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The Electronic Structures around Impurities in Monovalent Metals*

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The behaviours of electrons in binary alloys which form solid solutions are discussed on the basis of BLOCH's free electron theory. In this work the perturbation potential due to a solute atom is taken to be of the type $-Ze^2(1+\eta)r^{-1}\exp(-qr)$ *a priori*. The parameters q and η are determined self-consistently, and on the assumption that η is zero, q becomes identical with the shielding constant which MOTT obtained by THOMAS-FERMI's method. Further, the heat of formation of alloys in disordered state, the heat of solution of hydrogen in copper, and the work functions of alloys, are discussed.

§ 1. Introduction

The electronic theories of the binary alloys have been studied by MOTT, FRIEDEL and many others. They investigated the binary alloys in which both components are completely soluble with each other and one of the components is sufficiently sparse. MOTT¹⁾ obtained the potential produced by a solute atom in the form $Zer^{-1}\exp(-qr)$ using THOMAS-FERMI's method, and calculated the electronic conductivity and heat of formation of alloys. FRIEDEL²⁾ dealt with the electronic structure around a solute atom in terms of the phase shifts of free electrons, assuming that there are some bound states of electrons around a solute atom, and discussed the heat of solution of hydrogen and of polyvalent metals in noble metals, and also the magnetic susceptibility and x-ray emission and absorption of these alloys.

We shall treat here the electronic structure around a solute atom from the viewpoint of free electron theory for the case where the solvent metal (noble metal) contains few solute atoms (polyvalent or hydrogen atoms) which do not interact among themselves. It

* The main contents of the present paper were already reported at the meeting of the Physical Society of Japan held in October, 1953.

will be assumed that the perturbation potential energy due to a solute atom (impurity atom) in the solvent metal is $-Ze^2(1+\eta r)\exp(-qr)$ and that there is no bound level of the electrons around the solute atom. $Z+1$ is the valency of the solute atom, $-Ze^2r^{-1}\exp(-qr)$ is the COULOMB energy in the field of an impurity ion and electrons around this ion, and $-Ze^2\eta r\exp(-qr)$ is the exchange energy due to these electrons.

If plane waves are adopted as the wave functions of electrons in the conduction band of pure metal, this treatment reduces to that of BORN's approximation in the scattering problem³⁾, so that one may get a good approximation at least for the electrons which have high energy.

In the first place, the charge distributions will be calculated, the free electron model being used as the unperturbed system and $-Ze^2(1+\eta)r^{-1}\exp(-qr)$ as the perturbation term; the COULOMB part and the exchange part of the potential energy produced by the above charge distribution are then equated to $-Ze^2r^{-1}\exp(-qr)$ and $-Ze^2\eta r^{-1}\exp(-qr)$, respectively, and the equations thus obtained will be solved with respect to q and η , which yields the self-consistent solution.

Finally, by use of these values of q and η , the heat of solution of polyvalent metal atoms in noble metals, the heat of solution of hydrogen atoms in copper and the work functions of alloys will be calculated.

§ 2. Distribution of Electronic Charge

The wave function of an electron in a pure metal and the eigenvalue of the energy are

$$\psi_k^0 = V^{-1/2} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (2.1)$$

and

$$E_k = (\hbar^2/2m) k^2, \quad (2.2)$$

respectively, where V stands for the volume of the crystals, $\mathbf{k}$ the wave vector, $\mathbf{r}$ the coordinate vector of the electron and m the electron mass.

