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ON THE ELASTIC MODULI OF ALKALINE AND NOBLE METALS III

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A new term is given in the energy expression for the elementary cell of a monovalent metal under uniaxial tension. This term accounts for the interaction of the quadrupole moment of the deformed elementary cells. The calculated values of c_{11} and c_{12} for potassium and silver are given.

1. In the two previous papers of this series [1, 2] the author has described a method for obtaining the elastic moduli c_{11} and c_{12} of alkaline and noble metals using the theory of monovalent metals developed by GOMBÁS [3—8]. The method leads to an approximate expression for the energy of the Wigner—Seitz cell of a monovalent metal subjected to uniaxial elastic deformation, the elementary cell in this case being regarded as a rotational ellipsoid instead of a sphere. The ratio of the ellipsoidal axes is obtained at the minimum of the cell energy and this yields the Poisson ratio for the cell very near the unstrained equilibrium state, while the compressibility, the unstrained equilibrium energy and radius of the cell are known from GOMBÁS's theory. Then the elastic moduli c_{11} and c_{12} can be calculated from these quantities.

GOMBÁS's theory of monovalent metals accounts for the cohesion of the alkaline, alkaline earth and noble metals on a purely theoretical basis, without introducing any empirical or semiempirical parameter giving the energy of the elementary cell as a function of the cell radius, the Wigner—Seitz cell being approximated by a sphere of equal volume. The compressibility, energy and equilibrium lattice constants of the cell can be evaluated for the equilibrium case, when the cell energy is minimum, giving results in excellent agreement with experimental values measured at an adequately low temperature or even extrapolated to absolute zero.

The metal is treated in GOMBÁS's theory as a system composed of a positive metal ion lattice and an approximately free gas of valence electrons. The valence electrons are treated in a modified lattice potential consisting of the electrostatic potential of the ion cores and a nonclassical pseudopotential being the result of the Pauli principle. In calculating the energy of an elementary cell it is now unnecessary to orthogonalize the eigenfunctions of the valence electrons to those of the core electrons, since the pseudopotential automatically compensates for this, and thus one obtains the deepest possible energy states for the valence electrons.

Gombás's energy expression for an elementary cell can be written as follows:

$$U = U^E + U^W + H, \tag{1}$$

where U^E is the total self energy of the valence electrons, U^W the total interaction energy of the valence electrons with the ion cores and H the interaction energy of the ion cores.

U^E and U^W can be written further as

$$U^E = E_C + E_A + E_W + E_F \tag{2}$$

and

$$U^W = W_C + W_E + W_A + W_W + W_K, \tag{3}$$

where the indices are C for Coulomb-type, A for exchange, W for correlation, F for zero-point and E for non-Coulomb-type electrostatic energy, and the index K represents the energy resulting from the pseudopotential.

The interaction energy of the ion cores H is approximately zero for alkaline metals, and for noble metals can be given as an average value, so the elementary cells are to be regarded as electrically neutral in equilibrium configuration, since they can be approximated by spheres. Gombás has shown that in this case the calculations can be carried out using free-electron eigenfunctions for the valence electrons (while as regards the ion cores the results for free atomic ions calculated by the self-consistent field method were used). Expression (1) was calculated by Gombás for some monovalent metals at different elementary cell radii. For alkaline metals U can be given in a simple analytical form as a function of the cell radius:

$$U = -\frac{c_1}{R} + \frac{c_2}{R^3} \tag{4}$$

(for c_1 and c_2 see [3]). For noble metals the numerically computed values of U can be approximated analytically in the form:

$$U = -\frac{A}{R} + \frac{B}{R^n}, \tag{5}$$

where A, B and n are constants.

It must be stressed that the analytical forms [4], [5] are always connected with complete spherical symmetry, i.e. the shape of the Wigner—Seitz cell does not change. It follows that in calculating the energy of the elementary cell every elementary sphere has to be taken electrically neutral from the outside, so there is no direct interaction term between different cells, as the ion core interaction occurring in the unstrained symmetry conditions has been taken into account already with the term H in (1).

