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### Effect of semicore banding on heavy-alkali-metal lattice constants: Corrections to the frozen-core approximation

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Equilibrium lattice constants and bulk moduli of the heavy alkali metals K, Rb, and Cs were calculated using the Troullier-Martins pseudopotentials and plane-wave basis functions. The treatment of the outermost  $p$ -shell electrons as Bloch states yielded lattice constants 2–3% larger than those obtained within the frozen-core approximation (including the partial core correction of Louie, Froyen, and Cohen [Phys. Rev. B **26**, 1738 (1982)]), which narrows a long-standing discrepancy between local-density-functional theory and experiment. Predicted bulk moduli are 30–50% larger than measured values, within either treatment. The band dispersion of the semicore states (with bandwidths 0.067, 0.14, and 0.25 eV for K, Rb, and Cs) is attributed primarily to core-electron-conduction-electron hybridization rather than direct core-core overlap. The semicore density of states has a flat line shape, rather than the peaked shape expected for an idealized tight-binding band.

#### I. INTRODUCTION

Local-density-functional theory<sup>1</sup> (LDFT) has yielded accurate cohesive-property predictions for a wide variety of materials. Calculated lattice constants and bulk moduli are often within 1–2% and 5–10%, respectively, of the measured quantities, although predicted cohesive energies are typically somewhat less satisfactory. An exception to this pattern is the alkali metals, particularly K, Rb, and Cs, for which calculated lattice constants in the bcc structure are underestimated by as much as 6% or 7%.<sup>2</sup> Recent work by Sigalas *et al.*<sup>3</sup> has reconfirmed this trend, which had been noted in earlier results of Moruzzi, Janak, and Williams<sup>4</sup> and many others.<sup>5</sup> This behavior is insensitive to the particular form of the (local) exchange-correlation potential adopted, or whether all-electron or pseudopotential methodologies<sup>6</sup> are employed.<sup>7</sup> The apparent failure of LDFT to properly describe the alkali metals is disturbing, both for its possible implications regarding the validity of the general approach, and because of the importance of the heavy alkali metals to materials of current interest, such as the alkali-metal-intercalated fullerenes and graphites, to which LDFT is widely applied. Errors of the order of several percent in the bond length bode ill for the ability of LDFT to predict subtle

structural and vibrational properties in complex materials.

It is tempting to attribute the discrepancy between LDFT predictions and experiment for the alkali metals primarily to the local-density approximation for the exchange-correlation energy.<sup>8</sup> Gradient corrections<sup>9–11</sup> provide a computationally tractable way to go beyond the local-density approximation, and in some instances have been found to considerably reduce this discrepancy. Thus, although the efficacy of the presently employed forms of the gradient correction remains unclear,<sup>12,13</sup> it appears that nonlocal corrections to LDFT may be appreciable for the heavy alkali metals, perhaps a few percent in the lattice constant.<sup>14</sup>

We intend to show in this paper that, for the heavy alkali metals, corrections to the frozen-core approximation associated with core banding are of the same order of magnitude. Before we consider the issue of core bands, we discuss briefly the possible influence of relaxation and polarization for localized core states. von Barth and Gelatt<sup>15</sup> discussed the validity of the frozen-core approximation in pseudopotential-based total-energy calculations within LDFT. They demonstrated that, owing to the stationarity of the total-energy functional, the error incurred in the frozen-core approximation vanishes to first order in the relaxation of the core charge density in

the solid relative to a reference atomic core charge density. Therefore, although core polarization may nonetheless have a pronounced effect in systems of reduced symmetry, such as overlayers,<sup>16</sup> such effects are expected to be small in cubic systems.<sup>17</sup> The question may also be raised as to whether screened van der Waals core-polarization interactions,<sup>18</sup> which are correlation effects that may be poorly described by LDF'T, are significant for the alkali metals. This seems unlikely, and in any case such interactions are attractive and cannot explain the underestimation of lattice constants by LDF'T.