The perturbed wave function and the energy are respectively, in the approximation of the 2nd order perturbation,

$$\psi_k = V^{-1/2} e^{ikr} + V^{-1/2} \sum_{k'} \{H_{kk'}/(E_k - E_{k'})\} e^{ik'r} \quad (2.3)$$

and

$$W_k = (\hbar^2/2m) k^2 + H_{kk} + \sum_{k'} \{|H_{kk'}|^2/(E_k - E_{k'})\}, \quad (2.4)$$

where

$$H_{kk'} = -V^{-1} Z e^2 (1+\eta) \int (e^{-qr}/r) e^{-i(k'-k)r} d^3r. \quad (2.5)$$

A variation ρ' of charge density of electrons is caused by the impurity atom:

$$\rho' = \sum_k \psi_k^* \psi_k - \sum_k \psi_k^{0*} \psi_k^0 = 2 \sum_k \sum_{k'} \{H_{kk'}/(E_k - E_{k'})\} \psi_k^{0*} \psi_k^0. \quad (2.6)$$

The summation for k extends from 0 to the wave vector k_0 of Fermi-surface, and that for k' over all the k -space. From (2.1), (2.2) and (2.5), we get

$$\begin{aligned} & \sum_k \sum_{k'} \{H_{kk'}/(E_k - E_{k'})\} \psi_k^{0*} \psi_k^0 \\ &= -2 \frac{V}{(2\pi)^6} \int dk \int dk' \frac{8\pi m Z e^2 (1+\eta)}{V \hbar^2 (p^2 + q^2) (k^2 - k'^2)} e^{i(k'-k)r} \\ &= \frac{Z(1+\eta)}{4\pi^5 a_H} \int dk \int d\mathbf{p} \frac{1}{p^2 + q^2} \cdot \frac{e^{-i\mathbf{p}r}}{p^2 + 2(\mathbf{p} \cdot \mathbf{k})}. \quad (2.7) \end{aligned}$$

The factor 2 in the second expression of (2.7) arises from the spin degeneracy. a_H is the Bohr-radius, and $\mathbf{p}$ is defined as the difference

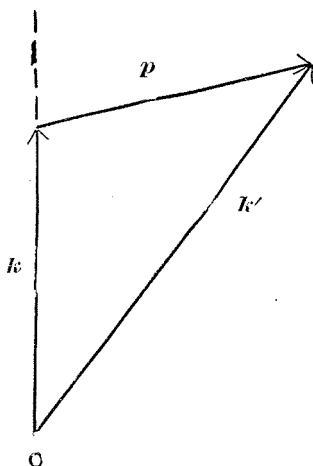


Fig. 1.

between k' and k (Fig. 1). With reference to Fig. 1, (2.7) can be integrated:

$$\begin{aligned} & \frac{Z(1+\eta)}{2\pi^4 a_H} \int d\mathbf{p} \frac{e^{-i\mathbf{p}r}}{p^2+q^2} \cdot \frac{1}{p} \int_0^{k_0} k^2 dk \int_{-1}^{+1} \frac{dx}{p+2kx} \\ &= \frac{Z(1+\eta)}{2\pi^4 a_H} d\mathbf{p} \frac{e^{-i\mathbf{p}r}}{p^2+q^2} \cdot \frac{k_0}{4} \left\{ 1 - \frac{p^2-4k_0^2}{4pk_0} \log \left| \frac{p+2k_0}{p-2k_0} \right| \right\} \\ &= \frac{Z(1+\eta)}{2\pi^3 a_H} \frac{k_0}{r} \int_0^\infty dp \frac{p \sin(pr)}{p^2+q^2} f(p, k_0) \end{aligned} \quad (2.8)$$

with

$$f(p, k_0) = 1 - \frac{p^2-4k_0^2}{4pk_0} \log \left| \frac{p+2k_0}{p-2k_0} \right|,$$

and therefore

$$\rho' = \frac{Z(1+\eta)k_0}{\pi^3 a_H r} \int_0^\infty dp \frac{p \sin(pr)}{p^2+q^2} f(p, k_0). \quad (2.9)$$

The function $f(p, k_0)$ has a maximum value 2 at $p=0$, and becomes smaller as p increases (the solid curve in Fig. 2). It will now be assumed that $f=2$ independent of p (the broken curve in Fig. 2). It is too large for large values of p , but it has little influence upon the value of (2.9) on account of the factor (p^2+q^2) . Thus the integration in (2.9) can easily be carried out, yielding

