RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 7 15 FEBRUARY 1993-I

Rapid Communications

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *should be no longer than four printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

Crystal binding energies from atomic-cluster calculations

Yang Jinlong and Wang Kelin
Center for Fundamental Physics, University of Science and Technology of China,
Hefei, Anhui 230026, People's Republic of China

F. Casula
Istituto di Fisica della Facoltà di Medicina, Università di Cagliari, I 09124 Cagliari, Italy

G. Mula
Dipartimento di Scienze Fisiche, Università di Cagliari, I 09124 Cagliari, Italy

(Received 23 April 1992; revised manuscript received 30 November 1992)

A parameter-free technique is proposed to estimate the binding energy of a crystal from the knowledge of the binding energy of suitably chosen small atomic clusters, the latter being computed by an all-electron discrete variational method within local-density-functional theory. Test calculations of the equilibrium static properties of several metals and semiconductors, including the third-row elements from Na to Si and the group-IV semiconductors from C to Sn, will be compared with previous experimental and theoretical results.

By the end of the 1980s a host of first-principles, accurate methods for computing the electronic and structural properties of solids have been shown[1] to be capable of quite accurate calculations of important ground-state properties such as the total energy. However, in the materials-design field a need still exists for simpler procedures[2] which would be extremely useful in guided searches for new materials with specified properties.

It is with this goal in mind that we set out to look for ways of incorporating the results obtained from atomic-cluster calculations into some suitable expression for determining the binding energy of a given crystal. Actually it is now possible to make first-principles calculations of the electronic structure and of the binding energy of small clusters in a time-effective way by using, e.g., a modern version of the discrete variational (DV) method.[3-5] In this paper we propose a method for estimating $E_b^{\rm cry}$, the binding energy per atom of a crystal, from the binding energy of small clusters. $E_b^{\rm cry}$ can be approximated in two different ways, namely, as the average binding energy of a small cluster or as the binding energy of the central atom of the same cluster. To be more precise let us refer to a monatomic kind of material and let us indicate with

$$E_b^{\rm clus}(n)=nE_{\rm at}-E_{\rm tot}^{\rm clus}(n)\ , \tag{1}$$

the binding energy of an n-atom cluster, where $E_{\rm tot}^{\rm clus}(n)$ and $E_{\rm at}$ are the total energy of the considered cluster and the isolated atom energy of its constituents. Since the contribution of the less bound surface atoms acts to reduce the average binding energy per atom, the quantity $(1/n)E_b^{\rm clus}(n)$ should give a lower bound for $E_b^{\rm cry}$. On the other hand, we could define the binding energy of the n' atoms belonging to the cluster core $(1\le n'<n)$ as the difference between the total cluster binding energies before and after their removal, *without allowing for any relaxation of the atomic positions,* i.e.,

$$\begin{aligned}E_c^{\rm clus}(n)&=\frac{1}{n'}\{[E_{\rm tot}^{\rm clus}(n-n')+n'E_{\rm at}]-E_{\rm tot}^{\rm clus}(n)\}\\&=\frac{1}{n'}[E_b^{\rm clus}(n)-E_b^{\rm clus}(n-n')]\ .\end{aligned} \tag{2}$$

Since this difference can be regarded, to a very good approximation, as given by $E_b^{\rm cry}$ plus the average excitation energy per atom of the final state of the unrelaxed $(n-n')$-atom cluster, $E_c^{\rm clus}(n)$ represents an upper bound to $E_b^{\rm cry}$. In the limit of an infinite cluster both methods should give $E_b^{\rm cry}$. Though it is well known that this limit means very large clusters[6] we would argue that the arithmetic mean of the two bounds should give quite good approximations for $E_b^{\rm cry}$.