The ionic radius provides one measure of the expected prominence of core effects. Plotted in Fig. 1 is the ratio of the ionic diameter to the nearest-neighbor spacing for several simple and noble metals. This ratio is larger for the heavy alkali metals than for Zn, whose  $3d$ -band width is about 1 eV. The relatively shallow outermost-core shell binding energies for the heavy alkali metals (about 1 Ry) also suggest that the frozen-core approximation may be unreliable for these systems.

In the present work, equilibrium lattice constants and bulk moduli are calculated for bcc K, Rb, and Cs, with the outermost filled  $p$ -shell ("semicore") electrons treated as Bloch states, so that seven band electrons are considered per atom. Relatively few calculations exist on the heavy alkali metals that include the band character of semicore electrons. FLMTO (full-potential linear-muffin-tin-orbital) calculations were done by Klepeis,<sup>19</sup> and FLAPW (full-potential linear augmented-plane-wave) calculations for Cs monolayers by Wimmer.<sup>16</sup> A  $Z = 9$  calculation for Cs dimers was performed by Moullet, Andreoni, and Gianozzi.<sup>20</sup> We note also a (non-LDF'T) consideration of excited core-hole bandwidths in Li and Na.<sup>21</sup> Semicore bands have been more widely studied in materials other than alkali metals, for example, the  $p$  bands in early transition metals,<sup>22,23</sup> and the  $3d$  electrons in semiconducting compounds.<sup>24,25</sup>

Our calculations employ norm-conserving pseudopotentials.<sup>26</sup> The use of pseudopotentials (as compared,

for example, with the FLAPW method) introduces additional uncertainties associated with the sensitivity to the precise form adopted. Nevertheless, the pseudopotential methodology has become increasingly prominent in the past few years because of its convenience for large-cell calculations.<sup>27,28</sup> The present authors are performing calculations<sup>29</sup> for alkali-intercalated graphites, which provided motivation for this study.

## II. METHOD OF CALCULATION

Norm-conserving soft-core pseudopotentials were generated with the codes of Troullier and Martins.<sup>26</sup> Most of the present work was based on  $Z = 7$ , but results are also presented for  $Z = 1$  and  $Z = 9$ . Some studies involving semicore pseudopotentials have appeared previously,<sup>20,30-32</sup> but such pseudopotentials have been applied relatively infrequently. The partial core correction of Louie, Froyen, and Cohen<sup>33</sup> was applied in the case of  $Z = 1$ . The exchange-correlation potential of Ceperley and Alder<sup>34</sup> was employed throughout. The atomic configurations and core radii employed in generating the pseudopotentials are listed in Table I. A non-relativistic pseudopotential was employed for K, whereas semirelativistic pseudopotentials were used for Rb and Cs. The pseudopotentials were cast in the Kleinman-Bylander fully separable form, convenient for use in conjunction with the conjugate-gradient optimization of Teter, Payne, and Allan.<sup>28</sup> Angular momenta up to  $l = 2$  were treated, with the local potential taken to coincide with the  $s$  wave ( $l = 0$ ).

One may have some concern about transferability, and in particular the accuracy of the  $p$ -wave potential in the valence region, for the semicore pseudopotentials. Such concerns motivated Teter and Allan<sup>30</sup> to employ extended norm conservation. The present pseudopotentials were tested by comparing an atomic calculation of the valence  $p$  electron energies (above the semicore  $p$  level) with an all-electron calculation. The results agreed to about 1 meV, which indicates that both the semicore and valence states are described correctly for an isolated atom; atomic  $s$  and (excited)  $d$  state valence-electron energies also showed agreement between pseudopotential and all-electron calculations. Whether application of the Kleinman-Bylander construction to semicore pseudopo-

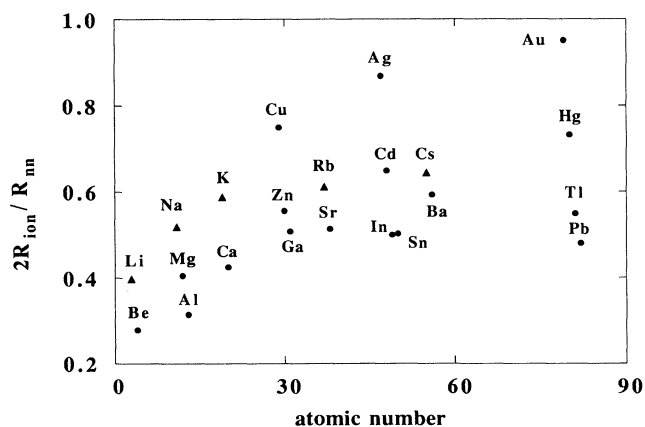


FIG. 1. Ratio of ionic radius to half the nearest-neighbor spacing for several simple and noble metals. The alkali metals are denoted by triangles.

