

A CONTRIBUTION TO THE THEORY OF MULTIVALENT METALS

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The paper deals with the extension of the statistical model of metals having one or two valency electrons as suggested by Gombás to multivalent metals. On the basis of this model a number of constants of metallic aluminium were calculated, no use being made of any empirical parameters. The results are in comparatively good agreement with experiment.

The statistical theory of metals was elaborated mostly by GOMBÁS [1], [2], who in a number of papers dealt with the calculation of the fundamental constants of most of the univalent and bivalent metals. This theory, which in its substance does not take into account the structure of the BZ (Brillouin zones) and the energy distribution of the valency electrons in reciprocal space, achieved its greatest successes for alkali metals, Cu and others (i. e. for metals having one valency electron) for which the effect of the BZ on the physical properties is mostly very small. The matter stands quite differently with bivalent metals, where this effect on the energetic spectrum of the valency electrons is considerable. Although for this case all assumptions of this theory are not fulfilled to the same degree as for univalent metals, where the average contributions of all valency electrons are concerned (e. g. for the total energy) good agreement with experiment can, however, still be expected; calculations confirmed this without exception. Quite analogous behaviour can, therefore, be expected for multivalent metals. In the following we shall first briefly outline the main ideas of the Gombás theory of metals and propose an extension of his equation for the total energy of the crystal to metals with several valency electrons. This equation we shall then use for the calculation of some physical constants of metallic aluminium.

It is a well-known fact that the grouping together of the atoms of a metal into a crystal lattice leaves the closed electron shells of the ion practically unchanged, while the wave functions and the energies of valency electrons are changed considerably. In the following we shall therefore assume that the state of the valency electrons in a metal is described by a wave function of the Bloch type, i. e. a wave function which is non-zero

practically throughout the whole of the crystal and the state of the core electrons by a wave function which is localised in the immediate vicinity of the atomic nucleus. This latter wave function is to a first approximation identical to the wave function of the free ion. We shall further limit ourselves in our assumptions to the atomic sphere the radius of which is denoted by R , thus considerably simplifying the whole problem.

In his theory of metals GOMBÁS assumes that to a first approximation, which without doubt corresponds to reality better in the case of a univalent than a bivalent metal, the wave functions of valency electrons are plane waves, i. e. the density of the valency electrons is uniform. It is, of course, obvious that the wave function of valency electrons of the type

$$e^{i\vec{k}\vec{r}}$$

in which \vec{k} denotes the wave vector, are generally not orthogonal to the functions of the core electrons. As a consequence the energy of the valency electrons would be lower than corresponds to reality where due to the validity of the Pauli principle valency electrons cannot occupy states already fully occupied by the core electrons. GOMBÁS avoided this difficulty in a simple way. Starting out from the statistical formulation of the Pauli principle he derived for this obviously non-classical repulsion between the valency electrons and the core electrons a potential by which he supplemented the potential in the Schrödinger equation. He was therefore not bound by orthogonality conditions between the wave function of the valency electrons and the wave functions of the core electrons. He derived two expressions for this repulsion potential which he denoted by F_i and G_i . In principle these potentials differ by the fact that while deriving G_i the core elec-

trons were consistently distinguished according to the azimuthal quantum number l , while in the case of the potential F_i this was not consistently adhered to. The potential G_i is, moreover, better suited for metals having several valency electrons and we shall therefore use it in the following [3].

The idea from which GOMBÁS [4] started when deriving the potential G_i is briefly this:

If the volume element is dv and $dp_x dp_y dp_z$ the element of momentum space, then — as is well known — the number of electrons in the volume element dv having momenta $\langle p_x, p_x + dp_x \rangle$, $\langle p_y, p_y + dp_y \rangle$, $\langle p_z, p_z + dp_z \rangle$ is given by the formula

$$\frac{2}{h^3} dp_x dp_y dp_z dv. \quad (1)$$

Let us now divide momentum space by coaxial cylindrical surfaces the axis of which is identical with the position vector \vec{r} of the volume element dv so that the individual hollow circular cylinders contain consecutively the points representing the states of electrons having an azimuthal quantum number $l = 0, 1, 2, \dots$. Let us further require that the radii p_l of the individual cylindrical surfaces should, according to semi-classical quantum theory, satisfy the following relation

$$|\vec{r}|p_l = l \frac{h}{2\pi}.$$

Let us further assume that the potential of the core electrons in a sufficiently small volume element dv is constant and that the electron density in this volume element is so great that statistical methods can be applied to the solution of the problem. It is obvious that this assumption loses validity in the vicinity of the nucleus and at the boundaries of the ion. As, however, these regions do not figure in our considerations they do not have to be specially considered.

