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Calculations showing a correlation between electronic density and bulk modulus in fcc and bcc metals

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The linearized augmented-plane-wave method is used to study the electronic density n_{WS} at the boundary of the Wigner-Seitz cell for bcc and fcc elemental metals. The calculated n_{WS} is generally in good agreement with the results derived from an empirical formula that was introduced by Miedema and co-workers. A formula is introduced to calculate the bulk modulus of materials using n_{WS}, and from it another formula for calculating the relationship between the external pressure and the volume of materials is derived. As an example, the pressure-volume compression curve for Cu is calculated. The limitations and features of the conventional method and our method for calculating the bulk modulus of materials are discussed.

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I. INTRODUCTION

The electronic density n_{WS} at the boundary of the Wigner-Seitz cell was introduced by Miedema, de Boer, and de Chatel[1] as a parameter to calculate the heat of formation ΔH of alloys through the formula

$$\Delta H = f(c)\{-P(\Delta\Phi)^2 + Q(\Delta n_{\mathrm{WS}}^{1/3})^2\}, \tag{1}$$

where $f(c)$ is an unknown function of the concentration and the proportionality constants P and Q do not depend on the type of metal system considered. $\Delta\Phi$ is the work function difference and Δn_{WS} is the difference in electronic density at the boundary of the Wigner-Seitz cell between the pure elemental metals. The work function of a material can be determined by experiments. However, measurement of the electronic density n_{WS} at the boundary of the Wigner-Seitz cell is difficult from experiment. Thus Miedema *et al.* did not use direct experimental information about n_{WS}. An empirical relationship between the bulk modulus B and the theoretical n_{WS} from five alkali metals was extended to other elemental metals in their calculations. The scheme successfully predicts the signs of ΔH for 500 binary alloys constructed from 53 metallic elements.

n_{WS} is also used to predict the crystal structure,[2] solid solubility for a specific solvent, heat of mixing of liquid alloys,[3] and melting points of metals.[4] Chelikowsky[5] successfully plotted the solid solubility maps of most elements in Mg, Pb, Be, Zn, Cd, Tl, and Hg with Miedema coordinates. n_{WS} is also used to describe the electronegativities[6,7] of metals, which can be compared with other methods by Pauling.[8] St. John and Bloch,[9] and Phillips and co-workers.[2,4,10]

Miedema *et al.*'s empirical results have been used in many calculations.[2,5,11,12] However, results for n_{WS} calculated from first principles are absent in the literature. In this paper, the linearized augmented-plane-wave (LAPW) method is used to calculate n_{WS} for all bcc and fcc pure elemental metals except the rare-earth elements. The calculated results are remarkably consistent with the empirical results of Ref. 1. Knowing either the bulk modulus B or n_{WS}, one can exactly deduce the other one. Hence a formula that is used to calculate the bulk modulus is introduced. n_{WS} under different uniform hydrostatic pressure strains is also calculated for Cu. Based on these results, a pressure-volume compression curve is plotted. Explanation of this empirical formula from the point of view of quantum mechanics will be the next challenge, which will help us to have a better understanding of the existence of such a relationship and its physical meaning.

The outline of the paper is the following. In Sec. II we give a brief overview of the computational approach. Then in Sec. III n_{WS} of pure elemental metals is calculated. In Sec. IV we investigate the relationship between the pressure and the volume of Cu by calculating n_{WS} under different uniform hydrostatic pressure strains. A discussion and concluding remarks are given in Secs. V and VI, respectively.

II. COMPUTATIONAL DETAILS

The LAPW method[13–15] is based on local-density-functional theory.[16,17] The essential idea of the method is to divide real space into different regions, namely, spheres around the nuclei and the remaining interstitial region. In each of these regions the natural form of the variational basis functions is adopted, that is, plane waves in the interstitial region, and a product of radial functions and spherical harmonics inside the spheres. In this method there are no empirical parameters. This theory involves only one approximation, namely, the assumed form of the density functional for the exchange and correlation energy treated within the local-density approximation. The Hedin-Lundqvist exchange-correlation potential[18] is adopted. The experimental lattice constants are used in our calculations. The representative points in the Brillouin zone are chosen according to the special points scheme.[19] Self-consistent convergence calculations were performed for a 216-*k*-point mesh in the irreducible portion (1/48) of the Brillouin zone. Convergence is assumed when the average root-mean-square differences between the input and output charge are less than $1\times10^{-5}\ e/(\mathrm{a.u.})^3$.