For each given structure the procedure of selecting a representative cluster is simple and straightforward. In the case of monatomic solids one can regard any atom of the solid as the center and include in the cluster as many shells of neighbors—*in the same positions they would have in the bulk*—as is deemed sufficient. In practice for most calculations presented here this means two shells

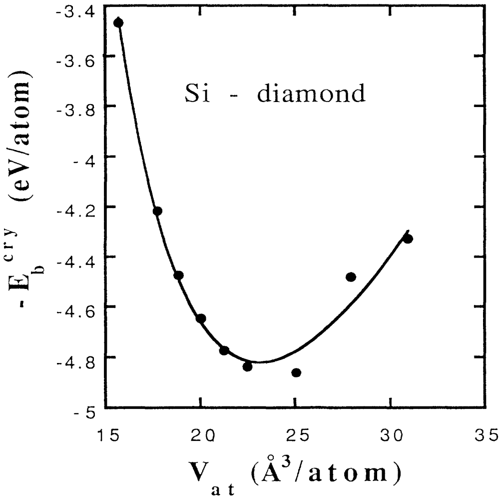

FIG. 1. Sign-reversed bulk Si binding energy per atom in the diamond structure plotted as a function of atomic volume. Dots are calculated points and the solid line is the result of fitting them to Murnaghan's equation. Minimum indicates theoretical equilibrium quantities.

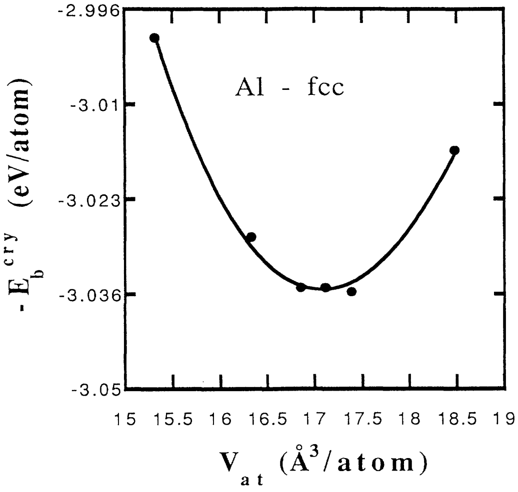

FIG. 2. Sign-reversed bulk Al binding energy per atom in the fcc structure plotted as a function of atomic volume. Dots are calculated points and the solid line is the result of fitting them to Murnaghan's equation. Minimum indicates theoretical equilibrium quantities.

and a cluster core reduced to the cluster central atom ($n'=1$). The use of larger n' values does not lead to significantly different results. In the case of the diamond structure, for instance, our cluster contains a central atom surrounded by four others located at the vertices of a tetrahedron, plus twelve further atoms arranged as the bulk second neighbors.[7] Analogous procedures can be easily followed for other crystal structures. Volume-dependent calculations can be made by varying the interatomic distances at fixed cluster symmetry.

The second step is the computation of $E_b^{\text{clus}}(n)$ and $E_b^{\text{clus}}(n-1)$. As we have stated in the Introduction, in the removal process the atomic positions of the remaining $n-1$ atoms are unchanged, while the cluster electronic states are obviously allowed to relax. The binding-energy calculations are done by using the first-principles discrete variational method. The method can be traced back to the early 1970s,[3] and its main idea is to use a discrete sample of points for integrating in real space the Hamiltonian and overlap matrix elements:

$$H_{ij}=\langle\chi_i|H|\chi_j\rangle=\Sigma_k\omega(\mathbf{r}_k)\chi_i^*(\mathbf{r}_k)H(\mathbf{r}_k)\chi_j(\mathbf{r}_k)\ ,$$

$$S_{ij}=\langle\chi_i|\chi_j\rangle=\Sigma_k\omega(\mathbf{r}_k)\chi_i^*(\mathbf{r}_k)\chi_j(\mathbf{r}_k)\ .$$

The choice of the grid and of the weights $\omega(\mathbf{r}_k)$ can be done according to Ref. 5: typically for the not too heavy atoms used in this work 300 points around each atom are sufficient for obtaining a good convergence.

The DV method is an all-electron one and typically only a minimal basis set is required. Moreover the innermost atomic core levels can often be frozen in cluster calculations. The exchange-correlation potential we used is after von Barth and Hedin.[8] An important point to be stressed is that the DV method allows us to compute the total energy and the atomic energy in the same program, so that the binding energy, which is their difference, should be particularly reliable.