TABLE I. Core radii (a.u.) employed in pseudopotential generation.

	$Z$	Configuration	$r_s$	$r_p$	$r_d$
K	1	$4s^1 4p^0 3d^0$	3.51	3.76	3.60
K	7	$3p^6 4s^1 3d^0$	3.51	1.06	3.60
K	9	$3s^2 3p^6 3d^0$	1.03	1.13	3.68
Rb	1	$5s^1 5p^0 4d^0$	3.82	3.82	3.72
Rb	7	$4p^6 5s^1 4d^0$	3.72	1.33	3.72
Rb	9	$4s^2 4p^6 4d^0$	1.30	1.36	3.90
Cs	1	$6s^1 6p^0 5d^0$	3.73	4.23	4.23
Cs	7	$5p^6 6s^1 5d^0$	3.74	1.53	4.23
Cs	9	$5s^2 5p^6 5d^0$	1.45	1.65	4.25

tentials in calculations for solids introduces additional inaccuracy deserves further study.

The plane-wave basis-set energy cutoffs were  $E_c$  of 60 Ry for K, and 65 Ry for Rb and Cs in the  $Z = 7$  calculations (for  $Z = 1$ , a cutoff of 12 Ry yields a highly converged result). The calculated total binding energies corresponding to these values of  $E_c$  differ by a few mRy from values obtained at 10–15 Ry higher cutoff energies. At these higher values of  $E_c$ , greater precision is achieved in the description of the semicore orbitals—however, the equilibrium lattice constant and bulk moduli are essentially unchanged.

The calculations for  $Z = 7$  require considerably more computational effort than those for  $Z = 1$ , because of the larger plane-wave basis set and the larger number of electrons in the unit cell. In pseudopotential calculations for compounds including alkali-metal elements, however, the cutoff energy will typically be dictated by one of the non-alkali-metal components. In calculations for the doped fullerenes, for example, the cutoff appropriate to the carbon pseudopotential of Troullier and Martins is of the order 60 Ry. In those circumstances, the additional computational overhead associated with  $Z = 7$ , as compared with  $Z = 1$ , is much smaller than in the pure alkali metals.

Energy integrations were performed using the Gaussian broadening method,<sup>35</sup> and Brillouin-zone sampling with  $\mathbf{k}$  points determined by the special-point method. A set with 68  $\mathbf{k}$  points reproduces the overall structure of the density-of-states curve; larger sets do not alter significantly the properties addressed in this work. Most of the results presented correspond to either 68 or 140  $\mathbf{k}$  points. In the former case, a Gaussian broadening parameter of 0.008 Ry was employed and in the latter case 0.005 Ry. Larger  $\mathbf{k}$ -point sets are normally employed in studies of the high-pressure phase diagram, but are not required in the present context.

### III. RESULTS

Although the semicore energy spectra calculated within local-density-functional theory have no *formal* physical interpretation, their qualitative features provide insights into the role played by such states. The calculated positions  $\langle \epsilon(k)_{\text{calc}} \rangle$  of the semicore bands (relative to the Fermi energy), which represent averages over 140 sampled  $\mathbf{k}$  points, are listed in Table II. In addition to

TABLE II. Properties of semicore bands of heavy alkali metals.  $\langle \epsilon(k)_{\text{th}} \rangle$  is the mean semicore band energy, in eV, below  $E_F$ . Experimental values taken from photoemission measurements (Ref. 36). The variance and bandwidth of the calculated semicore bands  $\epsilon(k)_{\text{th}}$  are given in the last two columns. The spatial-variation exponents  $\rho$  (Å) [cf. Eq. (1)] for variance and bandwidth are included in parentheses.

