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Calculation of theoretical strengths and bulk moduli of bcc metals

Y. Song,* R. Yang, and D. Li
Titanium Alloy Laboratory, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110015, China

W. T. Wu
State Key Laboratory for Corrosion and Protection, Institute of Corrosion and Protection of Metals, Chinese Academy of Sciences, 62 Wencui Road, Shenyang 110015, China

Z. X. Guo
Department of Materials, Queen Mary & Westfield College, University of London, Mile End Road, London E1 4NS, United Kingdom

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A first-principles method based on the local-density approximation using discrete variational clusters has been used to study the electronic structure of bcc metals, Li, Na, K, V, Nb, Ta, Cr, Mo, and W. The binding energy of these metals was calculated, and the relationship between the binding energy and the volume of a unit cell for a given metal was determined. The results show that the contribution of the interaction beyond the third nearest-neighbor atoms to the binding energy is small for transition metals, but large for alkali metals. The theoretical triaxial tensile strength and bulk modulus of these metals were estimated from the electronic structure and binding-energy calculations. The present results of the bulk modulus for Li, Na, K, Nb, Ta, Mo, and W are in good agreement with experiments and other available theoretical data, but the bulk modulus for V and Cr is somewhat overestimated. The theoretical strength obtained in the present work is in good agreement with the results of the linear muffin-tin-orbitals method. [S0163-1829(99)14521-1]

I. INTRODUCTION

By means of first-principles self-consistent calculations, it is now possible to calculate readily the binding energy vs volume curves for a group of atoms on a given lattice. Analysis of such curves for elements and for simple alloys yields theoretical ground-state properties such as cohesive energy, bulk modulus, and strength. The strength of an ideal crystal sets an upper limit of attainable stresses, and a knowledge of it is useful for the estimation of ideal work of fracture stresses needed for homogeneous nucleation of dislocations. Most calculations of the theoretical strength have been based on empirical potentials with the parameters adjusted to the experimental data corresponding to the equilibrium ground state. However, the theoretical strength is usually associated with an inflexion point on the total-energy curve in relation to deformation parameters, which is far from the equilibrium state. The calculation of ideal strength from first-principles electronic structure is rarely reported. Recently, Sandera *et al.* have conducted a calculation of ideal strength for some pure metals by using the linear muffin-tin-orbitals method.[1] The authors of this paper have estimated the theoretical strength of some practical and hypothetical binary β-type titanium alloys based on the calculations of electronic structure with the discrete variational cluster method.[2–4]

Elastic modulus is another quantity that determines the response of a crystal to external forces. The shear modulus provides valuable information on the bonding characteristics between adjacent atomic planes and the anisotropic character of the bonding. There are some calculations of bulk and shear moduli for pure metals with tight-binding interatomic potentials[5,6] and full-potential,[7] for intermetallic compounds with the full-potential linear-muffin-tin-orbital method,[8] and for practical and hypothetical β-type titanium alloys.[2–4]

In this paper, the electronic structure and binding energy of some bcc metals, Li, Na, K, V, Nb, Ta, Cr, Mo, and W, are calculated using the discrete variational cluster method. The theoretical strength and bulk modulus are estimated, and compared with experimental data and with relevant theoretical values obtained by other methods.

II. METHOD OF CALCULATION

The discrete variational cluster method (DVM) was originally introduced by Ellis and his co-workers.[9] Detailed documentation of the DVM can be found elsewhere,[9,10] so only the details pertinent to this work are given here. The clusters are chosen so that they contain 35 atoms including the fourth-nearest neighbors for light elements, such as Li, Na, K, V, and Cr, but only contain 15 atoms including the second-nearest neighbors for heavy elements owing to limited computing power. Both core states and valence states are treated nonrelativistically. The exchange-correlation interaction is represented by the Hedin-Lundqvist function for non-spin-polarized systems.[11] The elements of the Hamiltonian matrix and the overlap integrations are calculated by a weighted sum over a set of sampling points, and the number of the sampling points for the considered systems is 27 000 in the present calculations. The self-consistent charge approximation is introduced and the convergence criterion of charge self-consistent integration is chosen as lower than 10^{-4}.