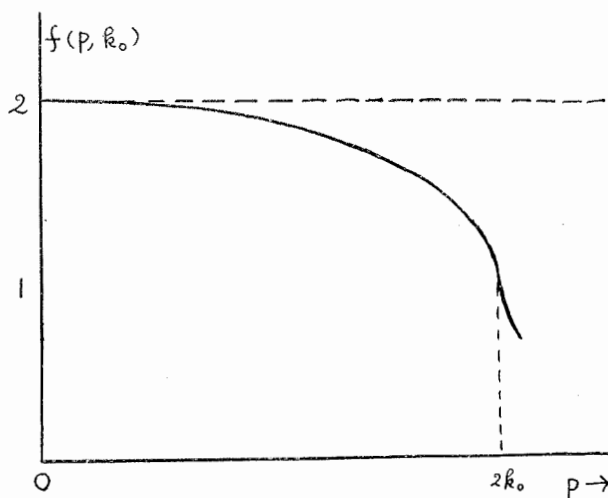


Fig. 2.

$$\rho' = \frac{Z(1+\eta)k_0}{\pi^2 a_H} \frac{e^{-qr}}{r}. \quad (2.10)$$

On the supposition that the distribution ρ' causes the perturbation potential which was adopted at first, q and η can be determined self-consistently. The Poisson-equation of the electrons around an impurity atom is given by¹⁾

$$\Delta Z e r^{-1} (e^{-qr} - 1) = 4\pi e \rho', \quad (2.11)$$

while according to SLATER's simplified theory⁵⁾, the exchange potential energy for a free electron is expressed as $-3e^2(3/8\pi)^{1/3}\rho^{1/3}$ (ρ : the density of the free electrons). On substituting the relation $\rho = \rho_0 + \rho'$ (ρ_0 : the density of free electrons in pure crystal) into this expression of exchange energy, one obtains the variation of the exchange energy caused by ρ' . This is equal to the exchange part of the perturbation energy:

$$-Ze^2\eta r^{-1}e^{-qr} = -e^2(3/8\pi)^{1/3}(\rho'/\rho_0^{2/3}). \quad (2.12)$$

Thus equations (2.11) and (2.12) yield q and η :

$$\frac{1}{q} = \sqrt{\frac{\pi a_H}{4k_0}} \left(1 - \frac{3}{2\pi k_0 a_H}\right) \quad (2.13)$$

and

$$\eta = \frac{3/2\pi k_0 a_H}{1 - 3/(2\pi k_0 a_H)}. \quad (2.14)$$

ρ' satisfies the condition of normalization

$$\int \rho' dr = Z. \quad (2.15)$$

If the exchange term is not contained in the perturbation energy, η is zero. Then ρ' and q turn out to be

$$\rho' = \frac{Zk_0}{\pi^2 a_H r} \int_0^\infty dp \frac{p \sin(pr)}{p^2 + q^2} f(p, k_0) \cong \frac{Zk_0}{\pi^2 a_H} \frac{e^{-qr}}{r}, \quad (2.16)$$

and

$$q^{-1} = \sqrt{\pi a_H / (4k_0)}. \quad (2.17)$$

Here it is also assumed that $f(p, k_0) = 2$. The results (2.16) and (2.17) are identical, so far as the shielding constant is concerned, with that derived by MOTT in 1936 and by FRIEDEL in 1953⁶⁾. It

is to be noticed that, in order to obtain the expression (2.17), it is necessary to assume that $f(p, k_0) = 2$.

In Fig. 3, the functions ρ' and $\rho'r^2$ are illustrated for different values of the parameter q , in order to see to what extent the second expression deviates from the first in (2.16).

