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ESTIMATE OF THE ENERGIES OF SYMMETRIC LATTICES OF NON-TRANSITION METALS BY THE PSEUDO-POTENTIAL METHOD

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The structure-sensitive part of lattice sums, in which the main role is played by the terms corresponding to the first coordination spheres, is investigated. By means of a universal pseudo-potential containing no adjustable parameters, the binding energies of non-transition metals are calculated, for five symmetric lattices, in the second approximation of perturbation theory. The results make it possible to exclude from each group the structures which do not occur in nature, but the prediction of the details of the polymorphism of simple metals requires considerable refinements.

1. Pseudo-potential theory has turned out to be extremely fruitful for understanding the properties of non-transition metals, the valence electrons of which are in s- and p-states[1]. It is fundamental to the theory that the dimensions of the region in which the effective self-consistent interaction potential of a conduction electron with the force centers of the lattice is great be small compared with the distances between the centers. In this case, in a large part of the volume of the metal, the electron moves as a free electron, and the effect of the potential is manifested here only through its scattering amplitude, so that one can introduce a comparatively small effective pseudo-potential and apply perturbation theory ($V_q \lesssim \epsilon_F$).

In principle, perturbation theory makes it possible to carry out a complete calculation of all the characteristics of the metal, including the electron spectrum, the total energy of the crystal and the phonon spectra. The expression for the energy of the metal is a sum over all the reciprocal-lattice vectors of expressions containing matrix elements of the pseudo-potential between these vectors, i.e., we require a knowledge of the behavior of the matrix element in the whole range of variation of its argument.

In practice, in the most successful of the pseudo-potential calculations that have been carried out, the semi-empirical expressions for the pseudo-potential have used one or several parameters, which have been adjusted individually for each metal[2]. It has been found that the influence of non-local effects[3] and of the third perturbation-theory approximation[4] are important.

In[5], a universal estimate-formula was obtained for the matrix elements of all the non-transition metals:

$$V_q = \frac{1}{\pi Z}\left(q^2 - \frac{8}{3}k_F^2\right) = -\frac{16}{3\pi Z}\left(1 - \frac{3}{8}\frac{q^2}{k_F^2}\right)\varepsilon_F \tag{1}$$

with the universal slope $\partial V_q/\partial q^2 = 1/\pi Z$. The experimental values of the matrix elements for simple metals, found from Fermi-surface measurements[6] and optical measurements[7], are satisfactorily described by the estimate-formula from[5]. In effect, formula (1) defines the position of the zero of the potential curve and its slope close to the zero. Outside the region about $q_0 \sim \sqrt{8/3}\,k_F$, the modulus of V_q is not small and a rigorous introduction of a pseudo-potential is impossible. The idea arises of using a model pseudo-potential, having selected its parameters so that it coincides with formula (1) close to the universal value q_0.

However, one can convince oneself that the model potentials usually used, which have in coordinate space the form of the Coulomb potential with a short-range potential (e.g., the Heine-Abarenkov potential), always give a slope at the point q_0 that is smaller than it should be from formula (1). This is connected with the fact that the matrix element (1) arose not as the result of some weak potential but as the result of cancellation of the effects of extremely strong resonance scattering of s- and p-waves.

Because of this, it is interesting to investigate the information about the energy of lattices that is given by the potential (1) without any adjustments. In this paper, values of the energies for five symmetric lattices (three cubic, the diamond and the hexagonal close-packed) are compared for all the non-transition metals of the periodic system. The calculational formulas are simplified and approximated so as to use only the region where the pseudo-potential is well defined.

2. We shall consider the expression for the band-structure (BS) energy in the second approximation of perturbation theory[1]:

$$E_{\mathrm{BS}} = \sum_{\mathbf{g}}{}' |S(\mathbf{g})|^2 F(g) = \sum_{\mathbf{g}} N_c(\mathbf{g}) F(g), \tag{2}$$

where F(q) is the characteristic function

$$F(q) = -\frac{\Omega_0 q^2}{8\pi}\langle \mathbf{k}+\mathbf{q}|w^0|\mathbf{k}\rangle^2 \frac{\varepsilon(q)-1}{\varepsilon(q)},$$

and N_c is a sort of weighting factor, equal to the number of reciprocal-lattice sites on a sphere of radius g. It is convenient to consider the function

$$N_t(q) = \sum_{|\mathbf{g}|<q} N_c(\mathbf{g}),$$

which is equal to the total number of reciprocal-lattice sites falling inside the sphere $|\mathbf{g}| = q$. For large q in the sum (2), the contribution that is sensitive to specific features of the lattice structure is relatively small and in the limit the function N_t is simply an integral corresponding to the volume of the sphere:

$$N_t = \left(\frac{4\pi}{3} q_s^3\right)^{-1} \int_0^q 4\pi q^2\, dq,$$

where $4\pi q_s^3/3$ is the volume of a unit cell of the reciprocal lattice.

