestimated the cohesive energy; their calculated value was 0.33 Ry. Using the HL form, Moruzzi *et al.*[25] overestimated the cohesive energy of vanadium, obtaining a value of 0.450 Ry. The cohesive-energy difference between these two calculations is about 0.12 Ry. We find that the cohesive-energy differences between the HL and $X\alpha$ results for Ti and Zr are of the same magnitude.

TABLE V. Ground-state properties of titanium in the hcp structure and a comparison with the experimental data. The experimental data are from Refs. 24, 27, and 28.

Property	Expt.	HL	$X\alpha$
V_0 (a.u.)	119.210	109.21	116.65
c/a	1.588	1.586	1.595
a (Å)	2.9508	2.866	2.925
c (Å)	4.6855	4.547	4.666
Bulk modulus (Mbar)	1.05	1.27	1.08
B'		3.59	3.82
Poisson's ratio	0.26	0.32	0.31
Cohesive energy (eV)	4.85	6.42	5.20

Poisson's ratio σ is the negative ratio of the transverse strain to the corresponding axial strain in a body subject to uniaxial stress. For a fixed value of c, the total energies at three (or more) different values of a were calculated and fit to a parabola. The value of a ($a_{\min}$) which corresponds to the minimum total energy was then used to evaluate σ directly from a linear fit of $a_{\min}$ versus c:

$$\sigma = -(\Delta a/\Delta c)(c/a) , \tag{3}$$

where $\Delta a/\Delta c$ is the slope of the fit and c/a is the equilibrium c/a ratio. Uniform meshes of nine values of c and a around the experimental c and a values were used except for the $X\alpha$ titanium calculation, for which a

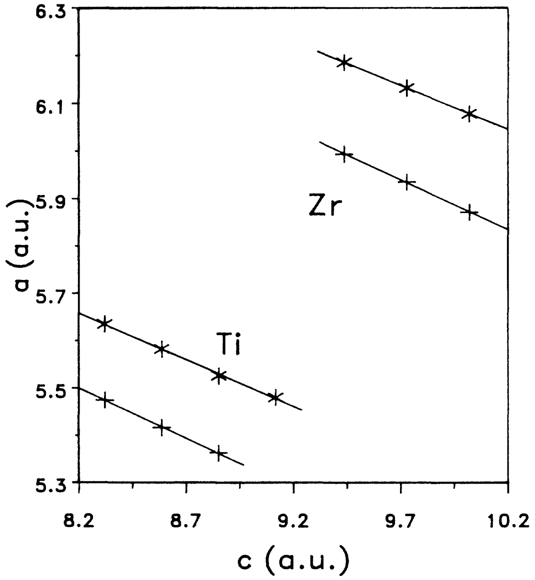

FIG. 4. Linear relationship between c and $a_{\min}$ gives the Poisson ratio (see text). Pluses represent the HL form, stars the $X\alpha$.

twelve-point mesh was used. The results are shown in Fig. 4 and in Tables V and VI along with the single-crystal Poisson ratio obtained from the elastic constants of Ref. 28. It may be noted that the HL exchange-correlation potential tends give a somewhat larger Possion ratio for both elements.

The sensitivity of the calculated results to the particular form of the exchange-correlation potential deserves some discussion. We find that for both titanium and zirconium the calculated V_0 and B_0 are in very good agreement with experiment when the $X\alpha$ $(\alpha=\frac{2}{3})$ exchange-correlation potential was used, the deviation for the equilibrium volume (V_0) being -2.2% for titanium and $+1.2\%$ for zirconium. However, when the Hedin-Lundqvist form was used, larger discrepancies in the equilibrium volumes are found, the deviations being -8% and -6% for titanium and zirconium, respectively. In this case the bulk moduli B_0 are about 20% larger than the experimental values, as might be expected based on the smaller calculated equilibrium volumes. Sensitivity of this magnitude has previously been reported for semiconductors.[29] The c/a ratios are all within 1% of the experimental values, except for zirconium with the HL form, where the discrepancy is about 2%. As we have discussed before, the $X\alpha$ form better predicts cohesive energies than the HL form for both titanium and zirconium, but in both cases the cohesive energies are overestimated except for Zr with the $X\alpha$ form, which underestimates the cohesive energy by about 3%.

B. Electronic properties

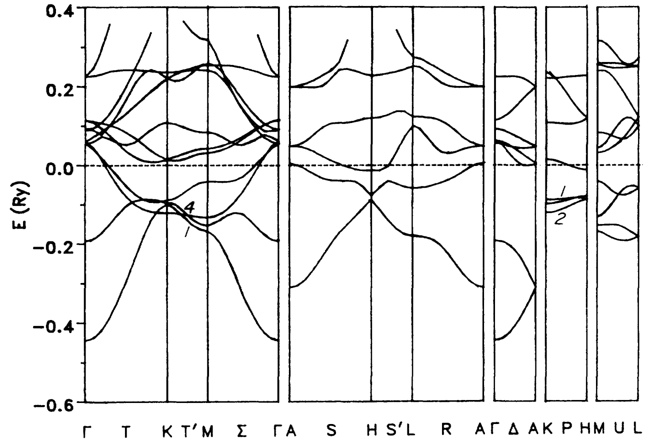

FIG. 5. Band structure for titanium using the HL exchange correlation.

