Total-energy calculations of solid H, Li, Na, K, Rb, and Cs

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Augmented-plane-wave calculations within the local-density approximation of the total energy of the solid alkali metals H, Li, Na, K, Rb, and Cs predict that except in Rb at $T=0$ K the fcc structure is more stable than the bcc, which agrees with experiments for Li and Na.

I. INTRODUCTION

A calculation of the total energy (TE) of a solid lets one find the equilibrium lattice constant and other ground-state properties of the solid, such as the bulk modulus and other elastic constants. In addition, it permits determination of the stable structure of the solid at least at $T=0$. Here, using total-energy calculations, we study the structural stability of the elements of the first column of the Periodic Table (H, Li, Na, K, Rb, and Cs) using the augmented-plane-wave (APW) method based on the local-density approximation (LDA). All the alkali metals crystallize in the bcc structure at room temperature. At $T=0$ K, however, the LDA predicts that the fcc structure is more stable than the bcc structure. This agrees with recent low-temperature experiments of Smith *et al.*[1] for metallic Li and Na.

II. METHOD OF CALCULATION AND APPROXIMATIONS

The total energy was calculated from the expression of Janak[2] which is valid within the muffin-tin (MT) approximation and needs as input the crystal potential, the charge density, and the eigenvalue sum. These were calculated self-consistently with the symmetrized APW method[3] using the muffin-tin approximation, which should be adequate for cubic materials. The crystal potential was calculated on a doubling linear mesh consisting of 750 points within the MT radius. We have found that for the alkali metals with large lattice constants, an integration with a smaller number of points leads to errors in the total energy of the order of 0.2 mRy. This small error would be sufficient to obscure the comparison of total energies between the fcc and bcc structures. The logarithmic derivatives were calculated on a mesh of at least 1000 points per Ry to ensure good eigenvalue convergence. To determine the charge density we treated the highest occupied s and p orbitals as band levels, but we found that our results were basically unchanged if we used only the s orbital as a band. All other states were treated as core levels because they form essentially flat bands. The core levels were obtained by performing a fully relativistic atomiclike calculation in each iteration. The band states were calculated self-consistently in the semirelativistic approximation[4] (the spin-orbit coupling is neglected), initially on an equally spaced mesh of 20 k points in the irreducible zone for the fcc structure, and 14 k points for the bcc structure. We found that for the bcc structure it was necessary to use a 55-k-point sampling to achieve acceptable convergence, while for the fcc structure using the corresponding 89-k-point mesh introduces negligible change on the total-energy value. Therefore, we performed the APW total-energy calculations with 20 k points for the fcc and with 55 k points for the bcc structure. A convergence in the energy levels of 0.5 mRy assured a convergence in TE of less than 0.05 mRy. In all our calculations the exchange potential was treated in the exchange and correlation formalism of Hedin and Lundqvist,[5] which is accurate for ground-state properties. To find the equilibrium lattice constant we calculated the TE at various lattice constants, and determined the minimum by fitting the results with a parabolic or cubic least-squares fit as proposed by Birch.[6] We also calculated the cohesive energy by subtracting the fitted equilibrium energy from the energy calculated by a full relativistic self-consistent atomic program.[7] We then calculated the fcc and bcc band structures using the equilibrium lattice parameters on a mesh of 89 k points for the fcc structure and 55 k points for the bcc structure in the irreducible $\frac{1}{48}$th of the Brillouin zone (BZ). The density of states was then calculated by the tetrahedron method.[8]

III. RESULTS AND DISCUSSION

The equilibrium atomic volume V that we calculated is almost the same in both the fcc and bcc structures. In

Figs. 1(a)–1(d) we show the TE as a function of the atomic volume for Li, Na, K, and Rb, respectively. The TE, the equilibrium lattice constant a_0, and the bulk modulus K_0 estimated by the fit are shown in Table I. Table II shows energy-band information at the equilibrium lattice constant especially for high-symmetry points of the fcc and bcc structures. In Fig. 2 we show the energy bands and densities of states for the fcc phase of Li and Na, in Fig. 3 the same quantities for K and Rb, and in Fig. 4 the fcc band structure of Cs. The bcc bands are not presented here since they are well documented in the litera-

ture.[9,10]