Binding energy E_b^s is estimated from the difference between the total energy of the system under consideration and the sum of energies of all the atoms constituting the system, i.e.,

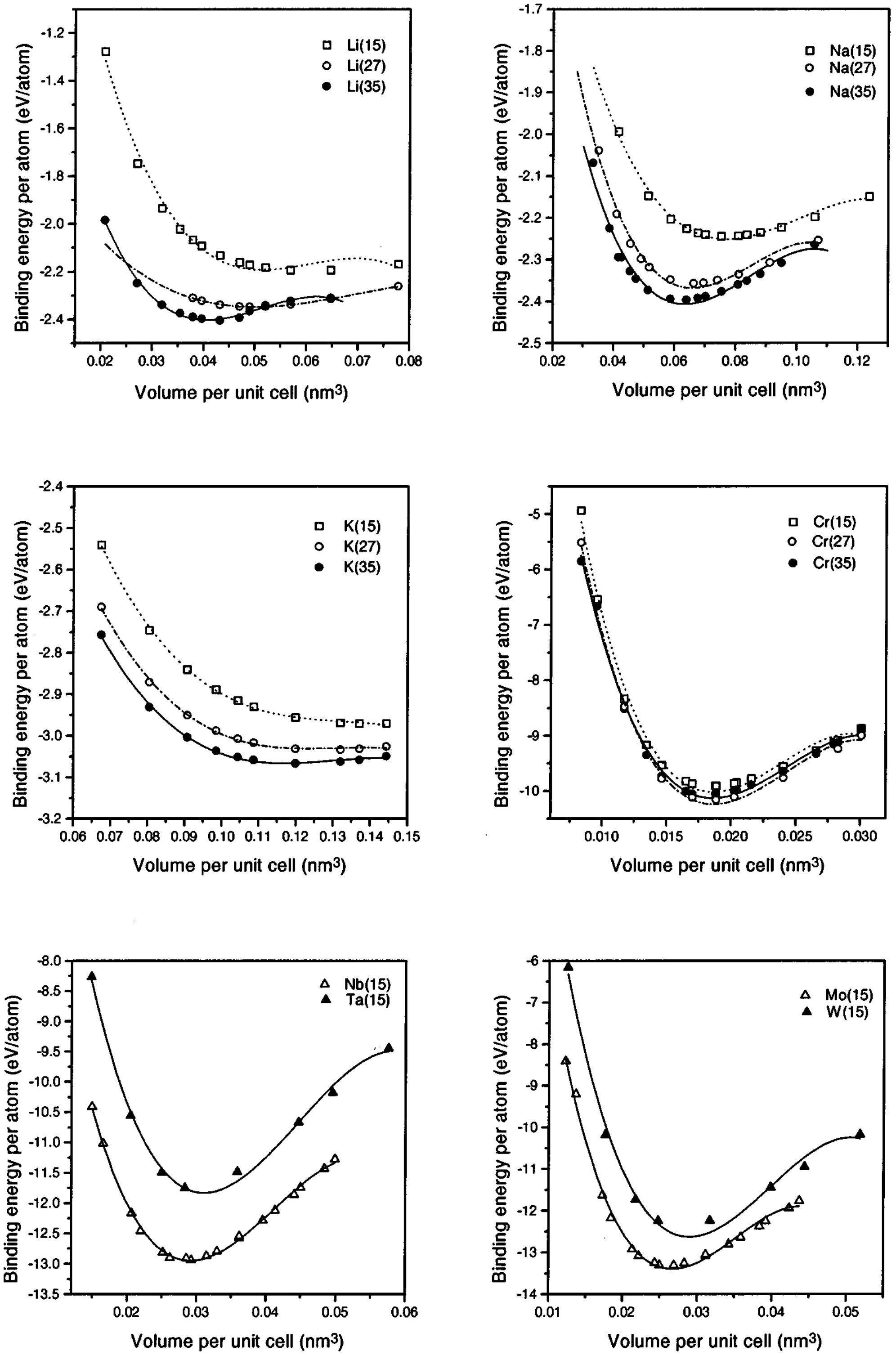

FIG. 1. Calculated binding energy per atom as a function of the unit-cell volume. The number in brackets indicates the number of atoms in the cluster employed here.