According to the discussion in the Introduction we will estimate E_b^{cry} as

$$E_b^{\text{cry}}\approx\tfrac{1}{2}\{(1/n)E_b^{\text{clus}}(n)+E_c^{\text{clus}}(n)\}\ . \qquad (3)$$

To illustrate the validity of our approach we have performed calculations on the third-row elements from Na to Si and on the fourth-column elements from C to Sn. Let us now discuss in detail the results we obtained for Si in the diamond structure. Our results for the binding energy, calculated according to Eq. (3), are reported in Fig. 1 as a function of the atomic volume. $E_b^{\text{clus}}(n)$ and $E_b^{\text{clus}}(n-1)$ have been obtained by performing all-electron DV-LDA (local-density approximation) calculations for 17- and 16-atom clusters, respectively. The dots in the figure denote the calculated values, while the continuous line is the result of a least-square fitting to Murnaghan's equation.[9] A separate fitting of $E_b^{\text{clus}}(n)$ and $E_b^{\text{clus}}(n-1)$ to an analytical form has been considered, as well as the direct fitting of their combination E_b^{cry}, but the results, as shown in Table I, are identical

TABLE I. The estimated equilibrium lattice constant a_0, binding energy E_b^{cry}, bulk modulus B_0, and its pressure derivative B_0' of diamond Si obtained by different fitting conditions compared to experimental and previous theoretical results: *a*, all-electron calculations: least-square fitting to Murnaghan's equation; *b*, all-electron calculations: least-square fitting to quadratic dependence; *c*, frozen-core calculations: least-square fitting to Murnaghan's equation; *d*, frozen-core calculations: least-square fitting to quadratic dependence; *e*, experimental results (Refs. 11 and 12); *f*, previous LDA pseudopotential calculations (Ref. 10).

	a	*b*	*c*	*d*	*e*	*f*
a_0 (Å)	5.70	5.81	5.86	5.73	5.429	5.451
E_b^{cry} (eV/at)	4.81	4.90	4.87	4.90	4.68	4.84
B_0 (Mbar)	0.96	1.32	0.60	1.92	0.99	0.98
B_0'	3.7	−1	4.1	−1	4.2	3.2

TABLE II. The estimated equilibrium lattice constant a_0, binding energy $E_b^{\rm cry}$, bulk modulus B_0, and its pressure derivative B_0' of fcc Al obtained by different fitting conditions compared to experimental and previous theoretical results: *a*, all-electron calculations: least-square fitting to Murnaghan's equation; *b*, all-electron calculations: least-square fitting to quadratic dependence; *c*, frozen-core calculations: least-square fitting to Murnaghan's equation; *d*, frozen-core calculations: least-square fitting to quadratic dependence; *e*, experimental results (Refs. 11 and 12); *f*, previous LDA pseudopotential calculations (Ref. 13); *g*, previous LDA pseudopotential calculations (Ref. 14).

	a	*b*	*c*	*d*	*e*	*f*	*g*
a_0 (Å)	4.09	4.09	4.05	4.06	4.02	4.41	4.01
$E_b^{\rm cry}$ (eV/at)	3.04	3.04	3.37	3.37	3.36	2.98	3.65
B_0 (Mbar)	0.60	0.58	1.36	1.10	0.72	0.65	0.71
B_0'	2.0	−1	4.1	−1			5

within three decimal figures. In the table we also show the result of a quadratic fitting of the same data, as well as the data obtained by a frozen-core DV-LDA calculation of $E_b^{\rm clus}(n)$ and $E_b^{\rm clus}(n-1)$. Finally our estimates are compared to those of previous LDA pseudopotential calculations[10] and the agreement appears to be within 5% for the lattice constant a_0, less than 1% for the binding energy $E_b^{\rm cry}$, and 2% for the bulk modulus. This agreement is practically unchanged if the comparison is made with the experimental results.[11,12] We also found that our theoretical a_0 and $E_b^{\rm cry}$ values depend only slightly on the use of the frozen-core approximation and on the analytical form actually chosen for the fitting, though of course the bulk modulus B_0 dependence is much more marked.