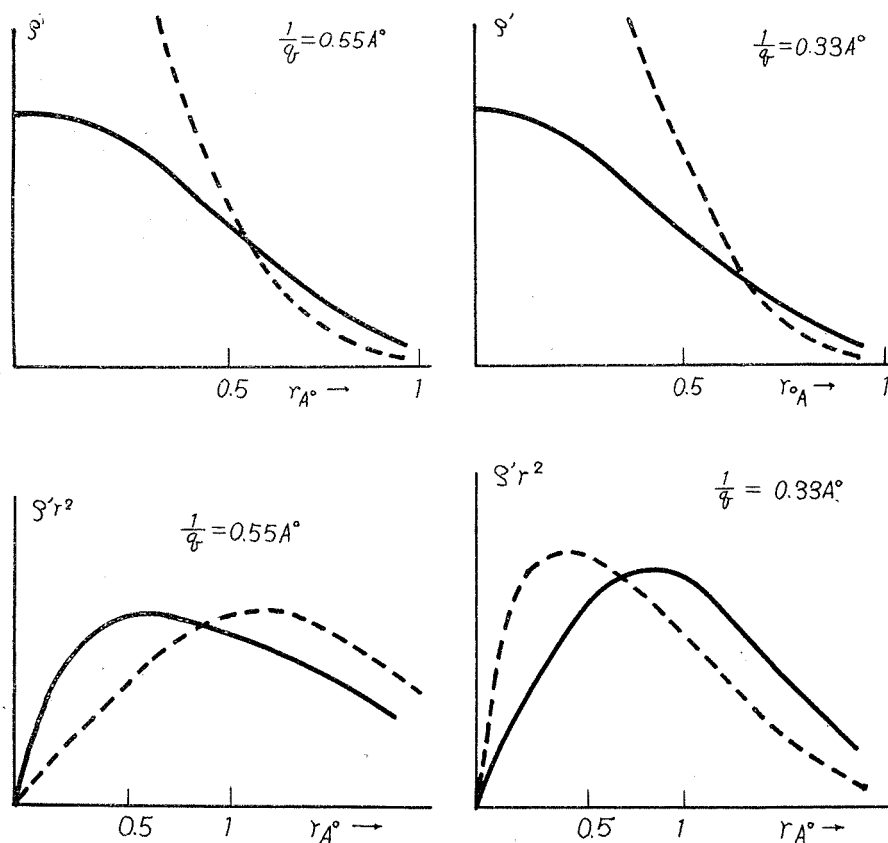


Fig. 3.

The solid curves: The first expression of (2, 16).
The broken curves: The second expression of (2, 16).

§3. Heat of Formation of Alloys

The AB alloy can be conceived to result through the following processes.

- 1) First, an A-ion is removed out from the lattice point of the metal A, and a free electron from the conduction band. (The energy H_1 is needed for this).
- 2) The ion and the electron thus taken out are brought together to form an A-atom (I_A : the ionization energy of the A-atom).
- 3) This atom A is added to another metal A (W_A : the sublimation energy of the metal A).
- 4) An atom B is removed out from the metal B (W_B : the sublimation energy of the metal B).
- 5) All the $Z+1$ valance electrons are removed from this atom B ($\sum^{Z+1} I_B$: the summation of the ionization energies of the atom B).
- 6) This B-ion is put into the hole from which the A-ion was removed, and at the same time $Z+1$ electrons are put into the conduction band, the number of conduction electrons thus increasing by Z as compared with that of the initial metal. (The energy H_2 is needed for this).

If these processes are repeated m' times, the metal turns into the alloy AB which contains m' solute atoms. Putting $\Delta E(m')$ equal to the difference between H_1 and H_2 , one obtains the heat of formation of alloy $\Delta E(m')$:

$$\Delta E(m') = m' \left\{ \sum^{Z+1} I_B - I_A + W_B - W_A \right\} + \sum^{m'} \Delta E(m'). \quad (3.1)$$

In case m' is very small and the solute atoms have no interaction among themselves, the heat of formation per one solute atom is given by

$$\Delta E = \sum^{Z+1} I_B - I_A + W_B - W_A + \Delta E. \quad (3.2)$$

ΔE is the average value of $\Delta E(m')$, that is, the difference between the crystal energies of the alloy and the pure metal.