TABLE I. The calculated and empirical values of n_{WS}.

Metal	Calculated n_{WS} $[10^{-2}e/(\mathrm{a.u.})^3]$	Empirical n_{WS} $[10^{-2}e/(\mathrm{a.u.})^3]$	V_m[a] (cm^3/g-at.)	B[a] (10^6 kg/cm^2)
Li	0.76	0.77	13.1	0.118
Na	0.43	0.44	23.8	0.069
K	0.24	0.22	45.6	0.033
Rb	0.19	0.19	56.1	0.032
Cs	0.15	0.14	69.2	0.021
Ca	0.73	0.6	26.2	0.155
Sr	0.57	0.5	33.9	0.118
Ba	0.56	0.4	38.1	0.105
Ac	0.94			
V	3.63	3.68	8.36	1.651
Nb	3.45	3.21	10.8	1.736
Ta	3.67	3.56	10.8	2.04
Cr	4.29	4.25	7.23	1.94
Mo	4.22	4.46	9.39	2.779
W	4.65	4.81	9.55	3.296
Fe	3.82	4.0	7.09	1.716
Rh	4.20	4.73	8.29	2.758
Ir	4.88	5.34	8.52	3.62
Ni	3.89	4.4	6.59	1.90
Pd	3.36	3.7	8.88	1.844
Pt	4.06	4.6	9.09	2.838
Cu	3.22	3.55	7.11	1.335
Ag	2.41	2.53	10.3	0.981
Au	3.05	3.4	10.2	1.766
Pb	1.46	1.3	18.3	0.438
Al	2.53	2.2	10.0	0.736

[a] Reference 20.

The calculations of n_{WS} were performed after the above self-consistent convergence calculations were finished. Because of the symmetry, the electronic density in the irreducible portion (1/48) of the surface of the Wigner-Seitz cell is calculated. The irreducible portion is divided into thousands of regions with equal areas in order to ensure that they have the same weight in the n_{WS} calculations. One point represents a region. The number of small regions was increased until the variation of the calculated n_{WS} was converged within $1\times10^{-5}e$. In all calculations we used 2583 points in the irreducible portion. The mathematical mean value of 2583 points was calculated to represent the electronic density n_{WS} at the boundary of the Wigner-Seitz cell.

III. CALCULATED AND EMPIRICAL n_{WS} FOR PURE ELEMENTAL METALS

Miedema *et al.*[1] assumed that the valence electrons could be considered to have an approximately uniform density throughout the atomic cell for five alkali metals. In that simple case the electron density at the Wigner-Seitz cell boundary was given by the ratio of the number of valence electrons per atom (N_0) and the atomic volume (V_m). The spatial distributions of the electrons of Fe, Cu, and Al were given by experiments or calculations at that time. From these eight values an empirical formula for calculating n_{WS} was developed:

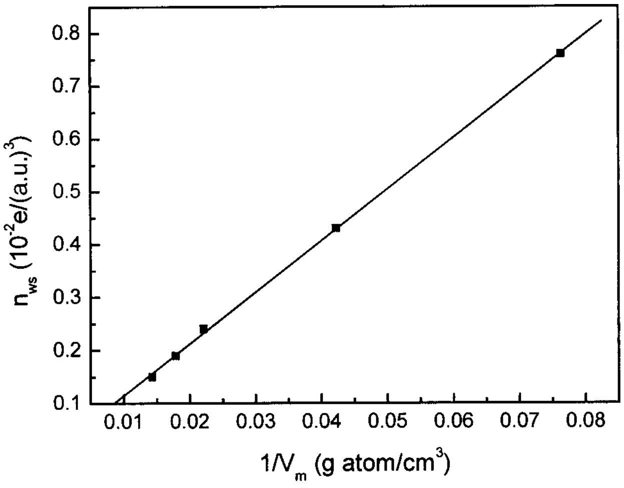

FIG. 1. Relation between the electronic density at the boundary of the Wigner-Seitz cell and the atomic volume for five alkali metals.

$$n_{\mathrm{WS}}=0.82\times10^{-4}(B/V_m)^{1/2}, \qquad (2)$$

where B is the bulk modulus in kg/cm^2, V_m is the atomic volume in cm^3/g-at., and n_{WS} is the electronic density in $e/(\mathrm{a.u.})^3$ at the boundary of the Wigner-Seitz cell.