The band structure and the density of states of titanium have been previously calculated by a number of authors using a variety of methods.[1-7] The band structure reported here was calculated at the experimental lattice parameters[24] using both the HL and $X\alpha$ exchange-correlation potentials, and the band structures thus obtained are almost identical. Our band structure (see Fig. 5) is very similar to that calculated by Jepsen,[4] using a non-self-consistent linear-muffin-tin-orbital method. In particular the crossings at the Fermi level are practically identical. Jepsen rather thoroughly reviewed and compared his results with earlier calculations, and he found that his Fermi surface was in agreement with the de Haas–van Alphen experiment of Kamm and Anderson.[30] Noticeable differences are found along the T' and P directions. One of the energy levels was degenerate in his band structure, but not in ours. This level is labeled by 1 and 4 in the T' band at the bottom and by 1 and 2 in the band at the bottom. It may have been just accidentally degenerate in his calculation, since in their Zr calculation[10] these bands were split. These bands were split in the self-consistent Ti calculation of Feibelman *et al.*,[5] which was obtained using a linear combination of Gaussian orbitals approach and yielded very similar band structures to those obtained here. Our calculated density of states ($X\alpha$) (Fig. 6) is very similar to Jepsen's.[4] The density of states at the Fermi level is 12.3 states/atom Ry while his number was 12.4

TABLE VI. Ground-state properties of zirconium in the hcp structure and a comparison with the experimental data. The experimental data are from Refs. 25, 27, and 28.

Property	Expt.	HL	$X\alpha$
V_0 (a.u.)	157.05	147.84	158.92
c/a	1.593	1.627	1.608
a (Å)	3.232	3.145	3.234
c (Å)	5.147	5.116	5.200
Bulk modulus (Mbar)	0.833	0.986	0.846
B'		3.00	4.02
Poisson's ratio	0.29	0.34	0.29
Cohesive energy (eV)	6.25	7.40	6.04

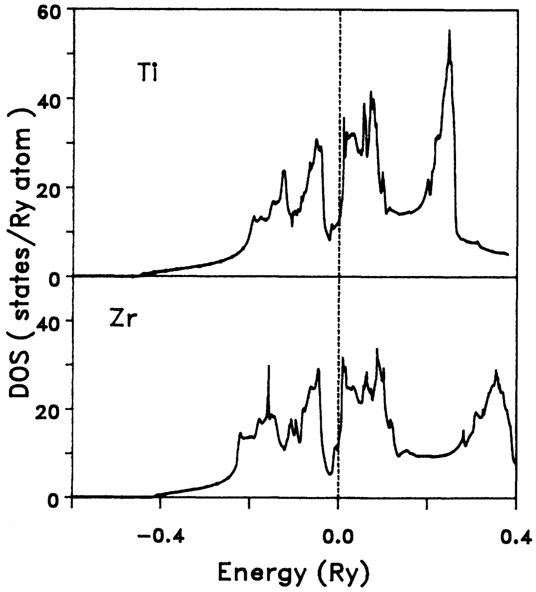

FIG. 6. Density of states for titanium and zirconium. The Fermi energy is indicated by the dashed line.

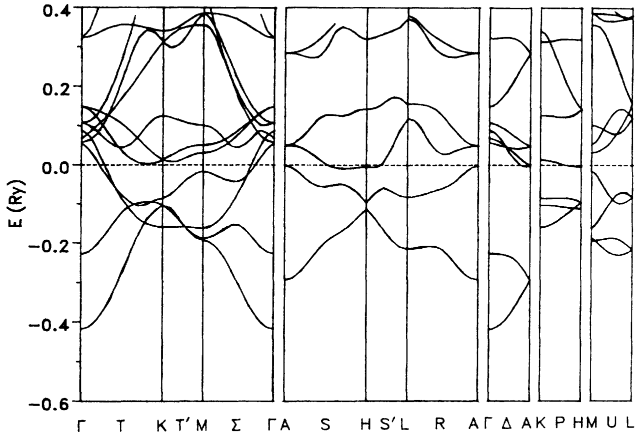

FIG. 7. Band structure for zirconium using the HL form.

states/atom Ry. The DOS is primarily d-like, the small peak just below the Fermi energy is due mostly to p-electron contributions.

The band structure and density of states of zirconium are shown in Figs. 6 and 7. As in the case of titanium, the band structures calculated using the HL and $X\alpha$ exchange-correlation potentials are very similar. A few previous calculations of electronic structure of zirconium have been reported.[6–12] We find that as for titanium our results for both the band structure and the density of states are very similar to those obtained by Jepsen *et al.*[10] The density of states ($X\alpha$) is shown in Fig. 6. We find the density of states at the Fermi level is 11.3 states/atom Ry, while the number in Ref. 10 was 13.1 states/atom Ry.

IV. CONCLUSIONS

In this paper, results of local-density-functional calculations of the energy band structures, equilibrium properties, cohesive energies, and densities of states for hexagonal-closed-packed titanium and zirconium are reported.

We find that the calculated equilibrium volumes are underestimated using the HL exchange-correlation potential, with deviations of about 8% for titanium and 6% for zirconium. The calculated c/a ratios are very close to the experimental value for titanium and about 2% larger for zirconium. The lattice parameters a and c are all about 3% smaller than experiment for both titanium and zirconium except for the c parameter of zirconium, where the discrepancy is 0.6%. The bulk moduli are found to be about 20% larger than the experimental values for both elements. The cohesive energies are overestimated as commonly found in the LDA calculations. The discrepancies between the experimental and the calculated values are 32% and 18% for titanium and zirconium, respectively. The Poisson ratios are about 20% larger than the measured values. We also find that there is considerable sensitivity to the exchange-correlation potential by comparing with parallel calculations using the exchange-only $X\alpha$ form. We find that the $X\alpha$ equilibrium volumes, lattice parameters, c/a ratios, and bulk moduli are in very good agreement with experiment for both titanium and zirconium; in this case the cohesive energies also being brought into better agreement with experiment.

The changes in the equilibrium volume due to the use of different exchange-correlation potentials ($X\alpha$ versus HL) are found to be about 6%. We take this to be an indication of the intrinsic accuracy of the LDA for these metals.

ACKNOWLEDGMENTS

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