Calculation of the principal volume part of the energy and of the bulk modulus by the perturbation-theory method is very unreliable and requires that the higher approximations be taken into account. Calculations by the Wigner-Seitz method[8,9] would be the most consistent. In the present paper, we shall take the values of the equilibrium specific volume Ω_0 from experiment.

The positions of the atoms in the lattice are smeared out because of the zero-point or thermal vibrations of the atoms. The structure factor is then simply multiplied by a damping factor

$$D(\Delta, q) = \exp\{-q^2\Delta^2/2\},$$

$D(\Delta, q) \equiv e^{-W}$ is the Debye-Waller factor[10], which multiplies the structure factor when the lattice vibrations are taken into account and is of the order of magnitude of the mean amplitude of the atomic vibrations. The Debye-Waller factor e^{-W} can be calculated rigorously for each specific lattice, if we know its vibration spectrum. One often uses the isotropic Debye model, for which, for high temperatures, $W = 3q^2T/2M\Theta^2$, where M is the ionic mass and Θ is the Debye temperature.

For orientation, we estimate the magnitude of W at the melting temperature by applying the rather crude "Lindemann criterion"[10], which states that symmetric lattices begin to melt when the ratio χ_m of the amplitude of the thermal vibrations to the radius r_s of the cell associated with one atom becomes approximately equal to $\frac{1}{4}$. Then the melting temperature is

$$T_m \approx {}^1/_9 \chi_m^2 r_s^2 M\Theta^2.$$

Using this T_m, we obtain for W an estimate from which we find the dependence on the lattice structure: $W \approx (qr_s)^2\chi_m^2/6$.

It is convenient to introduce and estimate the effective number of sites N_t^* making an important contribution to the sum (2) (and to relate Δ and N_t^* at the same time):

$$N_t^* = \frac{3}{q_s^3}\int_0^\infty e^{-2W} q^2\, dq = \frac{(3\pi)^{3/2}}{{}^4/_3\pi q_s^3 r_s^3 \chi_m^3}.$$

Finally, taking into account that $(4\pi r_s^3/3) \times (4\pi q_s^3/3) = (2\pi)^3$, we obtain for $\chi = \frac{1}{4}$ the value $N_t^* \sim 1/2\chi_m^3 \sim 30$. This value is unexpectedly small and shows that the most important role in the structure-sensitive part of the sum (2) is played only by the first three or four coordination spheres.

At low temperatures, the coefficient of q^2 in W[10] is approximately a factor of four smaller ($W = 3q^2/8M\Theta$) and the range of g contributing effectively to the structure-sensitive part of the sum (2) is correspondingly somewhat broadened (since $N_t^* \sim W^{-3/2}$, we have $N_t^*(T = 0) \sim 250$).

From a formal point of view, the combination of $w^0(q)$ with the damping factor $D(\Delta, q)$ generates a class of pseudo-potentials $w^*(q, \Delta) = w(q)e^{-W}$, depending on the smearing parameter Δ. Usually, the model pseudo-potential is chosen such that the contribution to the sum from the region $q \geq 5k_F$ is negligibly small.

To solve the question of which structure is stable under given conditions, we may expect the best results by applying the method of successive approximations. Given an estimate of the Debye-Waller factor, instead of the energy (2) we must calculate for a given temperature the free energy and phonon spectrum, and then repeat the calculations with a more accurate Debye-Waller factor, which can be calculated for an arbitrary phonon spectrum.

Since in the calculations we are going to use the rough-estimate pseudo-potential of[5], we can lower the requirements for the accuracy of the calculational formulas and reject the method of successive approximations. Actually, the matrix element of the pseudo-potential is uniquely defined only in the vicinity of q_0, where cancellation of the s- and p-scatterings occurs. Outside this region, perturbation theory is inapplicable; moreover, since the scattering amplitude becomes essentially complex, effects associated with the non-local nature of the pseudo-potential become important. By artificially increasing the "smearing" in such a way that the main contribution to the integral is only from the range about q_0 within which the potential of[5] is defined, we eliminate these complicated effects at the same time.

