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Compressibility and Binding Energy of the Simple Metals*

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A straightforward calculation of the compressibility, binding energy, and density of the simple metals yields good agreement with experiment. Effects of band structure are included in the perturbation theory, using an electron-ion interaction fitted to experimental data in the region of the zone faces.

I. INTRODUCTION

ALTHOUGH the electron-gas compressibility, when measured in units of the noninteracting electron-gas compressibility, is an increasing function[1,2] of r_s (see Fig. 1), the experimentally observed compressibilities for simple metals strongly show the opposite trend. The quantity r_s is, as usual, given by $\frac{4}{3}\pi r_s^3 = n^{-1}$, where n is the electronic density. It is well known, of course, that the ions play an important role in determining the compressibilities K of metals, and, in fact, detailed and quite accurate calculations have been made in isolated cases.[3] These calculations fall into two general classes: Those based on cellular methods, and those based on perturbation theory. The former have two distinct disadvantages: (1) They are complicated, must be applied to each metal separately, and hence do not elucidate the trend shown in Fig. 1; (2) They cannot be readily extended to polyvalent metals. On the other hand, there has been no assurance in the past that the latter method is sufficiently accurate to treat volume-dependent properties.

Here, we present a *simple* calculation, based on perturbation theory, of the total energy and hence the compressibility of the nearly-free-electron metals.[4] For the alkalis, our results are of accuracy comparable to that of the cellular methods for both binding energy and compressibility. Moreover, we find good agreement for polyvalent metals where few previous calculations exist. The accuracy and simplicity of our methods may be attributed to: (1) Use of a simple analytic form for the electron-ion potential fitted to metallic data near Bragg reflection planes; (2) The utilization of the zero-pressure condition to eliminate the less accurately known zeroth Fourier coefficient of this potential. Thus, we are able to derive simple formulas for the binding energy and compressibility, which apparently apply to all simple metals. Finally, we expect that similar considerations will be useful for a number of other solid-state properties; for example, calculations of phonon spectra.

II. CALCULATION

In addition to the usual kinetic, exchange, and correlation energies, the energy of a solid contains terms resulting from the electron-ion and ion-ion interaction. Our basic assumption is that band-structure effects can be included in perturbation theory. But the zeroth Fourier coefficient of the electron-ion potential is never small and must be treated exactly. Its contribution to the energy[5] is comprised of the potential field of the ions plus the Coulomb field of the other electrons, and may be written as $\alpha/\frac{4}{3}\pi r_s^3$, where

$$\alpha = \frac{1}{Z} \lim_{k\to 0}\left(V_k + \frac{8\pi Z}{k^2}\right). \tag{1}$$

Here Z is the valence, and V_k is the kth Fourier coeffi-

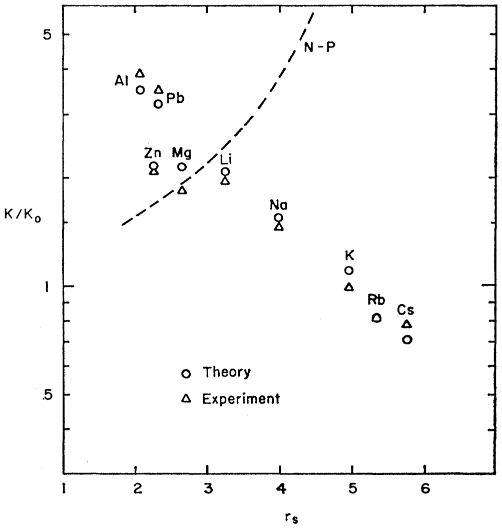

FIG. 1. Comparison of experimental and theoretical values of the compressibility K, measured in units of the free-electron compressibility, $K_0 = 1.7 r_s^5$, where $\frac{4}{3}\pi r_s^3 = n^{-1}$. The dashed line is the interacting electron-gas compressibility, according to the Nozières-Pines interpolation formula (Ref. 1).

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[1] D. Pines and P. Nozières, *The Theory of Quantum Liquids* (W. A. Benjamin, Inc., New York, 1966), Vol. I.

[2] We use atomic units throughout: $\hbar = 2m = e^2/2 = 1$.

[3] See, for example, J. Bardeen, J. Chem. Phys. **6**, 367 (1938), and, for recent reviews: H. Brooks, Trans. Met. Soc. AIME **227**, 546 (1963); F. S. Ham, Solid State Phys. **1**, 127 (1955); H. B. Huntington, *ibid.* **7**, 213 (1958); and W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

[4] By this we mean metals with principally parabolic band structure, and specifically exclude in this paper any discussion of the noble and transition metals.

[5] By energy we always mean energy per electron.

cient of the bare interaction of an electron with a single ion. That (1) is positive is of no concern, because we have included the electron-electron contribution twice; half of the latter is automatically subtracted again if we write the ion-ion interaction energy as[6]

$$\tfrac{1}{2}\sum_{k\neq 0}\frac{8\pi Z}{k^2}[S(k)-1], \tag{2}$$

where $S(k)$ is the structure factor for the ionic arrangement: $S(k)=\langle\rho_k\rho_{-k}\rangle/N$, where ρ_k is the kth Fourier coefficient of the ionic density, and N is the total number of ions. For hcp, fcc, and bcc structures, the numerical value of this term[7] is $-1.792Z^{\frac{2}{3}}/r_s$; for a liquid metal we obtain[8] $-1.73Z^{\frac{2}{3}}/r_s$.