The electronic density n_{WS} calculated by the LAPW method, the experimental bulk modulus B, the atomic volume V_m, and the empirical n_{WS} are listed in Table I. It is seen that the deviations between the n_{WS} calculated from first principles and the empirical n_{WS} calculated from Eq. (2) are mostly less than 5%. For some transition metals the errors become larger, but all of them are also within 15%.

In Fig. 1 the calculated n_{WS} is plotted versus atomic volume for five alkali metals in the 1A group. From the figure, it is seen that n_{WS} in the 1A group is inversely proportional to atomic volume, which indicates that the assumption of Miedema *et al.* is reasonable. For other elemental groups, the smaller differences between their ionic and atomic radii and the larger number of valence electrons result in nonuniform electron density throughout the atomic cell, and sometimes in the same group the configurations of the valence electrons are also different. These factors make the variations of n_{WS} complex, not simply inversely proportional to the atomic volume.

By a simple transform from Eq. (2) we have

$$B=\frac{1}{(0.82\times10^{-4})^2}V_m n_{\mathrm{WS}}^2=(1.487\times10^8)V_m n_{\mathrm{WS}}^2. \qquad (3)$$

It is known that the physical meaning of the atomic volume V_m is the volume per mole of elements, so the atomic volume V_m can be calculated in a cubic cell through the formula

$$V_m=\frac{6.02\times10^{23}}{n}(a\times10^{-8})^3=\frac{0.602}{n}a^3 \quad (\text{cm}^3/\text{mol}), \tag{4}$$

where 6.02×10^3 is Avogadro's number, n is the number of atoms in a cell (2 and 4 for bcc and fcc metals in the present study, respectively), and a is the lattice constant in angstroms. From Eqs. (3) and (4) we get

$$B=\frac{0.895\times10^8}{n}a^3 n_{\text{WS}}^2. \tag{5}$$

The units for the bulk modulus B, the lattice constant a, and the electronic density n_{WS} are kg/cm^2, Å, and $e/(\text{a.u.})^3$, respectively.

The magnitude of the bulk modulus reflects whether or not the compression of a material is easy. From Eq. (5) it is clearly seen that the bulk modulus B is proportional to n_{WS}^2. This indicates that the compression or tension of a crystal will closely correlate with the electronic density n_{WS} at the boundary of the Wigner-Seitz cell, or the parameter n_{WS} may be as an excellent index to measure the degree of difficulty of deformation of a material. It is thought that the boundary of the Wigner-Seitz cell is the interface between two atoms; the electrons in the interface are supplied by both atoms. So it is understandable that n_{WS} might reflect the strength of the bond between two atoms and some of the mechanical properties of the metal.

IV. PRESSURE-VOLUME COMPRESSION CURVES AND n_{WS}

The bulk modulus is the reciprocal of the compression coefficient, so one has

$$B=-V\frac{dP}{dV}. \tag{6}$$

From Eqs. (5) and (6), one gets

$$\frac{dP}{dV}=-\frac{0.895\times10^8}{n}n_{\text{WS}}^2. \tag{7}$$

By calculating n_{WS} at different volume, the pressure-volume compression curve can be obtained from Eq. (7). As a typical example, Fig. 2 plots the pressure-volume compression curves for Cu. From Table I it is known that the calculated n_{WS} is lower by about 10% than the empirical result for Cu, so the calculated bulk modulus obtained by Eq. (5) will be lower than the experimental result. If the empirical parameter 0.895 is adjusted to 1.095 in Eq. (5) according to the experimental bulk modulus of Cu, and then the pressure-volume curve is plotted again for Cu, it is found that the calculated compression curve is in good agreement with the experimental curve.[21]