In Fig. 2 we reported similar results for the binding energy of bulk fcc Al. $E_b^{\rm clus}(n)$ and $E_b^{\rm clus}(n-1)$ have been obtained from all-electron DV-LDA calculations for 19- and 18-atom clusters, respectively, i.e., we have taken into account the interactions of a bulk atom with its first and second neighbors in the fcc structure. The dots denote the calculated values, while the continuous line is the result of a least-square fitting to Murnaghan's equation. Our main results are reported in Table II and compared with the experiment[11,12] and with other theoretical results.[13,14] In comparison with the experiment the lattice parameter appears to be correct within 2% and the binding energy within 9%. Previous bulk LDA calculations gave the same degree of accuracy for $E_b^{\rm cry}$ and a_0, but we have to point out that in Ref. 13 the binding energy is underestimated, as in our calculations, while in Ref. 14 it is overestimated. For the bulk modulus B_0 the error is somewhat larger than in the case of Si, i.e., 17%, though not so different from the value obtained in Ref. 13. Again frozen-core calculations produce results of comparable quality for $E_b^{\rm cry}$ and a_0.

In Table III we display our results for the equilibrium properties of the third-row elements Na, Mg, Al, and Si. Since four different structures are involved, from the metallic bcc to the insulating diamond structure, this kind of test is particularly significant. We have already explained the details of Al and Si calculations; for Na and Mg, which crystallize in the bcc and hcp structures, we used 15- and 18-atom clusters, respectively, again including first- and second-neighbor shells. For Mg the minimization has been done in two steps: first, we have minimized with respect to a_0 at the experimental value of $\xi = c/a$ ratio and then a further minimization with respect to ξ has been performed.

We would like now to suggest an alternative use of Eq. (3), whenever the lattice constant, or some reliable guess for it, is already known. Table IV gives estimates for the bulk binding energies of the third-row and of group-IV elements, obtained by performing frozen-core calculations of $E_b^{\rm clus}(n)$, $E_b^{\rm clus}(n-1)$, and finally $E_b^{\rm cry}$ at the experimental value of the lattice constant. The accuracy of the results turns out to be comparable, and in most cases even better, than that obtained in the fully *ab initio* process, since the relative errors with respect to experiment do not exceed 7% for all crystals, but Ge and Sn. For Ge the error, i.e., 12%, is still acceptable, while it is somewhat higher for Sn, i.e., 26%, but both of them are comparable with other theoretical predictions.[10,16] The Sn theoretical values in particular may reflect the disregard of relativistic effects.[16] We do not attach any special meaning to the overall improvement of the results, obtained with this simplified version, but we stress that since the full procedure produces *good* $E_b^{\rm cry}$ and a_0 values quite close to experimental ones, it is quite reasonable to obtain still *good* values of $E_b^{\rm cry}$ by using exactly the exper-

TABLE III. The equilibrium atomic volumes $V_{\rm at}$ and binding energies $E_b^{\rm cry}$ of third-row elemental crystals, i.e., bcc Na, hcp Mg, fcc Al, and diamond Si, compared to experimental and previous theoretical results.

		bcc Na $n=15$	hcp Mg $n=19$	fcc Al $n=19$	diamond Si $n=17$
$V_{\rm at}$ (Å^3)	present calculation	50.59	21.97	17.10	23.15
	previous LDA results[a]	35.11	27.51	21.48	20.23
	experimental results[b]	37.64	23.31	16.58	20.01
$E_b^{\rm cry}$ (eV/at)	present calculation	1.35	1.62	3.04	4.81
	previous LDA results[a]	1.22	1.88	2.98	4.84
	experimental results[c]	1.11	1.52	3.36	4.63

[a] From Ref. 13.

[b] From Ref. 12.

[c] From Ref. 11.