$N_t^* \sim 10$ corresponds to this condition. In calculational respects, the method described is an application of the Ewald method to the calculation of lattice sums with arbitrary functions. Usually, the Ewald method has been applied to the calculation of the lattice-structure dependence of the Madelung constant in the electrostatic energy

$$E_e = -\alpha_M Z^2/2r_s.$$

A calculation of the dependence of α_M on the damping factor (the same factor as for E_{BS}) served as a check on the accuracy of the calculations. In order to ensure accuracy in the energy of the order of 10^{-3} atomic units (the order of magnitude of the melting temperature), it is sufficient to take $N_t^* > 10$.

Clearly, such calculations can no longer hope to explain effects connected with the influence of temperature and of small pressures $p \lesssim T_m/\Omega_0$, since the corresponding "Debye-Waller factor" formally corresponds to temperatures higher than the melting temperature T_m.

3. Thus, we arrive at the following calculational scheme. Assuming the value of the equilibrium density to be known from experiment, we calculate the BS energy from formula (2), but replace N_c everywhere by $N_c^* = N_c e^{-2W}$. In the calculations, for w(q) we have used the two expressions given in[5]:

1) a pseudo-potential estimated from first principles:

$$w(q) = \frac{32}{3\pi Z}\sqrt{\frac{3}{2}}\,\varepsilon_F\left(\frac{q}{2k_F} - \sqrt{\frac{2}{3}}\right); \tag{1a}$$

2) Harrison's model pseudo-potential with the parameter β determined from the condition $w(q_0) = 0$:

$$w^\beta(q) = -\frac{4\pi Z}{\Omega_0}\left(\frac{1}{q^2} - \frac{3}{8k_F^2}\right), \tag{1b}$$

Ω_0 is the volume of the unit cell and Z is the valency

$$2\frac{4\pi k_F^3}{3}\frac{\Omega_0}{(2\pi)^3} = Z.$$

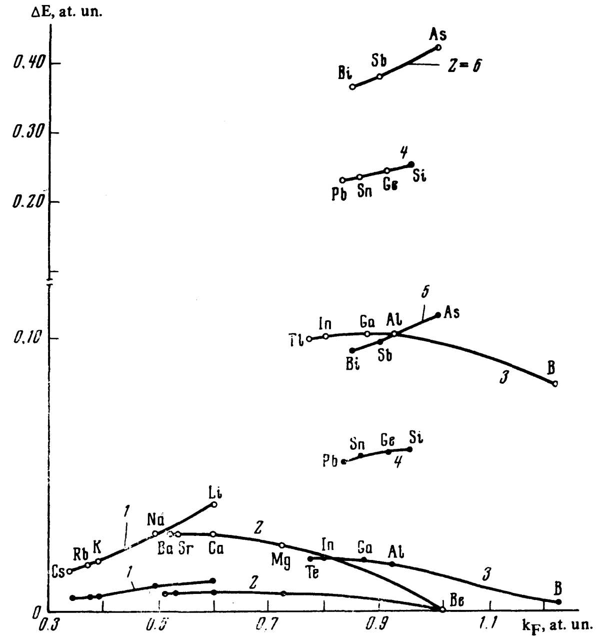

FIG. 1. Dependence of k_F of the energy difference between the diamond and hexagonal structures (○) and between the simple cubic and hexagonal structures (●) for the potential (1a) and $N_t^* = 13$.

It is sufficient to perform the calculations of the sums for fixed volume only in the second perturbation-theory approximation, since, because of the effect of the damping factor, $w^*(q) = we^{-W}$ and $w^{\beta *}(q) = w^{\beta} e^{-W}$ are everywhere small compared with ϵ_f, for the non-transition metals. In Fig. 1 are given the results of the calculations of the total energy $E = E_e + E_{BS}$ of different symmetric lattices as functions of k_F (i.e., in effect, of the specific volume) for the valency values $Z = 1, 2, 3, 4$ and 5 for the pseudo-potential estimated from first principles and with the damping-function parameter $N_t^* = 13$.

The values of k_F were chosen to correspond to the non-transition metals of each group. The symbols for the metals are shown in Fig. 1. The interpolation between the points corresponds to variation of the specific volume. For convenience, we have plotted the differences between the calculated energies of the structures and the energy of the close-packed hexagonal structure.