Now we have the elementary cell energy as a function of the sphere radius $U(R)$, the equilibrium cell radius R_0 and minimal cell energy U_0 can be obtained form the equilibrium condition

$$\frac{dU}{dR} = 0 . \tag{6}$$

For spherical symmetric deformation of the elementary cell (i.e. isotropic compression or dilatation) the cell radius is

$$R = R_0(1 + \Delta). \tag{7}$$

Near the equilibrium state Δ is a small quantity, and the cell energy can be given up to the second order as

$$U = U_0 + \frac{R_0^2}{2}\left(\frac{d^2 U}{dR^2}\right)_{R_0} \Delta^2 . \tag{8}$$

From (8) one gets for the compressibility $\varkappa$ (see [1])

$$\frac{1}{\varkappa} = \frac{1}{12\pi R_0}\left(\frac{d^2 U}{dR^2}\right)_{R_0} \tag{9}$$

or, introducing

$$V_0 = \frac{4\pi R_0^3}{3}$$

and

$$w_0 = -\frac{U_0}{V_0} \tag{10}$$

and using (5):

$$\frac{1}{\varkappa} = \frac{n w_0}{9} . \tag{11}$$

Thus

$$U = U_0\left(1 - \frac{9}{2 w_0 \varkappa}\Delta^2\right). \tag{12}$$

2. If a uniaxial tension stress deforms the Wigner—Seitz cell, the spherical symmetry is lost and hence the elementary cell is more accurately represented by a rotational ellipsoid than by a sphere. Let the two main axes a and b of the rotational ellipsoid be given, by

$$\left.\begin{aligned} a &= R_0(1 + \Lambda) \\ b &= R_0(1 + \mu\Lambda) \end{aligned}\right\} \tag{13}$$

and let the direction of the stress be the direction of the axis a.

To a first approximation (see [1]) the cell energy can be taken as

$$U_1 = U_0(1 - \varphi_\mu \Lambda^2), \tag{14}$$

where

$$\varphi_\mu = \frac{3}{10\, w_0\, \varkappa} (3 + 4\mu + 8\mu^2). \tag{15}$$

A further term has to be introduced into the energy expression (14) because of the change of the electrostatic interaction between the ion core and valence electronic charge, resulting from non symmetrical deformation of the elementary cells:

$$U_2 = U_0(1 - \Phi_\mu \Lambda^2), \tag{16}$$

where

$$\Phi_\mu = \varphi_\mu + \frac{4e^2}{75\, R_0\, U_0} (1 - \mu)^2 . \tag{17}$$

3. In the case of uniaxial tension stress plainly the whole lattice will be deformed. Every Wigner—Seitz cell or elementary sphere will change its shape to a rotational ellipsoid of parallel rotational axis, and with this there will be a change in the interaction energy of the ionic lattice. Let us assume, however, that the ion cores themselves do not alter during the deformation of the lattice and that even the eigenfunctions of the valence electrons remain the same as in the unstrained equilibrium (this assumption is similar to that used in the usual first order perturbation). The change in the ion core interaction energy can now be calculated as an electrostatic interaction between the deformed Wigner—Seitz cells because the rotational ellipsoids are not electrically neutral i.e. the deformed elementary cells have a linear electric quadrupole moment.

It is known [9] that a rotational ellipsoid with axes a and b ($a > b$) has a linear electric quadrupole moment directed along the a axis if it has a point charge $+e$ at the origin and a uniform negative charge density of

$$\varrho_0 = - \frac{3e}{4\pi a b^2} .$$

The quadrupole moment Q_{11} is then given as

$$Q_{11} = \frac{e}{5} (a^2 - b^2) \tag{18}$$

and all other Q_{ik} are zero.

Using (13)

$$Q_{11}=\frac{2}{5}eR_0^2(1-\mu)\Lambda \tag{19}$$

up to the first order in Λ.

Let $V(r)$ be the potential in the crystal due to all such quadrupole moments. Then, owing to this field, the energy of the elementary cell placed in the origin will be

$$W=\int_{(\text{cell})}\varrho V\,d\Omega=\frac{1}{2}\left(\frac{\partial^2 V}{\partial x_1^2}\right)_0 Q_{11} \tag{20}$$

up to the second order.

The electrical potential of a linear quadrupole moment Q_{11} at a point given relative to Q_{11} by (r, ϑ) is

$$V=\frac{Q_{11}}{2r^3}(3\cos^2\vartheta-1). \tag{21}$$

Let there be a quadrupole moment Q_{11} at the point (r, ϑ) and a parallel quadrupole moment Q_{11} at the origin. The interaction energy of these two quadrupole moments together can be calculated from (20) and (21). The half of this belonging to each moment is:

$$W_{r,\vartheta}=\frac{9}{8}\,\frac{Q_{11}^2}{r^5}\left(1-10\cos^2\vartheta+\frac{35}{3}\cos^4\vartheta\right). \tag{22}$$