From Fig. 1 and Table I we see that at $T=0$ the fcc structure is more stable than the bcc structure for all the alkali metals except Rb. The difference in the equilibrium value of the TE is large for H and Li, 6 and 2.4 mRy, respectively. This difference becomes much smaller for Na and Cs, and is negative for Rb, favoring the bcc structure. However, as we discuss in Sec. V, these differences are not precisely calculated by the APW method. So in the following we consider as a reliable result the preference towards the fcc structure for most of these metals.
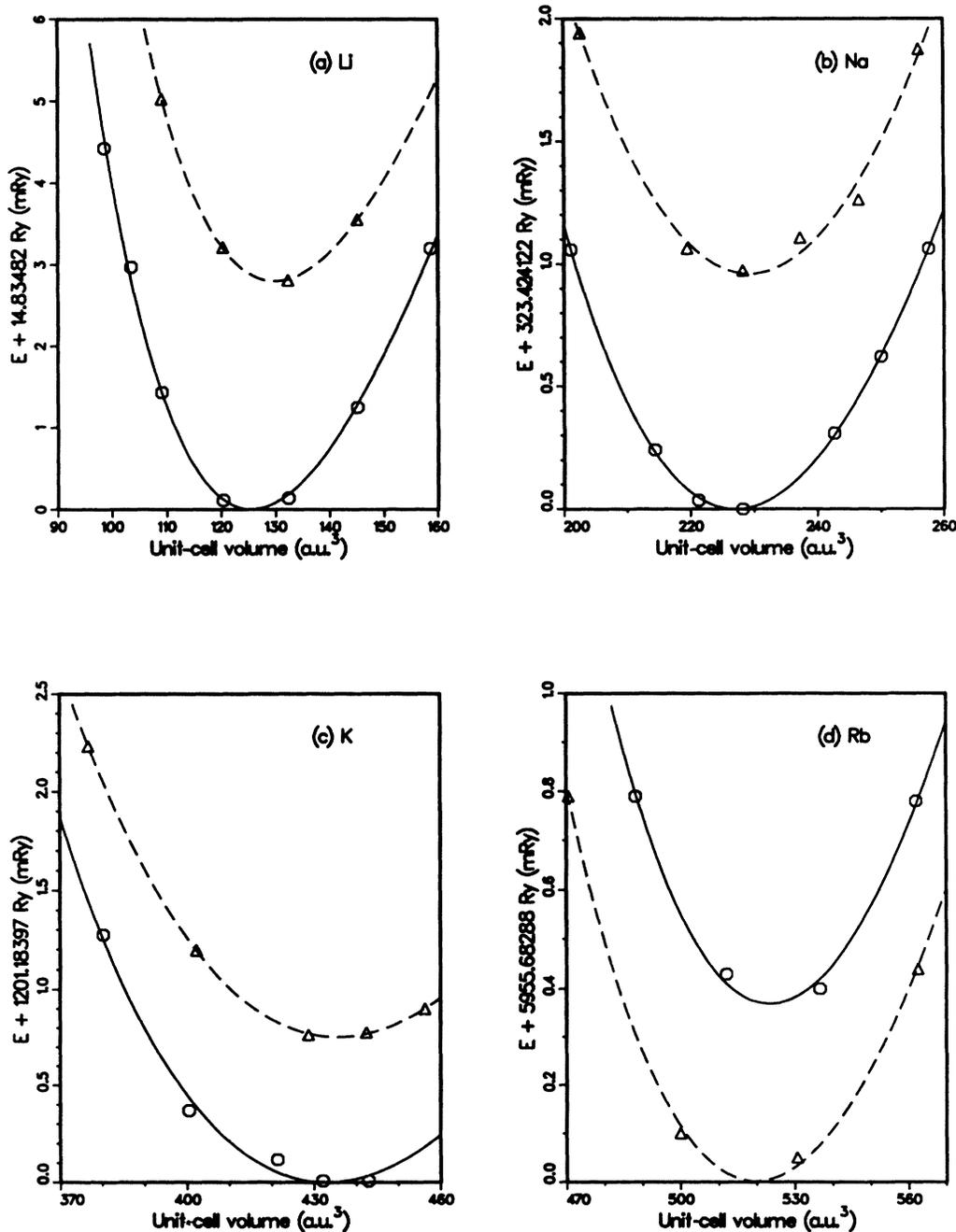
FIG. 1. Total energy (in Ry) of (a) Li, (b) Na, (c) K, and (d) Rb vs atomic volume (in a.u.) for the fcc (circles) and bcc (triangles) structures.