Band-structure effects add a term

$$E_B=\tfrac{1}{2}\sum_G\frac{G^2}{8\pi Z^2}|V_G|^2\left(\frac{1}{\epsilon_G}-1\right)n \tag{3}$$

to the energy, where ϵ_k is the Lindhard[1] dielectric function, and the sum extends over all nonzero reciprocal-lattice vectors G. The term (3) is readily derived in second-order perturbation theory treating screening in the Hartree approximation.[9] Further, we note that (3) may be written down immediately using the following considerations. According to the definition of the dielectric coefficient, the electronic-density fluctuation induced by ρ_k is

$$\rho_k{}^{\text{ind}}=(\epsilon_k{}^{-1}-1)(k^2V_k/8\pi)\rho_k.$$

This, in turn, acts back on the lattice with interaction energy

$$\tfrac{1}{2}\sum_{k\neq 0}\rho_kV_k\rho_{-k}{}^{\text{ind}}.$$

For a lattice of equivalent ions $\rho_{-k}\rho_k=N^2\delta_{k,G}$, so that (3) follows immediately. For the band parameters V_G, we have used a form recently proposed by one of us[10], namely,

$$V_G=(-8\pi Z/G^2)\cos|G|r_c, \tag{4}$$

where r_c is a radius close to the radius of the free ion. This form of the electron-ion interaction is known to give consistent results for Fermi surface and transport properties in simple metals, and for the ionization energies of the free atoms. We note that of the existing pseudopotentials, (4) is at least of comparable accuracy and is considerably easier to use. Pertinent values, given in Table I, are deduced from metallic data, as outlined in Ref. 10.

TABLE I. Values of r_c used in Eq. (4) (atomic units). The entries in the first column were deduced from Fermi-surface data, while those in the second column were derived from transport properties of the liquid. The value $r_c=2.00$ also fits the resistivity of liquid Li, but gives poor agreement for K/K_0 and E_g.

Metal	r_c	Metal	r_c
K	2.14	Li	1.06
Rb	2.61	Na	1.67
Al	1.12	Cs	2.93
Pb	1.12	Mg	1.39
...	...	Zn	1.27

The total energy of the solid can now be written

$$E=\frac{2.21}{r_s{}^2}-\frac{0.916}{r_s}-(0.115-0.031\ln r_s)-\frac{1.792Z^{\frac{2}{3}}}{r_s}+\frac{3\alpha}{4\pi r_s{}^3}+E_B, \tag{5}$$

where the first three terms are, respectively, the kinetic, exchange, and correlation energies, and atomic units are used throughout. For the latter, we arbitrarily choose the Nozières-Pines form,[1] noting that none of the several existing interpolation formulas differ by more than 10% over the range of r_s appropriate to Table I. If we assume that the zeroth Fourier component of the potential is also given accurately by Eq. (4), the limit (1) gives $\alpha=4\pi r_c{}^2$. Then the equilibrium condition $dE/dr_s=0$ predicts values of r_s in fair agreement with the observed densities. For calculations of the compressibility and binding energy, however, we use the more accurate procedure of eliminating α with the zero-pressure condition $dE/dr_s=0$. In this manner, we obtain[11]

$$E_g=\frac{0.737}{r_s{}^2}-\frac{2}{3}\frac{(0.916+1.792Z^{\frac{2}{3}})}{r_s}-0.105+0.031\ln r_s-0.0338\beta(r_s)[\cos^2y+\tfrac{1}{3}y\sin 2y], \tag{6}$$

and

$$K/K_0=22.1\{0.093r_s{}^2+2(0.916+1.792Z^{\frac{2}{3}})r_s-4.42-0.0338r_s{}^2\beta(r_s)[2y(\sin 2y-y\cos 2y)]\}^{-1}, \tag{7}$$

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[6] With this grouping, the divergent long-range parts of the ion-ion and electron-electron interactions precisely cancel. In writing (2), we neglect any deviations of the ion-ion interaction from Coulomb's law; at normal densities these deviations are surely unimportant. We also neglect the effects associated with the polarization of the ion cores; such neglect appears to be justified in all the metals we consider here, except possibly in Pb and Zn, where the core states are not so well separated in energy from the valence states.

[7] K. Fuchs, Proc. Roy. Soc. (London) **A151**, 585 (1935); W. Kohn and D. Schecter quoted by W. J. Carr, Jr., Phys. Rev. **122**, 1437 (1961).

[8] Obtained by numerical integration of the structure factor of N. W. Ashcroft and J. Lekner, Phys. Rev. **145**, 83 (1966).