When the crystal contains m' solute atoms, the energy of the electron with the wave vector k becomes, from the equation (2.4),

$$W_k = \frac{\hbar^2 k^2}{2m} - m' \frac{4\pi Z e^2 (1+\eta)}{V q^2} - m' \frac{4\pi Z e^2 (1+\eta)^2}{V a_{BQ} (4k^2 + q^2)}. \quad (3.3)$$

If the fraction of solute atoms per one atom in the crystal is defined as

$$x = m' / VN = (m' / V) (4\pi r_s^3 / 3), \quad (3.4)$$

W_k comes out

$$W_k = \frac{\hbar^2 k^2}{2m} - x \left\{ \frac{3Ze^2(1+\eta)}{r_s^3 q^2} + \frac{3Z^2 e^2(1+\eta)^2}{r_s^3 a_H q(4k^2 + q^2)} \right\}. \quad (3.5)$$

Supposing that there is no variation of repulsion energy between ion cores, one obtains, by the definition of $\Delta\epsilon$,

$$\Delta\epsilon = \frac{\partial}{\partial x} (\bar{W}_k - \bar{E}_k) + Z\epsilon_0 + \sum_i Ze^2 r_i^{-1} e^{-qr_i}, \quad (3.6)$$

where the bar means the average over all the electrons in the conduction band, ϵ_0 is the minimum energy of conduction band in the pure metal, and the last term is the static energy between an impurity atom and the ions in lattice points. The 2nd term is added to (3.6), because the number of electrons in the conduction band of alloy is larger by Z than that of pure metal. $\bar{W}_k$ and $\bar{E}_k$ become respectively as follows:

$$\begin{aligned} \bar{W}_k &= \frac{\sum_k W_k f_k}{\sum_k f_k} = \frac{\int_0^{k_0} (V k^3 / \pi^3) W_k dk}{\int_0^{k_0} (V k^3 / \pi^3) dk} \\ &= \frac{3\hbar^2 k_0^2}{10m} - x \frac{3Ze^2(1+\eta)}{2r_s^3 q^2} - x \frac{9Z^2 e^2(1+\eta)^2}{2r_s^3 a_H q k_0^3} \left(\frac{k_0}{4} - \frac{q}{8} \tan^{-1} \frac{2k_0}{q} \right) \\ &\quad - \frac{m'}{V} \int_0^\infty \frac{1}{2} \frac{Ze^2}{r} 4\pi r^2 dr \end{aligned} \quad (3.7)$$

$$\bar{E}_k = 3\hbar^2 k_0^{*2} / (10m), \quad (3.8)$$

where the distribution function of electrons, f_k , is assumed to be equal to unity, and k_0 and k_0^* are the maximum wave vectors of free electrons in the alloy and in the pure metal at 0°K, respectively. In the 2nd and 3rd terms of (3.7) the factor, 1/2, is multiplied to those of (3.5), because the one-electron approximation is adopted here, and so W_k contains twice the interaction energies of electrons without the interaction energies of electrons and impurity ions, which are the last term of (3.7) and diverge unfortunately. But, when m' impurities are contained in the volume V and a impurity ion occupies the volume $\frac{4\pi}{3} R^3 = \frac{V}{m'}$, the last term equals approximately to

$$\frac{m'}{V} \int_0^\infty \frac{1}{2} \frac{Ze^2}{r} 4\pi r^2 dr = x^{1/3} \frac{3Ze^2}{4r_s} \quad (3.9)$$

If x is much smaller than unity, the lattice constant a and k_0 can be written as

$$a = a_0(1 + bx) \quad (3.10)$$

and

$$k_0 = k_0^* \left(1 + \frac{Z}{3}x - bx \right) \quad (3.11)$$

where a_0 is the lattice constant of a pure solvent metal, and b is a constant. Then

$$\begin{aligned} \Delta\epsilon = & \frac{3\hbar^2}{5} \left(\frac{Z}{3} - b \right) k_0^2 - \frac{3Ze^2(1+\eta)}{2r_s^3q^2} \\ & - \frac{9Z^2e^2(1+\eta)^2}{2r_s^3a_Bqk_0^3} \left(\frac{k_0}{4} - \frac{q}{8} \tan^{-1} \frac{2k_0}{q} \right) - x^{-2/3} \frac{Ze^2}{4r_s} \\ & + Z\epsilon_0 + \sum_i Ze^2r_i^{-1}e^{-\eta r_i}. \end{aligned} \quad (3.12)$$

TABLE I.