TABLE I. Equilibrium lattice constant (a_0) in bohr, total energy (E_t) in Ry, bulk modulus (K_0) in Mbar, and cohesive energy (E_c) in Ry of metallic H, Li, Na, K, Rb, and Cs in fcc and bcc structures. ΔE is the difference $E_t(\text{bcc}) - E_t(\text{fcc})$ in Ry.

| | fcc | | | | bcc | | | |
	a_0	E_t (fit)	K_0	E_c	a_0	E_t (fit)	K_0	E_c	ΔE
H	4.33	-1.7025	1.150	0.174	3.46	-1.0669	1.07	0.169	0.0056
Li	7.95	$-14.834\,82$	0.156	0.157	6.38	$-14.832\,02$	0.148	0.149	0.0028
Na	9.68	$-323.424\,12$	0.090	0.107	7.69	$-323.423\,16$	0.087	0.106	0.000\,96
K	12.01	$-1201.183\,97$	0.046	0.085	9.54	$-1201.183\,22$	0.047	0.0893	0.000\,75
Rb	12.82	$-5955.682\,51$	0.049	0.0713	10.13	$-5955.682\,88$	0.042	0.0716	$-0.000\,37$
Cs	13.88	$-15\,567.988\,16$	0.033	0.0467	10.76	$-15\,567.987\,94$	0.020	0.0465	0.0022

We think that this behavior is to be expected because there are two compensating factors, local chemistry and solid cohesion. The alkali metals have one external s electron, so they consist of spherical atoms. The smaller the atom, the stronger the attraction between the outer electron and the neighboring nucleus. Hence, an increased number of neighbors around each atom results in a more stable local environment and the lowest energy. Since the fcc structure is more close packed than the bcc structure, the smaller the atom, the more the fcc structure is favored, due to local attractions. On the other hand, solid cohesion demands that the outer electron be free and delocalized. This happens for large atoms in which the local chemistry becomes insignificant. For spherically symmetric atoms, the denser the material, the larger the cohesion. Hence, the larger the alkali atom, the more favored the fcc structure. The local attraction is very strong for small atoms and decreases as Z increases. The solid cohesion is small for small atoms, which prefer to form molecules rather than solids, and increases slightly as Z increases, forming the electron sea more easily. It seems that these two factors, superposed, form a minimum for Na.

From Figs. 2, 3, and 4 and Table II we see that the larger the atom, the narrower the conduction band and the E_f-Γ_1 separation.

TABLE II. Energies (in Ry), with respect to the muffin-tin zero, of high-symmetry and directionally equivalent k points of H, Li, Na, K, Rb, and Cs in fcc and bcc structures, along with valence-band widths, at the equilibrium lattice constant.

fcc	H	Li	Na	K	Rb	Cs
Γ_1	$-0.493\,66$	0.056\,55	$-0.014\,24$	0.007\,36	0.003\,14	0.003\,68
L_1	0.788\,74	0.565\,37	0.317\,07	0.205\,11	0.174\,11	0.135\,60
L_{2p}	1.376\,87	0.315\,50	0.281\,12	0.229\,20	0.229\,09	0.215\,82
X_1	1.253\,13	0.688\,60	0.413\,04	0.238\,86	0.201\,56	0.150\,61
X_{4p}	1.863\,47	0.440\,54	0.381\,19	0.302\,67	0.298\,01	0.276\,96
W_1	1.431\,70	1.020\,04	0.602\,59	0.421\,70	0.371\,72	0.304\,49
W_{2p}	2.466\,03	0.654\,13	0.470\,23	0.280\,19	0.246\,79	0.192\,72
W_3	2.388\,06	0.593\,48	0.473\,84	0.320\,26	0.295\,43	0.243\,34
E_f	0.708\,00	0.316\,50	0.245\,00	0.185\,50	0.170\,00	0.143\,50
$E_f - \Gamma_1$	1.201\,66	0.259\,95	0.259\,24	0.178\,14	0.166\,86	0.139\,82
$L_{2p} - \Gamma_1$		0.258\,95	0.295\,36			
$L_1 - \Gamma_1$	1.282\,40			0.197\,75	0.170\,97	0.131\,92
$W_3 - \Gamma_1$	2.881\,72	0.536\,93				
$W_{2p} - \Gamma_1$			0.484\,47	0.272\,83	0.243\,65	0.189\,04