Points representing states of the core electrons having a certain quantum number l obviously occupy those places in momentum space which correspond to the lowest energies up to a certain maximum. At the same time due to (1) each cell of phase space having the size h^3 can at most contain two such points. It is thus obvious that each further (in our case valency) electron which should be placed in the volume element dv must have an initial energy greater than this maximum energy of the core electrons. This energy, which is a basic consequence of the Pauli principle can

be expressed by means of a potential which was derived by GOMBÁS and can be written

$$G_l(r) = -\frac{\pi^2}{4(2l+1)^2} D_l^2 - \frac{1}{2} \frac{1}{r^2}, \quad (2)$$

where D_l is the radial density of all core electrons having an azimuthal quantum number l . By introducing this potential into the Schrödinger equation — as mentioned above — the condition of orthogonality between the wave functions of the valency electrons and the wave functions of the core electrons is automatically fulfilled.

We shall now proceed with the calculation of the total energy of the valency electrons in the atomic sphere. As was shown by GOMBÁS [1, 2], it is possible to write the total energy of the valency electrons in a metal as the sum

$$U = E_K + E_G + E_A + E_W + W_G + W_B + W_A + W_K + W_W + H_S. \quad (3)$$

In contradiction to GOMBÁS, however, we supplemented the individual terms of this equation on the one hand by new expressions and on the other hand generalized them for the case of several valency electrons having a different azimuthal quantum number. The derivation of these expressions can be found in the cited book of GOMBÁS even though not always in this connection. Below there follows an explanation of the individual terms in equation (3).

E_K is the total kinetic energy of the valency electrons. As was mentioned above the individual electron levels in an atom split up into bands when the atoms group together. The width of these bands for the filled shells of the ion is negligible while this is not the case for valency electrons. We shall therefore assume in the following that the levels of the valency electrons having a certain azimuthal quantum number split up into one band. If we denote by ν_l the density of the valency electrons averaged over the angles ϑ and φ in the band formed from the level l , we can write for the total energy E_K the sum

$$E_K = E_K^0 + E_K^i + E_K^l. \quad (4)$$

*) The following units, if not otherwise stated, are used in this paper: The Bohr radius, i. e. the radius of the lowest electron orbit

$$a_0 = \frac{h^2}{4\pi^2 m e^2}$$

is used as the unit of length and Rydberg units

$$\text{Ry} = \frac{e^2}{2a_0}$$

are used for the energy.

E_K^0 is the kinetic energy of the electron gas in the individual bands at the absolute zero of temperature

$$E_K^0 = \sum_l 2\kappa_k \int \nu_l^{\frac{5}{2}} dv, \quad \kappa_k = 2.871, \quad (5)$$

where the integration is carried out throughout the whole volume of the atomic sphere (which will not be specially marked by limits of integration), and the sum is extended over all l for which $\nu_l \neq 0$.

E_K^i is the contribution to the kinetic energy from the non-uniform distribution of density.

$$E_K^i = \sum_l 2\kappa_i \int \frac{1}{\nu_l} (\text{grad} \nu_l)^2 dv, \quad \kappa_i = \frac{1}{8}. \quad (6)$$

E_K^l is the average minimum kinetic energy of the valency electrons in the quantum state l

$$E_K^l = \sum_l \int \frac{l(l+1)\nu_l}{r^2} dv. \quad (7)$$

This energy can also be interpreted as a consequence of the orthogonality between wave functions of the l -th state and wave functions of the valency electrons having a different azimuthal quantum number, because the term $\frac{l \cdot (l+1)}{r^2}$

corresponds to the angular part of the wave function of the electron.

E_o is the electrostatic energy which also includes the self energy of the valency electrons compensated by an identical term in the exchange energy E_A following from the interaction of the electron with its own self. It can be written in the form

$$E_o = \int \frac{\nu(\vec{r})\nu(\vec{r}')}{|\vec{r}-\vec{r}'|} dv dv', \quad (8)$$

where $\nu = \sum_l \nu_l$.