TABLE IV. Binding energies of third-row metals and of group-IV semiconductors in their experimental equilibrium structure calculated at their experimental lattice constant a_0 and compared with the corresponding experimental values E_b^{exp} (from Refs. 11 and 12) and with previous theoretical results E_b^{cal} (from Refs. 10, 13, 15, and 16). For the sake of completeness the size n of the clusters used in calculations, as well as the cluster binding energies appearing in Eq. (3), $E_b^{\mathrm{clus}}(n)$ and $E_b^{\mathrm{clus}}(n-1)$, are also reported.

	a_{exp} (Å)	n	$E_b^{\mathrm{clus}}(n)$ (eV/atom)	$E_b^{\mathrm{clus}}(n-1)$ (eV/atom)	E_b^{cry} (eV/atom)	E_b^{exp} (eV/atom)	E_b^{cal} (eV/atom)
diamond							
C	3.57	17	91.772	82.363	7.40	7.37	7.58
Si	5.43	17	55.298	49.386	4.58	4.68	4.84
Ge	5.66	17	52.343	46.783	4.32	3.87	4.26
α-Sn	6.49	17	45.517	40.285	3.95	3.13	3.78
bcc Na	4.29	15	15.434	14.079	1.19	1.11	1.22
hcp Mg	3.21,5.21	19	12.731	10.175	1.61	1.52	1.88
fcc Al	4.05	19	47.931	43.709	3.37	3.36	2.98

imental lattice constant.

Problems related with numerical convergence and cluster size will be discussed in detail elsewhere. We just anticipate that for large clusters, i.e., for large n values, it should be better to increase n' as well, in order to avoid in Eq. (2) numerical problems connected with the subtraction of two large and almost equal quantities such as $E_b^{\mathrm{clus}}(n)$ and $E_b^{\mathrm{clus}}(n-1)$. In this way one can easily check that our results are insensitive within a few percent, which is our method's accuracy, to the cluster size. We report here, e.g., that a 47-atom cluster calculation for C and Si produces E_b^{cry} values of 7.76 and 4.52 eV, respectively, to be satisfactorily compared with those of Table IV.

In summary we have shown the possibility of obtaining a reliable and reasonably accurate estimate of the crystal binding energy without using large cluster sizes, with obvious computational advantages. Our approach is accurate enough to bear comparison with pseudopotential calculations, with the added benefit of a direct computation of the binding energy. We stress that, even though approximate, the above calculations are completely parameter-free, no other input being required than atomic number and the chosen symmetry. A further interesting feature is that, whenever there is a discrepancy between experiment and first-principles LDA-based computations, our results closely follow the theoretical values. Finally, we stress that all the above results have been obtained by using just VAX-class minicomputers, namely, models DEC 11/750 and 6410. This should encourage extending the same method to systematic investigations on entire families of compounds.

This work was partially supported by CNR (PF#89.00006.69).

---

[1] For a review on LDA calculations see, e.g., R. O. Jones and O. Gunnarson, Rev. Mod. Phys. **61**, 689 (1989).

[2] R. Magri, J. E. Bernard, and A. Zunger, Phys. Rev. B **43**, 1593 (1991).

[3] D. E. Ellis and G. S. Painter, Phys. Rev. B **2**, 2887 (1970).

[4] B. Delley, D. E. Ellis, A. J. Freeman, E. J. Baerends, and D. Post, Phys. Rev. B **27**, 2132 (1989).

[5] G. L. Goodman, D. E. Ellis, E. E. Alp, and L. Soderholm, J. Chem. Phys. **91**, 2983 (1989).

[6] F. Casula, W. Andreoni, and K. Maschke, J. Phys. C **19**, 5155 (1986).

[7] Strictly speaking, it fails to distinguish between cubic and hexagonal diamond, but to achieve such a fine distinction is clearly out of the reach of our approach.

[8] V. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[9] F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 244 (1944).

[10] M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982).

[11] *CRC Handbook of Chemistry and Physics,* edited by R. C. Weast (CRC, Boca Raton, FL, 1988), p. D-50.

[12] R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1963), Vol. 1.

[13] J. R. Chelikowsky, Phys. Rev. B **21**, 3074 (1980).

[14] P. K. Lam and M. L. Cohen, Phys. Rev. B **24**, 4224 (1981).

[15] M. T. Yin and M. L. Cohen, Phys. Rev. B **24**, 6121 (1981).

[16] J. Ihm and M. L. Cohen, Phys. Rev. B **23**, 1576 (1981).