bcc	H	Li	Na	K	Rb	Cs
Γ_1	$-0.481\,44$	0.055\,09	$-0.003\,44$	0.010\,59	0.011\,68	0.023\,28
N_1	0.868\,58	0.573\,18	0.360\,09	0.215\,85	0.186\,00	0.156\,97
N_{1p}		0.333\,65	0.321\,34	0.247\,58	0.244\,71	0.250\,91
P_4		0.572\,10	0.476\,15	0.300\,35	0.274\,64	0.242\,75
H_{12}		0.907\,37	0.610\,95	0.300\,34	0.254\,12	0.194\,14
H_{15}		0.734\,50	0.658\,70	0.476\,49	0.449\,72	
E_F	0.810\,00	0.320\,80	0.266\,00	0.190\,00	0.176\,00	0.168\,40
$E_f - \Gamma_1$	1.291\,44	0.265\,71	0.269\,44	0.179\,41	0.164\,32	0.145\,12
$N_{1p} - \Gamma_1$		0.278\,56	0.344\,78			
$N_1 - \Gamma_1$	1.350\,02			0.205\,26	0.174\,32	0.133\,69
$H_{15} - \Gamma_1$		0.679\,41				
$H_{12} - \Gamma_1$			0.614\,39	0.289\,75	0.438\,04	0.170\,86

IV. COMPARISON WITH EXPERIMENTS
AND OTHER CALCULATIONS

There are a few experiments on the stable structure of Li as well as similar experiments on Na.[11] Overhauser[12] first concluded from the data of McCarthy *et al.*[13] that at $T=4.2$ K the stable structure of Li is closed packed in the $9R$ sequence $ABCBCACAB$. This was also verified by Smith *et al.*[11] who found that the transition temperature from $9R$ to bcc increases with pressure, or