$$E_b^s = E_{\mathrm{tot}} - \sum_i E^i_{\mathrm{atom}} . \tag{1}$$

For bcc crystals, the relationship between binding energy and the volume of a unit cell is determined by calculating the binding energy as a function of the hydrostatic strain ϵ that transforms the lattice vectors according to

$$\mathbf{a}' = \begin{pmatrix} 1+\epsilon & 0 & 0 \\ 0 & 1+\epsilon & 0 \\ 0 & 0 & 1+\epsilon \end{pmatrix} \mathbf{a}, \tag{2}$$

where $\mathbf{a}'$ and $\mathbf{a}$ are the new and old lattice vectors, respectively.

TABLE I. Comparison of calculated lattice constant a^c with experimental lattice constant a^e. The experimental data are taken from Ref. 16.

Metal	a^c(nm)	a^e(nm)	$\lvert(a^e-a^c)/a^e\rvert$(%)
Li	0.3471	0.3508	1.1
Na	0.4094	0.4291	4.6
K	0.4932	0.5344	7.7
V	0.2805	0.3026	7.3
Nb	0.3079	0.3294	6.5
Ta	0.3144	0.3303	4.8
Cr	0.2650	0.2884	8.1
Mo	0.2988	0.3147	5.1
W	0.3072	0.3165	2.9

Theoretical strength is related to the maximum force which may be applied to the material without perturbing its stability. In order to determine the theoretical triaxial tensile strength, the electronic structure was calculated under the condition given by Eq. (2) at zero temperature ($T=0$ K). The internal pressure was calculated according to $p=-dE_{\mathrm{tot}}/dV$, and the external stress $\sigma=-p$. The theoretical strength of triaxial tension can, therefore, be estimated by the relation[1]

$$\sigma_{\mathrm{th}}=n\frac{dE_b(V)}{dV}\bigg|_{V=V_i}, \tag{3}$$

where E_b is the binding energy per atom ($E_b=E_b^s/N$, N is the total number of atoms in the considered cluster system), V is the volume of a unit cell, V_i is the volume of a unit cell at the inflexion point of the binding-energy curve, and n is the number of atoms in the unit cell. The bulk modulus is determined as

$$B=nV\frac{d^2E_b(V)}{dV^2}\bigg|_{V=V_0}, \tag{4}$$

where V_0 is the volume of the unit cell at the equilibrium point.

TABLE II. Bulk modulus B (GPa): comparison of our results of discrete variational cluster method (DVM) with tight-binding total energy (TB) calculations, first-principles local-density approximation (LDA) results, pseudopotential model (PM) calculations, and experiment (Expt.).

	Theory				Experiment
Metal	DVM	TB [a]	LDA [a]	PM [b]	Expt. [c]
Li	10.6			13.5	11.57
Na	6.96			7.52	6.81
K	3.07			3.72	3.18
V	205	211	196		162
Nb	166	187	193		170
Ta	188	185	224		200
Cr	308	283			190
Mo	263	282	291		272
W	286	319	333		323

[a] Reference 6.

[b] Reference 12.

[c] Reference 13.

TABLE III. Calculated theoretical strength σ_{th} (GPa) as compared to values calculated by other methods (Ref. 1).

	First principles		Semiempirical theory		
Metal	DVM	LMTO [a]	Sinus [a]	Morse [a]	Polynomial [a]
Li	1.92				
Na	1.77	1.72	1.86	1.20	1.86
K	0.10				
V	38.3				
Nb	34.1				
Ta	41.3				
Cr	47.4				
Mo	42.2				
W	53.1	57.4	80.1	42.4	58.9

[a] Data taken from Ref. 1.

