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 Gombáš 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

\[ e^{i\vec{k}\cdot\vec{r}} \]

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 ele-
trons were consistently distinguished according to the azimuthal quantum number \( l \), while in the case of the potential \( F \) this was not consistently adhered to. The potential \( G_1 \) 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 \( G_1 \) is briefly this:

If the volume element is \( d\mathbf{r} \) 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 \( d\mathbf{r} \) having momenta \( \langle p_x, p_y + dp_y, p_z \rangle \), \( \langle p_x, p_y - dp_y, p_z \rangle \), \( \langle p_x, p_y + dp_y, p_z \rangle \) is given by the formula

\[
\frac{2}{h^3} \frac{dp_x \, dp_y \, dp_z}{dv}.
\]  

(1)

Let us now divide momentum space by coaxial cylindrical surfaces the axis of which is identical with the position vector \( \mathbf{r} \) of the volume element \( d\mathbf{r} \) so that the individual hollow circular cylinders contain consecutively the points representing the states of electrons having an azimuthal quantum number \( l = 0, 1, 2, \ldots \). 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

\[
[p_l] = \frac{\hbar}{2\pi}.
\]  

(2)

Let us further assume that the potential of the core electrons in a sufficiently small volume element \( d\mathbf{r} \) 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 \( d\mathbf{r} \) 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

\[
G_1(r) = - \frac{\pi^2}{4(2l + 1)^2} \frac{1}{D_l^2} \frac{1}{2} \left( \frac{1}{2} \right)^{l^2}.
\]  

(3)

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

\[
U = E_x + E_e + E_x + E_w + W_e + W_x + W_x + W_w + H_w.
\]  

(4)

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).

\( E_x \) 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 \( v_l \) the density of the valency electrons averaged over the angles \( \theta \) and \( \varphi \) in the band formed from the level \( l \), we can write for the total energy \( E_x \) the sum

\[
E_x = \frac{E_p^e + E_x + E_w}{v_l}.
\]  

(5)

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

\[
a_0 = \frac{\hbar^2}{4\pi^2 \epsilon_0 m_e}
\]  

is used as the unit of length and Rydberg units

\[
\text{Ry} = \frac{\epsilon_0}{2a_0}
\]  

are used for the energy.