Element	Level	$\langle \epsilon(k)_{\text{th}} \rangle$	$\epsilon_{\text{exp}}$	Variance	Bandwidth
K	3 <i>p</i>	15.77	18.3	0.018(11.0)	0.067(3.2)
Rb	4 <i>p</i>	13.04	15.8	0.040(13.6)	0.14(3.9)
Cs	5 <i>p</i>	10.62	13.0	0.073(8.7)	0.25(2.5)

the calculations for semicore  $p$  bands, based on  $Z = 7$  pseudopotentials, which are listed in the table, some calculations with coarser  $\mathbf{k}$ -point sampling for  $Z = 9$  pseudopotentials, which include both the semicore  $s$  and  $p$  bands, will be mentioned below. Values of semicore levels determined from photoemission measurements<sup>36</sup> are also listed in the table. The agreement between theory and experiment is reasonably close, particularly in view of the neglect of corrections such as the relaxation of the core hole in the calculations. The last two columns in Table II give the variance and the bandwidth (the difference between maximum and minimum eigenvalues) of the semicore bands. The values listed were calculated at the respective equilibrium lattice constants of the elements. The dependence of the semicore bandwidth (or the variance) on the lattice constant can be represented as an exponential

$$A \exp[(r_{\text{nn}} - R_{\text{nn}})/\rho], \quad (1)$$

where  $r_{\text{nn}}$  is the nearest-neighbor spacing, the equilibrium value of which is  $R_{\text{nn}}$  and  $A$  and  $\rho$  are parameters. Results for the exponential decay length  $\rho$  obtained by fitting our calculated values to this form are given in parentheses.

The ratio of the bandwidth to the variance, which we denote as  $S$ , provides a measure of the density-of-states line shape. For reference we consider two limiting cases: a rectangular density of states, for which  $S_{\text{rec}} = 2\sqrt{3} = 3.464$ , and an ideal  $s$ -wave tight-binding band in a body-centered-cubic crystal, for which (see the Appendix)  $S_{\text{tb}} = 5.28$ . The value for a  $p$ -wave tight-binding band would be somewhat smaller. Using the bandwidths and variances listed in the table, we find  $S$  of approximately 3.5, close to  $S_{\text{rec}}$ .

The calculated semicore bandwidths for the heavy alkali metals shown in Table II are of the order of one-tenth or two-tenths of an eV. This is at the borderline of applicability of the frozen-core approximation.<sup>15</sup> For comparison, these values are somewhat smaller than the calculated width of the 3*d* bands in Zn (greater than an eV), which lie about 8 eV below the Fermi energy,<sup>4</sup> but still within the valence band, and have essentially a rectangular density of states. The semicore  $p$ -band widths for Rb and Cs are smaller than the measured relativistic multiplet splitting<sup>36</sup> between  $p_{1/2}$  and  $p_{3/2}$ . (The pseudopotentials used in the present calculations are obtained by a weighted average over the atomic pseudopotentials corresponding to these levels, the standard procedure for generating semirelativistic pseudopotentials.) Some calculations were also performed for semicore  $s$  bands with  $Z = 9$  pseudopotentials. These levels lie at 25–35 eV below the Fermi energy and have bandwidths of several millivolts. The banding of the semicore  $s$  states is thus much less than for the  $p$  states, and our further discussion will refer exclusively to the  $Z = 7$  pseudopotentials.

In principle, the banding of the alkali-metal semicore states may originate from either of two mechanisms: core overlap on neighboring atomic sites, or core-electron-conduction-electron hybridization. One may distinguish between these two possibilities by examining the magnitudes of the line-shape parameter  $S$ , the length scale