III. NUMERICAL RESULTS AND DISCUSSION

A. Binding energy

Using the method described above, we calculated the electronic structure and the binding energy of bcc metals, Li, Na, K, V, Nb, Ta, Cr, Mo, and W. The calculated binding-energy data are shown in Fig. 1. The curves of the binding energy plotted against the volume of the unit cell were obtained by means of a polynomial fit. The polynomial fit was truncated after the third-order term. The correlation coefficient is in the range of 0.9960–0.9997. To investigate the contribution of the interaction beyond the third-nearest-neighbor atoms to the binding energy, the calculations for Li, Na, K, V, and Cr were performed by using the cluster that contains 15 atoms including the second-nearest-neighbor atoms (shown by open squares in Fig. 1), 27 atoms including the third-nearest-neighbor atoms (open circles in Fig. 1), and 35 atoms including the fourth-nearest-neighbor atoms (solid circles in Fig. 1), respectively. The alkali metals have one s valence electron and the interaction between the valence electron and the nucleus in alkali metals is weak. The characteristics of the interactions can be seen in Fig. 1. For alkali metals, the large separation between the curves in Fig. 1 indicates that the contribution from the interaction of the third- and fourth-nearest-neighbor atoms to the binding energy per atom cannot be ignored. For transition metals, on the other hand, the influence of these interactions on the binding energy per atom is smaller than that for alkali metals (Fig. 1). So in the present calculations, the cluster is chosen so that it contains 35 atoms including the fourth-nearest-neighbor atoms for light elements, Li, Na, K, V, and Cr, but only contains 15 atoms including the second-nearest-neighbor atoms for heavy elements, Nb, Mo, Ta, and W, mainly because of limited computing power. Fortunately, the contribution of the interactions beyond the third-nearest-neighbor atoms to the binding energy per atom is not so large and, therefore, does not seriously influence the accuracy of