Metal & Alloy	I_1 e.v.	I_2 e.v.	I_3 e.v.	W e.v.	ϵ_0 e.v.	a Å	b
Cu	7.68			3.52	-15.44	3.609	
Ag	7.54			2.95	-13.80	4.078	
Zu	9.35	17.89		1.59			
Cd	8.96	16.84		1.16			
Al	5.96	18.73	28.31	2.39			
Cu-Zn							0.05 ⁽⁷⁾
Ag-Cd							0.05 ⁽⁷⁾
Cu-Al							0.47 ⁽⁸⁾

From equation (2.13) (2.14), (2.17) (3.2) and (3.12) one obtains the values of q , η and ΔE shown in the table II, where the entropy term in ΔE is neglected. In the table I, the experimental values of I , W , ϵ_0 , a_0 and b are contained.

TABLE II.

Cu-Zn ($Z = 1$)

Zx	$k_0 \times 10^{-1}$ cm $^{-1}$	$\frac{1}{q} \times 10^8$ cm	$\eta = 0$	η	ΔE e.v.	$\eta = 0$	exp. ⁽⁹⁾
0.10	1.40	0.324	0.545	1.82	- 12.0	- 10.0	- 0.29
0.20	1.44	0.327	0.537	1.69	- 7.4	- 5.3	

Ag-Cd ($Z=1$)

Zx	k_0	$\frac{1}{q}$	$\eta = 0$	η	ΔE	$\eta = 0$	exp. ⁽⁹⁾
0.10	1.24	0.301	0.579	2.70	- 10.3	- 8.2	- 0.2
0.20	1.27	0.307	0.571	2.46	- 6.0	- 4.1	

Cu-Al ($Z=2$)

Zx	k_0	$\frac{1}{q}$	$\eta = 0$	η	ΔE	$\eta = 0$	exp.
0.10	1.37	0.321	0.550	1.93	- 36.7	- 29.3	- 1.3
0.20	1.39	0.320	0.447	1.87	- 22.4	- 15.2	

§ 4. Heat of Solution of Hydrogen in Copper

When the hydrogen atom is dissolved in copper, it is split up into a proton and an electron, the former occupying an interstitial position in the lattice and the latter being in the conduction band. The heat of solution of hydrogen in the monovalent metal, ΔE_H , reduces to, owing to (3.2),

$$\Delta E_H = \Delta E' + I_H. \quad (4.1)$$

$\Delta E'$ is equal to ΔE plus the correction energy due to the motion of the proton. In order to treat the motion, the adiabatic approximation is used. One takes the equilibrium point of the proton as an origin, and $\mathbf{R}(X, Y, Z)$ as its coordinate vector (Fig. 4). Denote the wave function of free electron and the mass of proton by $\phi_k(\mathbf{r}, \mathbf{R})$ and M , respectively, then SCHRÖDINGER's equation becomes

$$\left(H_0 + H' - \frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 \right) \phi_k(\mathbf{r}, \mathbf{R}) = E_k' \phi_k(\mathbf{r}, \mathbf{R}), \quad (4.2)$$

where H_0 is the Hamiltonian of pure crystal, and H' the perturbed

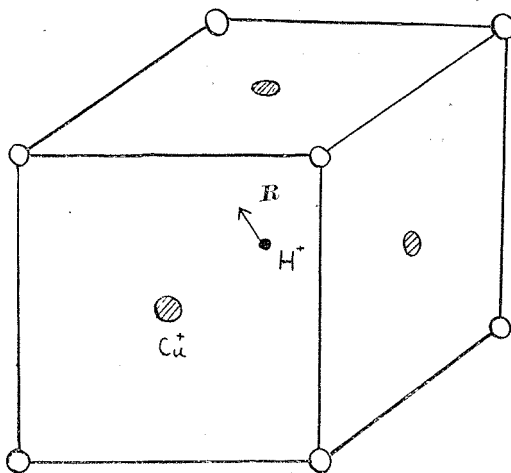


Fig. 4.