$\rho$ , and the preexponential  $A$ . Core-electron-conduction-electron hybridization appears to be the relevant mechanism for semicore band broadening. Nearest-neighbor core overlap would give rise to tight-binding bands with peaked densities of states and larger values of  $S$  than those obtained in the present calculations, which show a more rectangular density of states. Note from Table II that the value of the decay length  $\rho$  corresponding to the variance is larger than that for the bandwidth, indicating that the line-shape parameter  $S$  increases at smaller nearest-neighbor separations, as core overlap and the tight-binding character start to become more significant. Furthermore, the value of  $\rho$  appropriate to Born-Mayer core overlap potentials for  $\text{Rb}^+$  is about  $0.26 \text{ \AA}$ ,<sup>37</sup> much smaller than the value given in Table II. Therefore, if core overlap were the source of banding, the dependence of bandwidth on  $r_{\text{nn}}$  would be a great deal stronger than we find in our calculations. Finally, the preexponential in the Born-Mayer interaction  $A_{\text{BM}}$  multiplied by the coordination number would be comparable to the bandwidth for tight-binding bands. In the case of Rb, for example,  $A_{\text{BM}}$  is less than a meV,<sup>37</sup> too small to account for the bandwidth in Table II. All of these considerations indicate that banding of the semicore states results primarily from hybridization of conduction and core electrons.

In addition to introducing semicore bands, which have been the subject of the preceding discussion, the calculations for  $Z = 7$  also alter the valence bands, relative to those corresponding to  $Z = 1$ . For example, the band gaps at the  $N$  point of 0.94 and 1.53 eV are somewhat larger than literature values (based on  $Z = 1$ ) of 0.41 and 0.9 eV for K (Ref. 4) and Cs,<sup>38</sup> respectively. Correspondingly, the  $Z = 7$  Fermi surfaces show greater anisotropy (and for Cs even exhibits a small neck at the zone faces) than those obtained for  $Z = 1$ . The Fermi surfaces in alkali metals calculated within local-density-functional theory are known<sup>39,40</sup> to have greater anisotropy than the true quasiparticle Fermi surfaces. The disparity between the LDFT Fermi surface and the quasiparticle one is therefore greater for  $Z = 7$  than for  $Z = 1$ . The errors incurred by the neglect of semicore banding and the neglect of nonlocality in the mass operator<sup>39</sup> may partially compensate each other in the  $Z = 1$  LDFT calculations, thus yielding a result in closer agreement with the quasiparticle Fermi surface than might have been expected at that level of approximation.

We turn now to the effect of semicore bands on bulk cohesive properties, the primary focus of the present work. Calculated equilibrium lattice constants for the heavy alkali metals in the bcc structure are listed in Table III.

TABLE IV. Calculated and measured bulk moduli (Mbar) of the heavy alkali metals. Gradient-corrected (GC) results are based on the Langreth-Mehl form (Ref. 9). Measured value for Cs from G. Simmons and H. Wang, *Single Crystal Elastic Constants* (MIT, Cambridge, MA, 1971), and for K and Rb from H. Ledbetter, in *Dynamic Elastic Modulus Measurements in Materials*, edited by A. Wolfenden (ASTM, New York, 1990), p. 145.

	LDFT ( $Z = 1$ )	LDFT ( $Z = 7$ )	GC ( $Z = 7$ )	Expt.
K	0.040	0.043	0.040	0.033
Rb	0.036	0.036	0.034	0.026
Cs	0.023	0.025	0.023	0.017

Results are given both for  $Z = 7$  and  $Z = 1$ . The results for Rb and Cs with  $Z = 1$  correspond closely to previous LDFT calculations such as those of Sigalas *et al.*,<sup>3</sup> although our lattice constant for K is 2% larger (a similar result for K was obtained by Troullier and Martins<sup>41</sup>). Comparing the results for  $Z = 7$  and  $Z = 1$ , we find the lattice constants are increased by 2–3 % when the semicore electrons are treated as Bloch states. Not surprisingly the influence of the semicore bands on the lattice constant increases with atomic number, as does the relative atomic radius, cf. Fig. 1, and the semicore band position, Table II. The column of Table III labeled “GC” refers to results including the Langreth-Mehl gradient correction.<sup>9</sup> The gradient correction appears to have a relatively small effect on the heavy-alkali-metal lattice constants. The last column in Table III gives low-temperature experimental values of the K, Rb, and Cs lattice constants for the bcc structure. The values calculated in the present work for  $Z = 1$  are all lower than experiment, in agreement with previous work.<sup>3</sup> The results for Rb and Cs with  $Z = 7$  show improved agreement with experiment as compared with those for  $Z = 1$ . On the other hand, calculated lattice constants of K for both  $Z = 1$  and  $Z = 7$  are both within about 1% of experiment. Calculated and measured bulk moduli for the heavy alkali metals are listed in Table IV. Results for  $Z = 1$  and  $Z = 7$  are both about 30–50 % higher than experimental values.