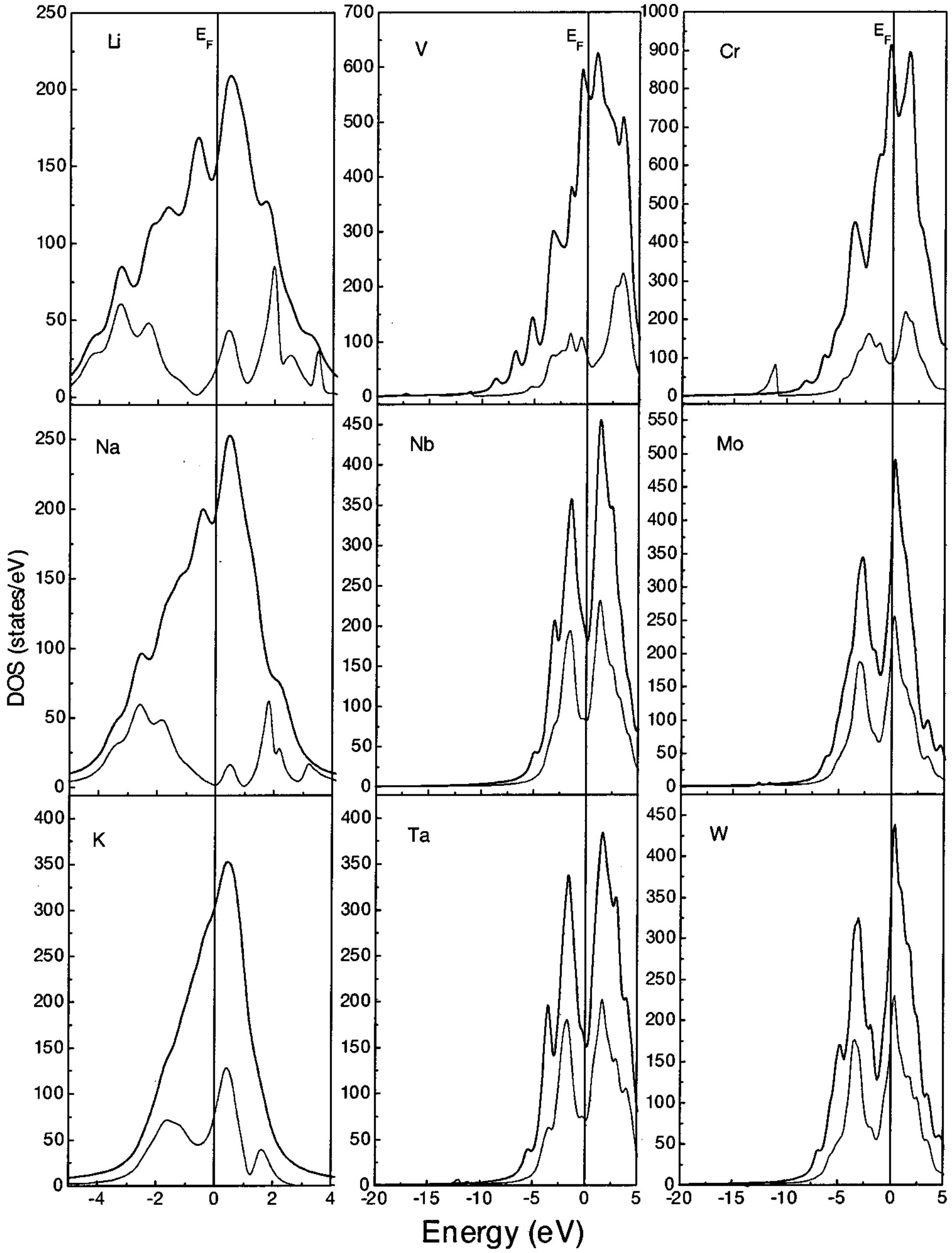

FIG. 2. Total (thick curve) and local (thin curve) density of states of the center atom at the equilibrium states of some bcc metals.

the calculations, as is clearly seen in the case of Cr illustrated in Fig. 1. The calculated lattice constants, obtained from the binding energy vs volume curves in Fig. 1, are compared with experiments in Table I. The calculated results underestimate the lattice constants by as much as 8.1%. It is noted that the errors in the lattice constants calculated in the present work are larger than that with the standard local-density approximation (LDA) approaches, which is typically less than 3% for transition metals.[15] In the *k*-space LDA approaches, a super unit cell is chosen to simulate a bulk material under periodic boundary conditions. In the DVM, however, an atomic cluster with the same structure as the bulk material is used to perform the simulation, without applying the periodic boundary conditions. In practical DVM calculation, interactions beyond a certain nearest-neighbor atomic shell are usually ignored (for example, beyond the fourth-nearest-neighbor shell for alkali metals in the present calculation). This procedure would cause an overestimation of the interactions between atoms included in the cluster, resulting in an underestimation of the lattice constants as compared to the *k*-space LDA approaches.

B. Bulk modulus and theoretical strength

The results of calculation for the bulk modulus are listed in Table II. The bulk modulus and theoretical strength are estimated with the binding energy vs volume curves obtained using the 35-atom cluster for Li, Na, K, V, and Cr, and the 15-atom cluster for Nb, Mo, Ta and W, respectively. For comparison, the theoretical values obtained by the tight-binding total energy (TB) calculations,[6] the first-principles local-density approximation calculations,[6] the pseudopotential model calculations[12] and the experimental modulus measurements[13] are also listed. In the present paper, the bulk modulus was calculated at the theoretical equilibrium volume, obtained by minimizing the binding energy per atom. The present bulk moduli are in good agreement with experimental measurements within 10% for alkali metals Li, Na, K, and for $4d$ and $5d$ transition metals, Nb, Mo, Ta, and W, the exception being for $3d$ transition metals V and Cr. The calculated bulk moduli for V and Cr show a large discrepancy with experiments, but are in good agreement with the TB and LDA results within 5%. The large discrepancy for $3d$ transition metals might be due to the poor treatment of the $3d$ states. The results are expected to improve if the generalized gradient approximation[14] for the exchange-correlation function is used.