[9] In deriving (3), care must be exercised in excluding the doubly counted part of the electron-electron interaction. The effect of any deviations from our Hartree (random-phase-approximation or self-consistent-field) treatment of the screening must be small, since the screening is small to begin with. Finally, we note that (3) contains not only a shift of the band minimum, but also a modification of the electronic kinetic energy. See, for example, Harrison (Ref. 3), Eqs. 2.32 and 2.60.

[10] N. W. Ashcroft, Phys. Letters **23**, 48 (1966).

[11] Ignoring negligible contributions arising from differentiating the denominator of $(\epsilon-1)/\epsilon$.

TABLE II. Summary of numerical results, and comparison with experiment.

	K/K_0		$-E_g$ (Ry/electron)	
Element	Theory	Experiment	Theory	Experiment
Al	3.5	3.9	1.41	1.38
Pb	3.2	3.5	1.55	1.79
Zn	2.1	2.1	1.10	1.05
Mg	2.1	1.9	0.860	0.890
Li	2.1	2.0	0.564	0.511
Na	1.6	1.5	0.454	0.460
K	1.1	1.0	0.383	0.390
Rb	0.82	0.82	0.344	0.366
Cs	0.71	0.78	0.318	0.345

where $y=3.84xr_c/r_s$, K_0 is the free-electron compressibility, and

$$\beta(r_s)=\sum_x \frac{1}{x^4}\,\frac{F(x)}{1+0.166r_sF(x)/x^2}. \qquad (8)$$

Here x is a reciprocal-lattice vector measured in units of twice the Fermi wave vector, and

$$F(x)=\tfrac{1}{2}+\frac{1}{4x}(1-x^2)\ln\left|\frac{x+1}{x-1}\right|.$$

Except for E_B, the relative sizes of the various contributions to E_g and K may be gleaned from inspection of (6) and (7). To obtain an estimate of the size of E_B, it is sufficient to take $y\sim\pi/2$, and $\beta=N_x/3x^6$, where N_x is the number of shortest reciprocal-lattice vectors and x is their length. It follows that the term [ ] in (6) is very small, and E_B has but little contribution to E_g. On the other hand, the term [ ] in (7) is of order unity, thereby giving to K: (i) in the polyvalent metals, a substantial contribution (more than 100% in Al); (ii) in the alkali metals, still a small contribution. The different behaviors result from the characteristic x's found in alkali and polyvalent metals. Since the polyvalent metals include such a large contribution from band structure to K, we regard the results for this group to be least accurate.

In evaluating the contribution from (8) to E_g and K/K_0, we have included in the sum only the nearest sets of Bragg planes to the zone center.[12] We have applied Eqs. (6) and (7) to a number of simple metals, and for every case attempted, we have found at least fair agreement with experiment as shown in Table II and Figs. 1 and 2. Since we have treated all the metals with the same approximation, a detailed comparison with the few previous calculations (attempted by different methods) is difficult. As to the accuracy of the results, however, we remark the following: Inaccuracies arising from uncertainties in the band-structure terms are clearly important, as mentioned earlier. For the alkalis, a cellular method would probably be more accurate than our calculation, provided the potential was known with some precision. The present calculation, on the other hand, makes best use of the limited information on the potential that can be deduced from direct experimental evidence.

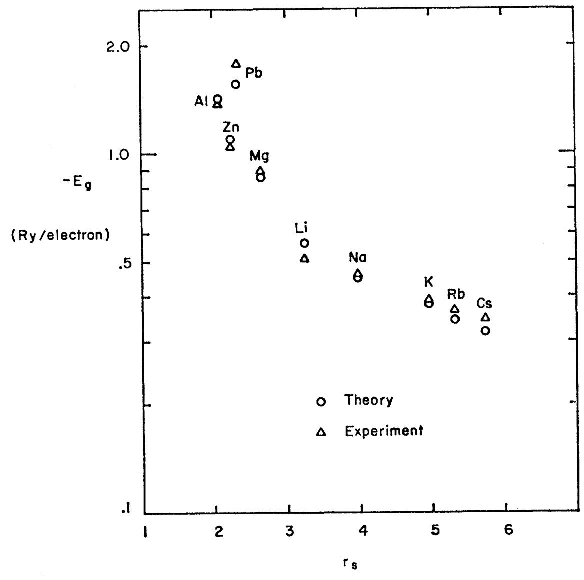

FIG. 2. Comparison of experimental and theoretical binding energies, measured in rydbergs per conduction electron. The experimental points represent the average of the first Z-ionization energies plus the observed heat of sublimation.

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[12] For the hexagonal structures, we carry out an equivalent procedure in keeping the {1001} and {0002} sets. Although the contribution from the omitted terms is generally not as much as an order of magnitude less than the terms retained, we note that they tend to be cancelled by terms of opposite sign in third-order perturbation theory (for both hexagonal and cubic structures). For Mg and Zn, each term in the sums (3) and (8) is weighted by the normalized-structure factor for the unit cell. The quantity calculated for the hexagonal case is not strictly the compressibility, but rather what the compressibility would be if the c/a ratio did not change on compression. This latter quantity, easily expressible in terms of the elastic constants, is the one plotted in Fig. 1 for both experimental and theoretical points.