#### IV. DISCUSSION AND CONCLUSIONS

The treatment of semicore  $p$  states in K, Rb, and Cs as valence electrons gives rise to core bandwidths of the or-

TABLE III. Calculated and measured lattice constants (a.u.) of the heavy alkali metals. Gradient-corrected results are based on the Langreth-Mehl form (Ref. 9). Measured values from N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, New York, 1976).

	LDFT ( $Z = 1$ )	LDFT ( $Z = 7$ )	GC ( $Z = 7$ )	Expt.
K	9.77	10.00	10.05	9.88 (5 K)
Rb	10.15	10.35	10.45	10.56 (5 K)
Cs	10.80	11.10	11.15	11.43 (78 K)

der of a tenth of an eV. Evidence was presented that this banding results from core-electron-conduction-electron hybridization. We find a 2–3 % increase in equilibrium lattice constant for the heavy alkali metals when semicore banding is included, relative to results based on the frozen-core approximation.

The influence of semicore bands on cohesive properties has previously been studied for transition metals<sup>22,23</sup> and stoichiometric semiconducting compounds.<sup>24,25</sup> A recent precise calculation for fcc and bcc La (Ref. 23) shows increases in the lattice constants due to 5*p* semicore banding in both cases. Hybridization of the semicore 3*d* bands with the upper valence bands in II-IV and III-V semiconducting compounds is found to increase the calculated lattice constant in most cases.<sup>24,25</sup> The present work, in which hybridization of semicore *p* bands with valence *s* bands increases the lattice constant, is therefore consistent with previous results.

The precise mechanism responsible for the lattice-constant increase is somewhat elusive. Discussions of the mechanism by which unfreezing the semicore orbitals affects cohesive properties were given by Wei and Zunger,<sup>24</sup> and by Fiorentini, Methfessel, and Scheffler.<sup>25</sup> In considering Zn, Cd, and Hg tellurides, Wei and Zunger<sup>24</sup> suggest that the antibonding *d* character in the upper valence bands is responsible for lattice-constant expansion and cohesive energy reduction. On the other hand, Fiorentini, Methfessel, and Scheffler<sup>25</sup> attribute such shifts in the case of GaN and ZnS to *d-p* core-overlap repulsion, which is neglected in frozen-core treatments.

Let us consider the similarities and differences between the heavy alkali metals and the semiconducting compounds with regard to semicore-band effects. Since our present results indicate that core overlap is small in the heavy alkali metals, the mechanism proposed by Fiorentini, Methfessel, and Scheffler does not appear operative in these systems, and we therefore turn our attention to the effect of hybridization. A simple perturbation analysis<sup>24</sup> shows that, to lowest order, hybridization shifts the semicore bands to lower energies and the valence bands to higher energies. We note two differences between the alkali metals and semiconducting compounds in this regard. First, although cation *d* and anion *p* states couple at the zone center in compounds with zinc-blende structure, no coupling occurs in the (body-centered-cubic) alkali metals between *p* and *s* states at the zone center. This would suggest that the overall effect of *p-s* hybridization in the alkali metals may be smaller than that of *d-p* hybridization in the zinc-blende compounds, and indeed the calculated *d*-band widths in the latter are of the order of a few tenths of an eV,<sup>24,25</sup> larger than the alkali-metal *p*-band widths listed in Table II. Further, whereas the sum of the orbital energies is, to lowest order, unchanged by *d-p* hybridization in the semiconducting compounds, the sum of occupied orbital energies in the alkali metals decreases as a result of *p-s* hybridization, because not all of the (upwardly shifted) conduction-band states are occupied. Thus, to lowest order, hybridization is expected to produce an attractive effective interaction in the alkali metals, contrary to our calculated results, which show expanded lattice con-

stants. As mentioned above, Wei and Zunger<sup>24</sup> emphasize the destabilizing effect of the hybridization-induced antibonding character in the upper valence-band orbitals. In the alkali metals, this “higher-order” effect would compete with the eigenvalue-sum shift, which to lowest order is attractive.