E_A is the exchange energy of the valency electrons and is given by the expression

$$E_A = -2\kappa_a \int \nu^{\frac{3}{2}} dv, \quad \kappa_a = 0.7386. \quad (9)$$

E_w is the correlation energy given to a first approximation by the expression

$$E_w = -\int g(\nu^{\frac{1}{2}}) \nu dv, \quad (10)$$

where the function $g(x)$ is defined by

$$g(x) = \frac{a_1}{x+a_2} x, \quad a_1 = 0.11294, \quad a_2 = 0.1216.$$

W_o and W_E is the contribution of the Coulomb potential and its deviation from the true ion potential. If we denote the potential of the ion by V we can write

$$W_o + W_E = -\int V \nu dv. \quad (11)$$

W_A is the exchange energy between the core electrons and the valency electrons. In the first approximation it can be written

$$W_A = -2\kappa_a \int_0^{r_g} [(\rho + \nu)^{\frac{3}{2}} - \rho^{\frac{3}{2}} - \nu^{\frac{3}{2}}] dv, \quad (12)$$

where r_g is the radius for which the ion density ρ equals the limiting ion density of the Thomas-Fermi-Dirac model $\rho_0 = 0.002127$. It was shown by GOMBÁS that for $\rho < \rho_0$ equation (12) ceases to correspond to reality.

W_K is the repulsion energy of the valency electrons being a consequence of the Pauli principle. Due to (2) it is given by the expression

$$W_K = -\sum_l \int G_l \nu_l dv. \quad (13)$$

W_w is the correlation energy due to the interaction between core electrons and the valency electrons. This energy is fairly small and GOMBÁS derived for it the approximate expression

$$W_w \doteq 0.130 W_A.$$

H_s finally is the energy due to ion-ion interaction the electron shells of which overlap. The expression for this energy will be found in the already cited book by GOMBÁS [1] or in his recent paper [2].

As was mentioned above, GOMBÁS calculated inter alia the total energy of univalent and bivalent metals on the assumption that the density of the valency electrons in these metals is uniform, i. e. $l = 0$, $\nu_0 = \text{const}$. After substituting these values into equation (3) there remains in the expression for the kinetic energy only the term E_K^0 and it is completely identical to that of GOMBÁS derived for the total energy of univalent or bivalent metals. It is, however, necessary to stress that this agreement is only formal since Gombás' assumption does not necessarily correspond in our case to that state of the crystal for which its total energy is a minimum. We shall deal with this question in greater detail in a future paper.

The assumption of uniform density of the valency electrons considerably simplifies numerical calculations of the individual terms of equation (3). It is obvious that this assumption which is only very approximate for univalent metals is without question much less suited for metals having two valency electrons, while for the rest of the metals uniform valency electron distribution hardly corresponds to reality. Probably the only exception

in this group of metals is aluminium some physical properties of which point to the fact that the valency electrons are to a great extent "free". We shall therefore retain the assumption that the three electrons of aluminium which in the free atom are in the $3s^2 3p$ state are to a first approximation uniformly spread over the atomic sphere with a density

$$\nu_0 = \frac{6}{4\pi R^3}, \quad \nu_1 = \frac{3}{4\pi R^3}. \quad (14)$$

On the above assumption we can easily evaluate those terms of equation (3) which contain the mutual interaction of the valency electrons

$$E_K^0 = \frac{9.2263}{R^2}, \quad (15)$$

$$E_K^1 = \frac{6}{R^2}, \quad (16)$$

$$E_C = \frac{10.8}{R}, \quad (17)$$

$$E_W = -\frac{2.4922}{7.3555 + R}, \quad (18)$$

$$E_A = -\frac{3.9650}{R}. \quad (19)$$

For the calculation of further terms of equation (3) Hartree's calculations of the radial densities D_i and the potential for Al^{+++} [5] was used, r_g being determined from the same calculations.

In the expression for the energy W_K the limits of integration may be extended to infinity, because from $r = 2.2$ the integrand is equal to zero. This energy can therefore be written (for $R \geq 2.2$) in the form

$$W_K = \frac{38.3034}{R^3} + \frac{4.5}{R^2}. \quad (20)$$

The terms W_A and $W_C + W_K$ cannot be expressed as functions of R in a sufficiently simple and precise analytical form. It can also be easily shown that the terms W_W and H_S can be neglected for aluminium. The error thereby omitted does not exceed the error with which the energy E_W is determined. Substituting into equation (3) we obtain for the total energy

$$U = \frac{6.8350}{R} - \frac{2.4922}{7.3555 + R} + \frac{19.7263}{R^2} + \frac{38.3034}{R^3} + \frac{27.110}{R^4} - \frac{9}{R^3} \int 2Z_p r dr - 18.5630 \int_0^{r_g} [(\rho + \nu)^{\frac{4}{3}} - \rho^{\frac{4}{3}}] r^2 dr. \quad (21)$$

The energy U was calculated for various R in the range $\langle 2.4, 3.4 \rangle$ the value 1.898 being substituted for r_g . The results of these calculations are given in table I.