energy due to a hydrogen atom :

$$H' = -e^2(1+\eta) \frac{e^{-q|r-R|}}{|r-R|} + V(\mathbf{R}). \quad (4.3)$$

$V(\mathbf{R})$ is the static energy between copper-ions and the hydrogen, expressed by the last term of (3.6)

Putting

$$\phi_k(\mathbf{r}, \mathbf{R}) = \psi_k(\mathbf{r}, \mathbf{R}) \cdot \chi(\mathbf{R}), \quad (4.4)$$

in which $\psi_k(\mathbf{r}, \mathbf{R})$ and $\chi(\mathbf{R})$ are the wave functions of a free electron and of the proton, respectively, one obtains from the equation (4.2)

$$(H_0 + H') \psi_k(\mathbf{r}, \mathbf{R}) = E'_k(\mathbf{R}) \psi_k(\mathbf{r}, \mathbf{R}) \quad (4.5)$$

and

$$\{ -(\hbar^2/2M) \nabla_{\mathbf{R}}^2 + E'_k(\mathbf{R}) \} \chi(\mathbf{R}) = E'_k \chi(\mathbf{R}) \quad (4.6)$$

provided $-(\hbar^2/M) \nabla_{\mathbf{R}} \psi_k(\mathbf{r}, \mathbf{R}) \nabla_{\mathbf{R}} \chi(\mathbf{R})$ and $-(\hbar^2/2M) \chi(\mathbf{R}) \nabla_{\mathbf{R}}^2 \psi_k(\mathbf{r}, \mathbf{R})$ are neglected. By removing the coordinate origin from the equilibrium point of proton to the point $\mathbf{R}$, one can get the eigenvalue E'_k of (4.5):

$$E'_k = W_k + V(\mathbf{R}). \quad (4.7)$$

The distribution of free electrons in the pure metal is uniform,

and therefore W_k does not depend on $\mathbf{R}$. Suppose that only the ions of the nearest neighbours of the proton are summed up in $V(R)$, then the distances of copper-ions from the proton are $\{(a_0/2) \pm X, (a_0/2) \pm Y, (a_0/2) \pm Z\}$. We retain only the second order of R in the expansion of $V(\mathbf{R})$, obtaining

$$V(\mathbf{R}) = e^2(a_0/2)^{-1}e^{-qa_0/2}\{6 + (q^2 + 4q/a_0)R^2\} = AR^2 + B. \quad (4.8)$$

Substitution of (4.7) and (4.8) in (4.6) yields

$$\{-(\hbar^2/2M)\nabla_{\mathbf{R}}^2 + W_k + B + AR^2\}\chi(\mathbf{R}) = E_k''\chi(\mathbf{R}). \quad (4.9)$$

The lowest eigenvalue E_k'' is therefore given by

$$E_k'' = W_k + B + (3/2)\hbar \sqrt{A/2\pi^2 M}, \quad (4.10)$$

and the heat of solution of hydrogen in the monovalent metal comes out

$$\begin{aligned} \Delta E_H = & \frac{\hbar^2 k_0^2}{5m} - \frac{3e^2(1+\eta)}{2r_s^3 q^2} - \frac{9e^2(1+\eta)^2}{2r_s^3 a_H q k_0^3} \left(\frac{k_0}{4} - \frac{q}{8} \tan^{-1} \frac{2k_0}{q} \right) - x^{-2/3} \frac{e^2}{4r_s} \\ & + 6e^2(a_0/2)^{-1}e^{-qa_0/2} + \frac{3\hbar}{2} \sqrt{\frac{e^2}{2\pi^2 M} \left(q^2 + \frac{4q}{a_0} \right)} e^{-qa_0/2} \left(\frac{a_0}{2} \right)^{-1} \\ & + \epsilon_{0\text{cu}} + I_H. \end{aligned} \quad (4.11)$$

Let us consider the quantity of hydrogen absorbed in copper to be very small so that k_0 may be put equal to k_0^* and the lattice constant does not vary. One obtains the numerical values of ΔE_H as shown in table III.