In summary, the precise origin of the observed hybridization-induced change in the calculated heavy-alkali-metal lattice constants (cf. Table III) is not entirely clear at this time, although the mechanism (hybridization-induced antibonding character in upper valence bands) identified by Wei and Zunger may be relevant. All-electron calculations, e.g., with the FLAPW method, would be more suitable than pseudopotential treatments for further investigation of this question.

The observed 2–3 % increase (cf. Table III) in calculated equilibrium lattice constants narrows the longstanding discrepancy between LDFT calculations of the lattice constants of heavy alkali metals in the bcc structure and experiment. The discrepancy is not, of course, eliminated entirely. For example, although core effects are relatively negligible for Li and Na, the LDFT predicted lattice constants for Li and Na are still considerably smaller than observed values. A great deal of recent work has focused on the effect of gradient corrections on cohesive properties. The present results indicate that any such future study on the alkali metals should not neglect the effect of the semicore banding, which is of the same order of magnitude. The influence of the semicore bands on properties of compounds such as the alkali-metal-intercalated fullerenes and graphites is expected to be greater than in the pure alkali metals because in many such systems the semicore states lie within the valence band of the host. Although the treatment of semicore states as valence electrons of course greatly increases the computational effort in calculations on the pure alkali metals, the additional overhead in calculations for compounds is much smaller. Therefore doing the more “correct” procedure of treating the semicore electrons as Bloch states (rather than invoking the frozen-core approximation) should be computationally feasible in many instances.

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## APPENDIX: TIGHT-BINDING LINE SHAPE

The normalized density of states for a tight-binding  $s$  band in the bcc structure is<sup>42</sup>

$$g(\epsilon) = \frac{4}{\pi^3} \int_{|\epsilon|}^1 \frac{K(\sqrt{1-x^2})}{\sqrt{x^2-\epsilon^2}} dx, \quad (\text{A1})$$

where  $K$  is the complete elliptic integral of the first kind; note the energy unit is one-half the bandwidth.

Then the mean-squared energy is found from<sup>43</sup>

$$\begin{aligned} \langle \epsilon^2 \rangle &= \frac{4}{\pi^3} \int_0^1 dx K(\sqrt{1-x^2}) \int_{-x}^x d\epsilon \frac{\epsilon^2}{\sqrt{x^2-\epsilon^2}} \\ &= \int_0^1 dx E(x)/\pi^2 = (\frac{1}{2} + G)/\pi^2 \approx 0.14347, \end{aligned} \quad (\text{A2})$$

where  $G$  is Catalan's constant and  $E$  is the complete elliptic integral of the second kind. The line-shape parameter  $S_{\text{tb}}$  is then given by the ratio of bandwidth to variance:

$$S_{\text{tb}} = 2/\sqrt{\langle \epsilon^2 \rangle} \approx 5.28. \quad (\text{A3})$$

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- <sup>1</sup>W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).  
<sup>2</sup>The prediction of martensitic phase transformations in the alkali metals is a much more subtle issue and will not be addressed here.  
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<sup>5</sup>See also J.C. Boettger, S. B. Trickey, and J. A. Nobel, *Phys. Rev. B* **45**, 7503 (1992); D. A. Papaconstantopoulos and D. J. Singh, *ibid.* **45**, 7507 (1992).  
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<sup>7</sup>Calculations for the heavier alkali metals are normally done semirelativistically, with spin-orbit interaction neglected.  
<sup>8</sup>Zero-point vibrations and nonadiabatic effects come into consideration for Li and Na [N. W. Ashcroft, *Phys. Rev. B* **39**, 10 552 (1989)], but are not expected to be significant for the heavier alkali metals.  
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