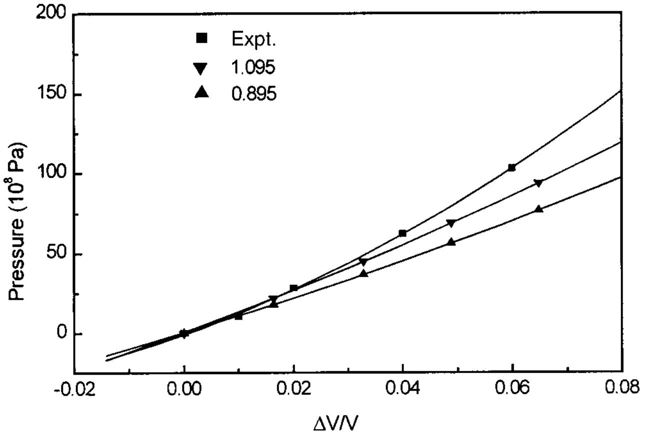

FIG. 2. The calculated and experimental relation between the external pressure and the volume for Cu.

V. DISCUSSION

The bulk modulus of a material is obtained from the curvature of the total-energy–strain curve in the conventional method. The physical meaning of this is clear. However, there exist some limitations in the conventional method. For example, a very accurate total-energy calculation is required, and the calculated results are sensitive to the number of basis functions; in general six or more self-consistent convergence calculations for different uniform hydrostatic pressure strains are required for calculating a bulk modulus. Our method does not have these limitations because the bulk modulus is obtained from n_{WS}, and only one self-consistent convergence calculation is required. Its deficiency is that its physical meaning is unclear.

VI. CONCLUSIONS

In this paper, the LAPW method has been used to study the electronic density n_{WS} at the boundary of the Wigner-Seitz cell for bcc and fcc elemental metals. We found that n_{WS} calculated from first principles is remarkably consistent with the results derived from the empirical formula of Ref. 1. Most differences between the calculated n_{WS} and empirical n_{WS} derived from the Miedema *et al.* empirical formula are less than 5%. A formula has been introduced for calculating the bulk modulus of materials from n_{WS} and the lattice constant. According to this formula and the definition of bulk modulus, we propose a formula to calculate the relationship between the external pressure and the volume of materials. The pressure-volume compression curve for Cu was obtained from the calculated n_{WS}.

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[1] A. R. Miedema, F. R. de Boer, and P. F. de Chatel, J. Phys. F: Met. Phys. **3**, 1558 (1973).

[2] J. R. Chelikowsky and J. C. Philips, Phys. Rev. Lett. **39**, 1687 (1977).

[3] R. Boom and F. R. de Boer, J. Less-Common Met. **45**, 237 (1976); **46**, 271 (1976).

[4] J. R. Chelikowsky and J. C. Philips, Phys. Rev. B **17**, 2453 (1978).

[5] J. R. Chelikowsky, Phys. Rev. B **19**, 686 (1979).

[6] A. R. Miedema, R. Boom, and F. R. de Boer, J. Less-Common Met. **41**, 283 (1975).

[7] A. R. Miedema, J. Less-Common Met. **46**, 67 (1976).

[8] L. Pauling, *Nature of the Chemical Bond*, 3rd ed. (Cornell University Press, Ithaca, NY, 1960).

[9] J. St. John and A. N. Bloch, Phys. Rev. Lett. **33**, 1059 (1974).

[10] E. S. Machlin, T. P. Chow, and J. C. Philips, Phys. Rev. Lett. **38**, 1292 (1977).

[11] Ray H. Baughman, Justin M. Shacklette, Anvar A. Azkhidov, and Sven Stafström, Nature (London) **392**, 362 (1998).

[12] A. R. Miedema, P. F. de Chatel, and F. R. de Boer, Physica B & C **100B**, 1 (1980).

[13] H. Krakauer, M. Posternak, and A. J. Freeman, Phys. Rev. B **19**, 1706 (1979).

[14] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981).

[15] H. Jansen and A. J. Freeman, Phys. Rev. B **30**, 561 (1984).

[16] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[17] W. Kohn and L. J. Sham, Phys. Rev. A **140**, A1133 (1965).

[18] L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).

[19] D. J. Chadi and M. L. Cohen, Phys. Rev. B **8**, 5747 (1973); S. Froyen, *ibid.* **39**, 3168 (1989).

[20] K. A. Gschneidner, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1967), Vol. 16, p. 275.

[21] D. E. Munson and L. M. Barker, J. Appl. Phys. **37**, 1652 (1966).