equivalently, the transition pressure from bcc to $9R$ increases with temperature. Although the transition with pressure from bcc to a more close-packed structure is expected, the preference of $9R$ instead of, say, fcc, is not obvious. Similar conclusions from quantitatively different results have been deduced by other workers.[14] Moreover, Smith *et al.*[1] observe that between $T=140$ and 175 K at a pressure of 6.5 kbar the $9R$ structure disappears, whereas the fcc phase partially appears ($\sim 20\%$). Smith *et al.* also find that at $T=140$ K and $P=6.5$ kbar the bcc
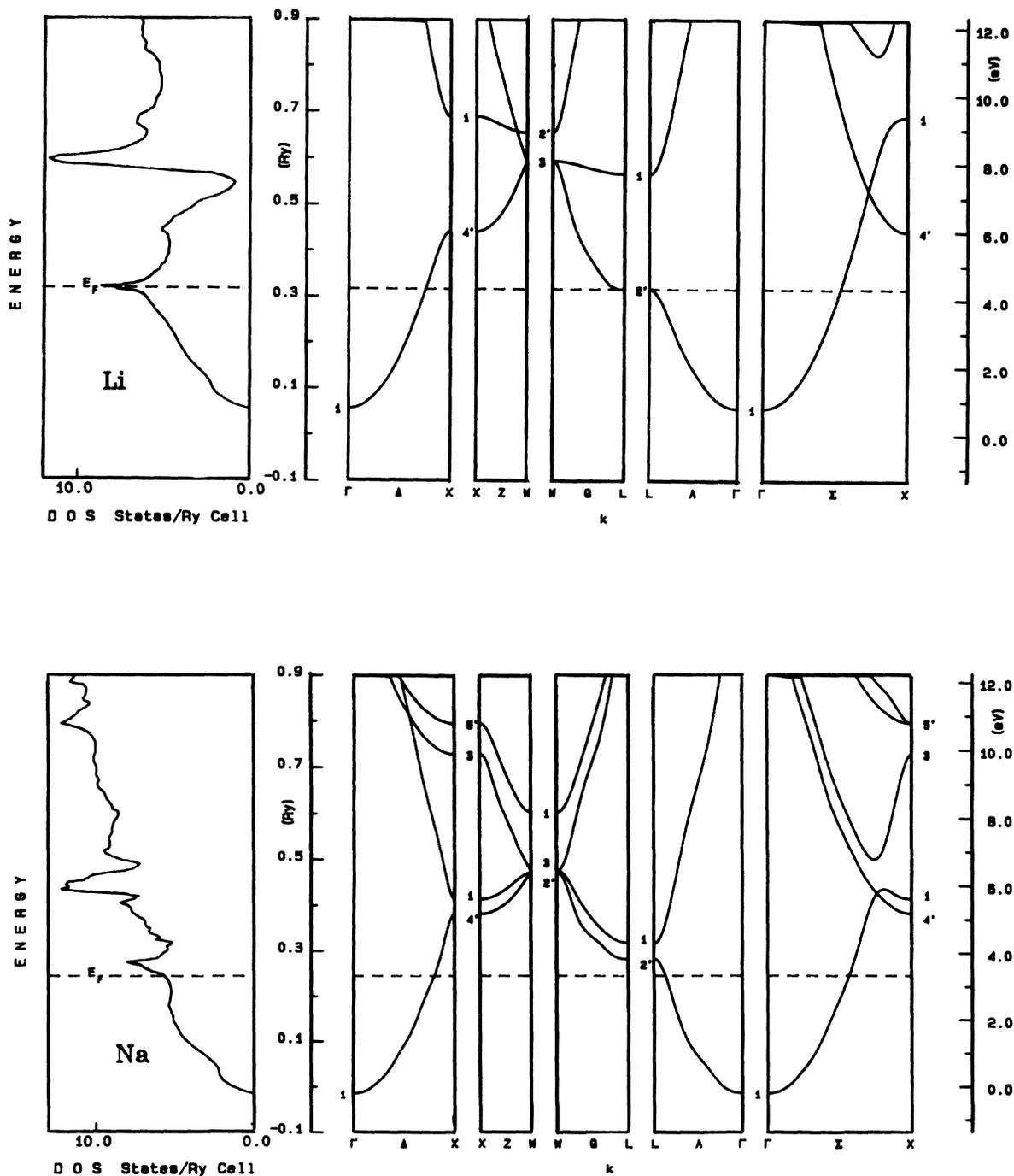
FIG. 2. Band structure of Li and Na in the fcc structure.

lattice constant of Li is 6.49 a.u. Our calculation (at $T=0$ K) gives an equilibrium lattice constant of 6.38 a.u. For the fcc structure of Li, Smith et al. found a lattice constant of 8.17 a.u., whereas we find an equilibrium lattice constant of 7.95 a.u.

For the bcc structure there are previous calculations by Moruzzi et al.[9] They found the equilibrium lattice constants to be 6.42, 7.70, 9.45, and 10.21 a.u. for Li, Na, K, and Rb, respectively, whereas we find them equal to 6.38, 7.69, 9.54, and 10.13 a.u., respectively, with corresponding total energies of -14.84, -322.98, -1196.45, and