TABLE III.

x	$k_0 \times 10^{-8}$ cm ⁻¹	$\frac{1}{q} \times 10^8$ cm	$\eta = 0$	η	ΔE_H e.v.	$\eta = 0$	exp.
0.01	1.36	0.320	0.552	1.98	-58.0	-51.0	-1.6

§ 5. The Work Function of Alloys

From the equation (3.5), one gets for the work function of alloy

$$\begin{aligned} \phi = & -\epsilon_0 - \frac{\hbar^2 k_0^2}{2m} - \left\{ 1.2 \frac{e^2}{r_s} - \frac{3Ze^2(1+\eta)x}{r_s^3 b^2} \right\} \\ & + \left\{ 0.612 \frac{e^2}{r_s} + \frac{3Ze^2(1+\eta)^2 x}{r_s^3 a_H q (4k_0^2 + q^2)} \right\} - 4\pi e P_n, \end{aligned} \quad (5.1)$$

and for that of pure metal

$$\varphi_0 = -\epsilon_0 - \frac{\hbar^2 k_0^{*2}}{2m} - 1.2 \frac{e^2}{r_{s0}} + 0.612 \frac{e^2}{r_{s0}} - 4\pi e P_{n0}. \quad (5.2)$$

In (5.1) and (5.2) the 3rd term is the COULOMB energy, the 4th term the exchange energy and the last term is the surface dipole term, which is usually small in monovalent metals⁽⁹⁾, and so P_n seems to be nearly equal to P_{ns} when x is very small.

If the variation of the lattice constant is considered, the difference between φ and φ_0 is

$$\Delta\varphi = x \left\{ -\frac{\hbar^2}{m} \left(\frac{Z}{3} - b \right) k_0^2 + \frac{1.2 e^2 b}{r_s} - \frac{0.612 e^2 b}{r_s} + \frac{3Ze^2(1+\eta)}{r_s^3 q^2} + \frac{3Z^2 e^2 (1+\eta)^2}{r_s^3 a_{Hq} (4k_0^2 + q^2)} \right\}. \quad (5.3)$$

In table IV, several values of $\Delta\varphi$ are shown in unit of e.v..

TABLE IV

Zx	Cu-Zn		Ag-Cd		Cu-Al	
	$\eta = 0$		$\eta = 0$		$\eta = 0$	
0.01	0.051	0.023	0.060	0.020	0.16	0.095
0.05	0.25	0.10	0.028	0.089	0.76	0.45
0.10	0.88	0.27	0.83	0.15	1.44	0.85
0.20	0.62	0.25	0.83	0.23	2.60	1.53

§ 6. Conclusion

The present calculation shows a contribution of the exchange energy to the heat of solution of alloys which have a few solute atoms. But in the more concentration of impurity atoms than several per cent it should be treated as the problem of two center scattering. It was shown in our previous work¹⁾ that the exchange energy should be taken into consideration for the electric conductivity and the paramagnetic susceptibility of alloys. The large deviation of the heat of solution arises from the circumstances that the interaction energy of the impurity-ion and free electrons diverges.

The approximation adopted in this work is that due to BORN,

and is invalid for the electrons having lower energies. In the calculation of ρ' and $\Delta\epsilon$, however, the integration with respect to k contains the factor k^2 , so that the contributions of low energy electrons are not too large, while in the scattering problem of low energy electrons the calculation must be carried through more strictly.

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