As can be seen from the Figure, for all the elements the diamond and simple cubic lattices can be eliminated as energetically unfavored. The same results were obtained in calculations with Harrison's model potential and with the damping-function parameters $N_t^* = 13$ and $N_t^* = 35$. The differences between the energies of the close-packed lattices (see Fig. 2) were found to be much smaller than the upper bound of the error of the calculations (which is of order 10^{-2} eV). These small differences are more sensitive to the parameters N_t^* and to the choice of expression for the pseudo-potential. Nevertheless, unexpectedly good general agreement with the available experimental information on the polymorphism of metals, collected in the survey by Evdokimova[11], is obtained. Thus, for the second group, all the variants of the calculation predict the hexagonal close-packed structure in agreement with experiment.

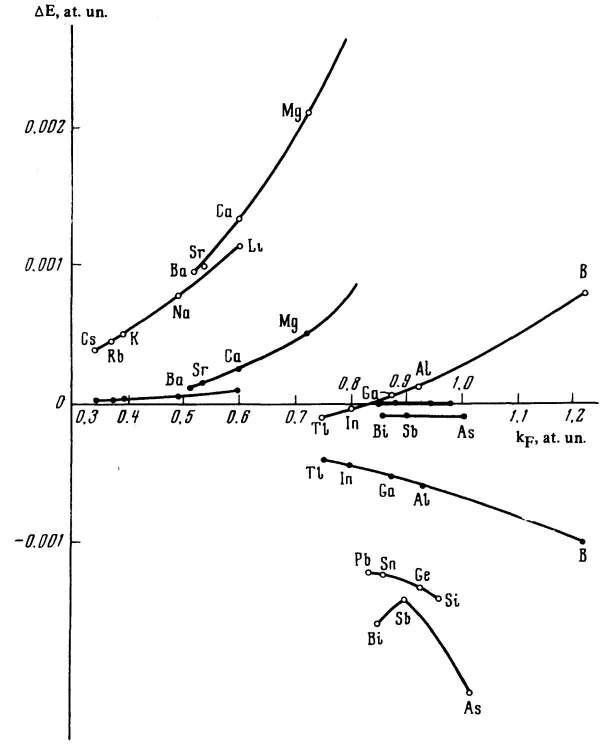

FIG. 2. Dependence of k_F of the energy difference between the BCC and HCP structures (○) and between the FCC and HCP structures (●) for the potential (1a) and $N_t^* = 13$.

For the metals of the first, third and fourth groups, by varying the parameters N_t^* and choosing an appropriate form of the pseudo-potential, we can always select the correct alternation of close-packed phases for each metal. In this sense, the statement by Heine and Weaire[2] that the preferred close-packed structure is determined entirely by the positions of the node of the pseudo-potential is too categorical.

The light group-four elements C, Si and Ge are dielectrics and form a lattice of the diamond type with strong covalent bonds. Carbon in the metallic phase forms the graphite lattice, which has not been studied in this work. Pb and Sn give close-packed lattices.

Of the group-five elements, Sb displays a hexagonal close-packed lattice under pressures greater than 90 kbar. In general, however, for metals of this group, different forms of distortion of a lattice of the simple cubic type are characteristic. Allowance for the distortions of the lattice for arbitrary deformations is intimately connected with the analysis of the phonon spectra and has not been made here. It is possible that the discrepancy of the order of 0.1 eV per atom between the calculated values and the experimental data is due not only to the presence of distortions, but also to the presence of covalent bonds.

4. The purpose of the present work was to investigate the information given about the most favored structure of metals by the "ab initio estimate" pseudopotential obtained in[5]. The separation of the structure-sensitive part of the total energy by means of a crude "smearing" procedure made it possible for sufficiently large "smearings" (small values of N_t^* of order 10) to use the pseudo-potential (1a) obtained from first principles, and to establish that, among the symmetric structures, the close-packed structures (BCC, FCC and HCP) are indeed energetically more favored than the diamond and simple cubic structures.

Harrison's model potential gives the same alternation of phases, but, possessing better convergence than potential (1a), is less sensitive to the choice of the quantity N_t^*.

There is no doubt that adjustment of the parameters w^* for each individual element can make it possible to achieve complete agreement with experiment. On the other hand, it is unlikely that any single pseudo-potential for all the metals could improve the general agreement with the experimental data for the whole periodic system. We should like to emphasize that, from the point of view of the method of successive approximations, referred to above, the effective potential should include a Debye-Waller factor calculated using the actual phonon spectrum of the given lattice. The effective pseudo-potential is thus found to depend on the specific lattice structure, and an improvement of the results of the calculations of the present work should contain not only a replacement of the estimate-formula (1) by a more accurate formula taking into account the deviation from exact resonance in the expressions for the scattering amplitude, but also a consistent calculation of the phonon spectra.

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