-5872.52 Ry from Moruzzi et al.,[9] and -14.83, -323.42, -1201.18, and -5955.68 from our calculation. The differences are due to the relativistic effects that we take into account, but which are not included in the work of Moruzzi et al. Our calculated bulk moduli are also in good agreement with those given by Moruzzi et al. and with experiment. In Table I we list our calculated values of the cohesive energy for both the fcc and bcc structures. For the bcc structures, Moruzzi et al.[15] reported nearly perfect agreement with the measured cohesive energies. Our values are somewhat greater than theirs.
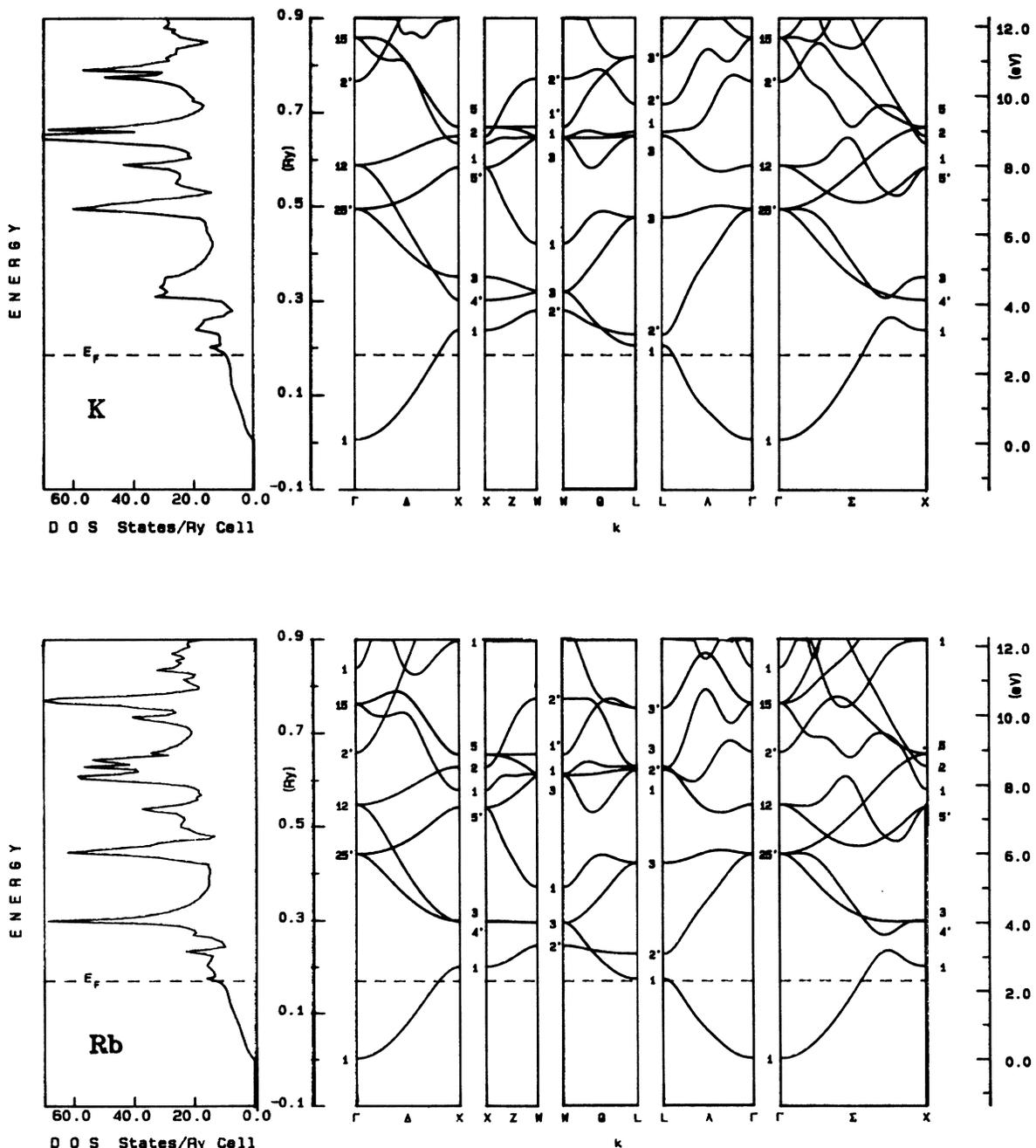
FIG. 3. Band structure of K and Rb in the fcc structure.
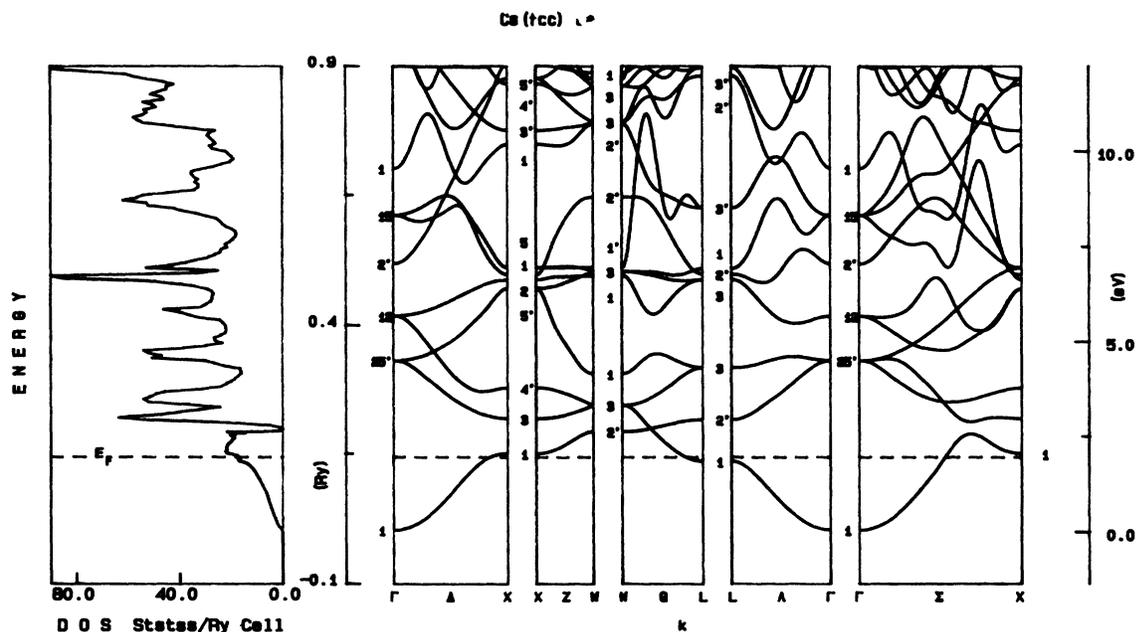
FIG. 4. Energy bands and densities of states for fcc Cs.