Table I.

R	2.4	2.6	2.8	3.0	3.2	3.4
$-U$	3.8922	4.0545	4.1179	4.1212	4.0852	4.0234

Knowing the dependence of U on R we can easily calculate the radius of the atomic sphere for equilibrium state R_0 if we put

$$\left(\frac{dU}{dR}\right)_{R=R_0} = 0. \quad (22)$$

For this purpose the function $U(R)$ was approximated by a polynomial and after substituting condition (22) the value

$$R_0 = 2.911,$$

was obtained. The experimental value is

$$R_0^{\text{exp}} = 2.984.$$

The minimum energy corresponding to this radius of the atomic sphere is

$$U_0 = -4.1255.$$

from which we can easily calculate the binding energy, i. e. that energy per atom which is needed to decompose metallic aluminium into free ions and free valency electrons. The binding energy per atom S can therefore be written as the absolute value of the sum of U_0 and the absolute value of the sum of the ionisation energies of the valency electrons I

$$S = |U_0 + |I||. \quad (23)$$

Substituting into equation (23) the value (22) and the sum of the ionisation energies [6]

$$I = 3.8971,$$

we obtain for the binding energy the value

$$S = 71.6 \text{ kcal/mol.}$$

The experimental value reduced to absolute zero is (7)

$$S^{\text{exp}} = 67.6 \text{ kcal/mol.}$$

It was mentioned above that the lattice constant or the radius of the atomic sphere and the binding energy are two constants which to a certain extent depend considerably less on the structure of the BZ and on the distribution of energy in

reciprocal space than other constants of a metal. It is also found that the agreement of the two values with experiment is very good.

From the statistical model of the atom we can comparatively easily calculate the compressibility κ defined by the following relation

$$\kappa = -\frac{1}{v_0} \frac{dv}{dp} = 12\pi R_0 \frac{1}{\left(\frac{dU}{dR}\right)_{R=R_0}}. \quad (24)$$

After substituting into this formula we obtained for the compressibility the value

$$\kappa = 0.65 \cdot 10^{-12} \text{ cm}^2/\text{dyn}.$$

The experimental value reduced to absolute zero

of temperature is according to GRÜNEISEN [8]

$$\kappa^{\text{exp}} = 1.3 \cdot 10^{-12} \text{ cm}^2/\text{dyn}.$$

We cannot but stress the fact that the compressibility and in general all the elastic constants depend considerably in the BZ so that as far as these are concerned only an estimate of the order of magnitude can be obtained. Although for the compressibility the agreement with experiment is considerably worse than for R_0 and S , the deviation of the value is only a little larger than the deviation for elements having two valency electrons, where according to GOMBÁS (9) it amounts to 30% to 40%.

Received 15. 9. 52, First Published (in Czech) 15. 1. 53.

К ВОПРОСУ СТАТИСТИЧЕСКОЙ ТЕОРИИ МНОГОВАЛЕНТНЫХ МЕТАЛЛОВ

(Содержание предыдущей статьи)

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В настоящей работе статистическая модель одновалентных или двухвалентных металлов распространена на металлы со многими валентными электронами. Автор различил валентные электроны согласно азимутальному квантовому числу, что привело к несколько иному выражению для кинетической энергии валентных электронов в элементарной сфере (4). Общую энергию валентных электронов при этом можно выразить в виде (3). На основании этой модели металла автор выяснил некоторые константы металлического алюминия, предполагая, что валентные электроны в металле равномерно рас-

пределены с плотностью (14). Оказалось, что вычисленные значения радиуса элементарной сферы R_0 и энергии связи S_0 хорошо согласуются с измеренными значениями R_0^{exp} и S_0^{exp} . Что же касается значения коэффициента сжимаемости κ , то его согласованность с экспериментом в основном хуже, что и нужно было ожидать, т. к. статистический метод не принимает во внимание влияние Бриллюэновых зон на константы упругости, которое в случае многовалентных металлов будет значительным.

Поступило 15. 9. 1952, в первый раз опубликовано (на чешском языке) 15. 1. 1953.

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*) Note added on proof: the paper was meanwhile published: R. GÁSPÁR, Ueber die Bindung des Metallischen Aluminiums, Acta Phys. Hung. 2 (1952) 31.