The interaction energy for one elementary cell is found by summing up (22) for the whole lattice and using (19):

$$W=\frac{9}{5}e^2R_0^2(1-\mu)^2\Lambda^2\sum_i\frac{1}{r_i^5}\left(1-10\cos^2\vartheta_i+\frac{35}{3}\cos^4\vartheta_i\right). \tag{23}$$

Let the smallest distance between two atoms in a given lattice be δ,

$$r_i=\delta\xi. \tag{24}$$

It is known that

$$\delta=\beta R_0, \tag{25}$$

where

$$\beta=(\sqrt{3}\,\pi)^{1/3} \quad \text{for s.c.c. lattices}$$

and

$$\beta=\sqrt{2}\left(\frac{2\pi}{3}\right)^{1/3} \quad \text{for f.c.c. lattices.}$$

Let us take

$$S = \sum_i \xi_i^{-5} \left(1 - 10 \cos^2 \vartheta_i + \frac{35}{3} \cos^4 \vartheta_i\right) \tag{26}$$

and

$$\eta = -\frac{27}{8} \beta^{-5}. \tag{27}$$

The U_2 in (16) has to be corrected further by W given by (23) and so the total cell energy will be

$$U = U_0(1 + \Psi_\mu \Lambda^2), \tag{28}$$

where

$$\Psi_\mu = \varphi_\mu - h(1-\mu)^2(1+\eta S) \tag{29}$$

and

$$h = -\frac{4e^2}{75 R_0 U_0}.$$

The energy term (28) has its minimum if

and

$$\left.\begin{aligned} &\left(\frac{\partial U}{\partial \mu}\right)_\Lambda = 0 \\ &\left(\frac{\partial U}{\partial \Lambda}\right)_{\Lambda \to 0} = 0 . \end{aligned}\right\} \tag{30}$$

From (30) we obtain the equilibrium Poisson ratio as

$$\mu_0 = -\frac{1}{4} \frac{1 + \frac{5}{3} \varkappa w_0 h(1+\eta S)}{1 - \frac{5}{12} \varkappa w_0 h(1+\eta S)}. \tag{31}$$

Let us finally introduce another constant g as in [2], with

$$g = \frac{5}{12} w_0 h = \frac{e^2}{60 R_0^4}. \tag{32}$$

Then

$$\mu_0 = -\frac{1}{4} \frac{1+4g\varkappa(1+\eta S)}{1-g\varkappa(1+\eta S)}. \tag{33}$$

The elastic moduli c_{11} and c_{12} can now be obtained in the same form as in [2], i.e.

$$c_{11} = \frac{3}{5\varkappa} [4 - 8 g\varkappa(1+\eta S)] \tag{34}$$

and

$$c_{12}=\frac{3}{5\varkappa}[1+4g\varkappa(1+\eta)S]. \tag{35}$$

Eq. (26) was then calculated for s.c.c. and f.c.c. lattices.

The numerical results are given in Table I, where c_{11} and c_{12} were calculated from Eqs. (34) and (35) assuming s.c.c. lattice for potassium and f.c.c. lattice for silver. The results of FUCHS' calculation for potassium and the available experimental values were quoted already in [1] and [2].

Table I

All data in 10^{11} dyne/cm^2

		K	Ag
c_{11}	(34)	0.479	17.87
	FUCHS	0.440	—
	experiments	0.457*	12.4
c_{12}	(35)	0.374	7.63
	FUCHS	0.380	—
	experiments	0.374*	9.34

* Measured at 73°K

As can be seen, the results are far better for potassium than for silver. There is, however, a quite remarkable overlapping of the ion cores with silver and so some of the basic assumptions of this and of the previous articles are only rough approximations for noble metals, even when the cells are at the equilibrium state. For unstrained equilibrium or for spherically symmetric deformations these discrepancies can be corrected by using a more sophisticated pseudopotential [10], but for nonspherically symmetric deformations the present method is only adequate for alkaline metals, where such overlappings are practically negligible.

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О МОДУЛЕ УПРУГОСТИ ЩЕЛОЧНЫХ И БЛАГОРОДНЫХ МЕТАЛЛОВ III.

Й. АНТАЛ

Резюме

В данной работе, являющейся продолжением предыдущих двух статей [1, 2], выведен новый член выражения энергии элементарной ячейки одновалентных металлов в случае одноосного растяжения. Появление этого члена вызвано взаимодействием квадрупольных моментов деформированных элементарных ячеек. Рассчитаны значения c_{11} и c_{12} для калия и серебра.