V. LAPW CALCULATIONS

The energy differences between the fcc and bcc phases of the alkali metals are quite small, on the order of 1 mRy or less. Although we believe our calculations to be well converged with respect to basis set size and number of k points, it is possible that systematic errors in the APW method could produce energy differences of this order between the two phases. To check the reliability of the method, we have performed a set of linearized augmented-plane-wave (LAPW) (Ref. 16) calculations on the fcc and bcc structures in Li and Na. The LAPW program used here[17] treats the core states fully relativistically and the valence and conduction bands in the semirelativistic approximation,[4] just as our APW code does. Both methods also use the Hedin-Lundqvist parametrization of the LDA.[5] However, in the LAPW calculations we are not making the muffin-tin approximation. Instead, the charge density and potential are expanded in spherical harmonics to angular momentum $l=8$ within the muffin tins, and expanded in Fourier series in the interstitial region. For this reason the muffin-tin radii are kept fixed, at 2.5 bohr for Li and 3.0 bohr for Na. A further difference is that we used the method of Monkhorst and Pack[18] to generate the k points.

We carefully checked the convergence of the total energy with respect to the number of basis functions and k points. Our calculations used 28 k points for the fcc structures and 40 (for Li) or 55 (for Na) points for the bcc phases. Approximately 60 basis functions were used at each k point. Tests done with a larger number of basis functions lead us to believe that the total energies are converged to within 0.1 mRy at all volumes.