The possibilities of experimental verification of calculated theoretical triaxial tensile strength are rather limited. There are some theoretical results based on the semiempirical potential, but few studies were based on first-principles calculations.[1] The present results of the theoretical strengths of bcc metals, Li, Na, K, V, Nb, Ta, Cr, Mo, and W, are listed in Table III. The semiempirical results and the linear muffin-tin orbitals-atomic-sphere approximation calculations are also listed in this table. The present results, obtained with the DVM, are in good agreement with available data obtained in other theoretical calculations for Na and W.

C. Electronic structure

The ideal strength of materials is ultimately due to the atomic bonding strength. The shearing along a certain direction involves the stretching of bonds, and the termination of the elastic regime involves the breaking of bonds. In order to gain insight into the microscopic origin of the bonding between atoms, it is helpful to examine the total density of states (DOS). In Fig. 2, we plot the total and local density of states for the bcc metals investigated here. The thick and thin curves indicate the total density of states and the local density of states at the central atom, respectively. It can be seen from Fig. 2 that the amplitude of the total DOS is higher than that obtained by Moruzzi *et al.*[15] This might be due to an insufficient number of atoms in the clusters used to simulate the bulk materials in the present work. Another feature seen in Fig. 2 is that the total DOS is different from the local DOS at the central atom. This means that the surrounding atoms have an effect on both the shape and the amplitude of the total DOS. It can be seen from Fig. 2 that the difference between the total and local DOS is larger for alkali metals Li, Na, and K than for $4d$ and $5d$ transition metals Nb, Mo, Ta, and W. This implies that the influence of the surrounding atoms on the total DOS reduces with the number of electrons of the metals, consistent with the results of binding-energy calculations (Fig. 1). A further point worth clarifying relates to the shape of the DOS curves. As shown by the work of Moruzzi *et al.*,[15] the DOS in alkali metals is parabolic in shape, and no peaks should be present under the Fermi level. To identify the origin of the abnormal peaks seen in Fig. 2, we have studied the variation of the shape of the total DOS in lithium with the cluster size. The results show that the amplitude of the abnormal peaks under the Fermi level reduces with increasing number of atoms in the cluster; but the peaks are still present for a cluster containing as many as 59 atoms. We, therefore, conclude that these small peaks are due to a deficiency of the method used in the present work. The foregoing discussion also suggests that the total DOS is more representative of the electronic structure of the metals investigated in this work. For transition metals, there exists a valley near the Fermi energy level separating the bonding and antibonding states, and the depth of the valley increases with the number of valence electrons in the metals. In general, the deeper the valley, the stronger the bonds between the atoms.

IV. CONCLUSIONS

The electronic structure and binding energy of bcc metals, Li, Na, K, V, Nb, Ta, Cr, Mo, and W, were calculated using the first-principles discrete variational cluster method based on the local-density approximation. The relationship between the binding energy and the volume of a unit cell was determined for the group of metals. The results show that the contribution of the interaction beyond the third nearest-neighbor atoms to the binding energy is small for transition metals, but is relatively large for alkali metals. The ideal strength and bulk modulus of these metals were estimated on the basis of the binding-energy curves. It was found that the strength and modulus of both the alkali and transition metals are determined by the characteristics of bonding between atoms. The bonding feature can be qualitatively described by the total density of states in metals. The resulting predictions of modulus and theoretical strength from the present work compared reasonably well with experiments and with other available theoretical work in the literature. This suggests that the DVM is a suitable method for the investigation of the mechanical properties of metals, even though the atomic configuration is far from the equilibrium state.

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*Also at the State Key Laboratory for Corrosion and Protection, Institute of Corrosion and Protection of Metals, Chinese Academy of Sciences, 62 Wencui Road, Shenyang 110015, China.

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