We calculated the fcc and bcc equations of state for Li and Na, and fitted the resulting total-energy versus volume data to the Birch form.[6] The fits are accurate to better than 0.01 mRy. Our results are presented in Table III. The difference in equilibrium energies is 0.47 mRy for Li and 0.27 mRy for Na. If we assume that the fcc↔bcc transition is thermally activated, these energy differences correspond to transition temperatures of 74 and 47 K, respectively, in very close agreement to the observed transitions from close-packed (not necessarily fcc) phases to bcc at 72 K in Li and between 36 and 51 K in Na.[17]

Comparing these results to the APW results in Table I, we see that the APW fcc-bcc energy difference is considerably larger than that predicted by the LAPW method. The Na energy versus volume curves for both methods are shown in Fig. 5. We see that the curves calculated by

TABLE III. LAPW equation-of-state data for the fcc and bcc phases of Li and Na.

| | Equilibrium parameters | | | | |
| | \multicolumn{3}{c}{fcc} | | \multicolumn{3}{c}{bcc} |
	a_0 (bohr)	E_0 (Ry)	K_0 (Mbar)	a_0 (bohr)	E_0 (Ry)	K_0 (Mbar)	ΔE (Ry)
Li	8.01	−14.834 79	0.147	6.37	−14.834 32	0.151	0.000 47
Na	9.66	−323.425 51	0.092	7.65	−323.425 24	0.092	0.000 27
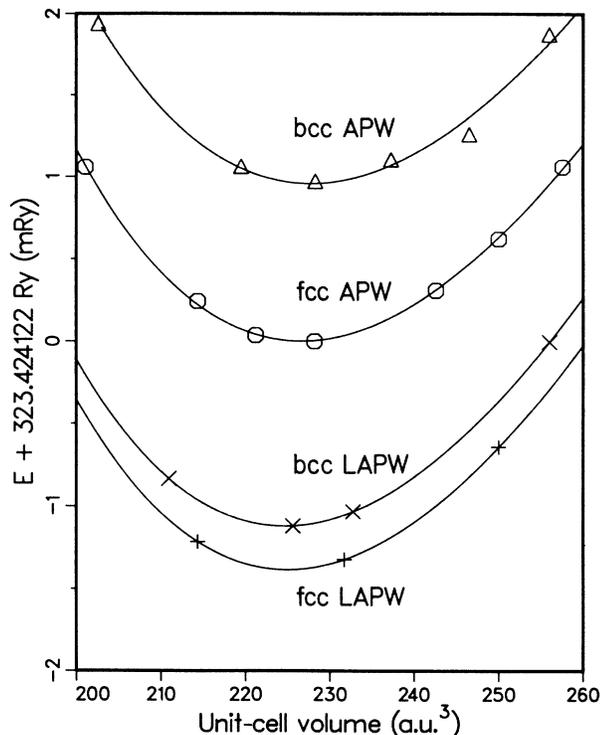
FIG. 5. Total energy (in Ry) of Na vs atomic volume for the fcc and bcc structures using the APW and LAPW methods.

(due to the use of the no-shape approximation potential) would not alter the basic result of this work, i.e., that the fcc structure is more favorable for H and the lighter alkali metals.

VI. CONCLUSIONS

We performed APW calculations of the total energy of solid H, Li, Na, K, Rb, and Cs within the LDA approximation. We predict that at $T=0$ K the fcc structure is more stable than the bcc structure for H, Li, Na, and K, a result that agrees with the existing experiments for Li and Na. At equilibrium the difference between the fcc and bcc total energies is larger for H and Li (6 and 2.18 mRy, respectively), and much smaller for the heavier elements. A comparison with our LAPW calculations which were done with a no-shape approximation potential for Li and Na leads to the following assessment of our APW calculations. The APW calculations (within the muffin-tin approximation) accurately give the equilibrium lattice constant, the bulk modulus, and the cohesive energy. However, the energy difference ΔE between the fcc and bcc structures is reliable only to the extent of predicting the stable structure, but should not be used to extract a structural transition temperature. It appears that the LAPW results (perhaps further convergence tests are needed) may be capable of accurately predicting transition temperatures as well.

each method are nearly identical, but that the difference between the fcc and bcc phases depends on the method used. In view of the small ($\lesssim 1$ mRy) difference between the phases and the fact that the sign is the same, we conclude that the superior accuracy of the LAPW results

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