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Theory of Influence of Order-Disorder Transformations on the Electrical Resistivity in Alloys.

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§ 1. Introduction.

It is well known that in many binary alloys the atoms are arranged in an ordered manner at low temperatures, whereas at high temperatures the two sets of atoms are distributed at random over the lattice. As the temperature is raised the transition from the ordered to the disordered state manifests itself in many ways. The specific heat and the electrical resistance, for exemple, behave anomalousely. The first method of approximating to the partition function of an alloy, and hence of obtaining its properties, was given by Bragg and Williams.*) This theory on order-disorder transformation was based upon the consideration of the ordering as a co-operative phenomenon characteristic for large assemblies of atoms, i. e. the long distance order. Bethe,**) on the other hand, has developed the statistical theory based on the local order, taking into account the only mutual interactions between the neighbouring atoms. It is difficult to apply his statistical problem here and furthermore, the physical properties now under consideration, such as electrical conductivity, should mainly depend on the order at long distances, showing a rapid change below the transition temperature. Hence, for the present purpose, we have adopted the theoretical results of the Bragg and Williams' statistics on superlattice.

The present paper is almost entirely concerned with the binary alloy Cu_3Au. The X-ray analysis shows that this alloy has a face-centred cubic structure like pure gold or copper, and that, in the superlattice state, the gold atoms occupy the corner

*) Proc. Roy. Soc. A vol. 145, (1934), p. 669; A vol. 151, (1935), p. 540.
**) Proc. Roy. Soc. A vol. 150, (1935), p. 552.

positions of the elementary cells, while the copper atoms occupy the remaining positions of the face-centred cube, as shown in Fig. 1. This crystal structure remains unchanged during the order-disorder transformation.

Let N be the total number of atoms in the crystal and $F_A N$ ($F_A = \frac{1}{4}$) the number of gold atoms (Au) to be distributed among these N lattice points. The number of copper atoms (Cu) is therefore $(1 - F_A) N = F_B N$ ($F_B = \frac{3}{4}$). For complete disorder the proba-

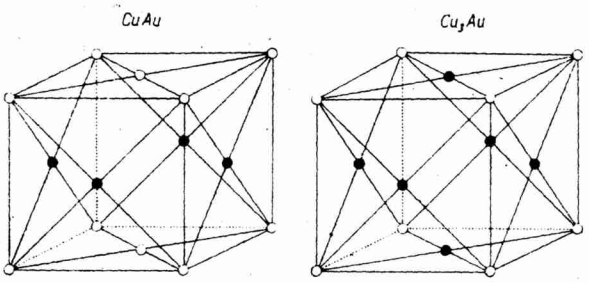

Fig. 1.

bility of any one of the N positions being occupied by a gold atom is F_A and that by a copper atom is $1 - F_A = F_B$. In the perfect ordered alloy on the other hand, both the Au and the Cu atoms form their own superlattices, the two lattices interpenetrating with each other. Let the number of lattice points in the gold superlattice be $F_A N$ (α — sites), then the number in the copper superlattice is $(1 - F_A) N$ (β-sites).

When the perfectly ordered arrangement is disturbed, some of the gold atoms will move into β-sites, displacing an equal number of copper atoms, which move into α-sites. We describe such situations by stating the fraction of α-sites still occupied by „right" atoms; let this fraction be r_α. Then the degree of superlattice order (Bragg-Williams long distance order) Φ may be written

$$\Phi = \frac{r_\alpha - F_A}{1 - F_A} = \frac{r_\alpha - F_A}{F_B}. \tag{1}$$

We see that Bragg-Williams' order parameter is so defined that it is unity for perfect order and zero for random state.

In an equilibrium state defined by Φ let V be the energy which is neccessary for the interchange of two neighbouring atoms from a position of order to one of disorder. Then V is a function of Φ. Bragg and Williams made, for the sake of simplicity, the following assumption:

$$V(\Phi) = V_0 \Phi, \tag{2}$$

where V_0 is the energy required for the creation of a pair of „wrong" atoms in a perfectly ordered alloy. By an elementary consideration of statistical mechanics we obtain the following condition of equilibrum*):

$$ln\left(\frac{1}{F_A(1-\Phi)}-1\right)+ln\left(\frac{1}{F_B(1-\Phi)}-1\right)=\frac{V}{kT}, \qquad (3)$$

wher k is Boltzmann's constant.

Eliminating V in the simultaneous equations (2) and (3), we obtain the equilibrum value of Φ corresponding to each value of T. The method of solution is a graphical one and was given by Bragg and Williams.**) The values of Bragg-Williams' parameter Φ for different temperatures obtained in this way are given in table I.

§ 2. Influence of order on the electrical resistivity of Cu_3Au alloy.

A. Experimental results.

Fig. 2 shows the effect of uniform long distance order on the resistivity of a Cu_3Au alloy. At room temperature the specific

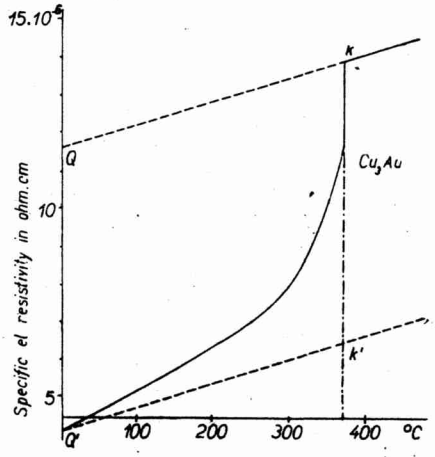

Fig. 2.

resistivity of the rapidly cooled disordered alloy, which is free from large volumes of long distance order, was found to be

*) Bragg-Williams: loc. cit.; Nix-Shockley: Rev. of Mod. Physics, Vol. 10, (1938), p. 16.

**) Bragg-Williams: loc. cit.

11,4 . 10^{-6} ohm . cm; on the other hand an alloy cooled sufficiently slowly to posses a uniform scheme of long distance order of high degree, has a specific resistivity of 3,9 . 10^{-6} ohm . cm. The smooth curve below shows the equilibrium resistance-temperature curve of the alloy with coherent schemes of long distance order.*) We see that upon the normal linear dependence on temperature there is superimposed a rapidly increasing rise terminated by a discontinnous jump at the temperature 372° C. Thus the difference of ordinates between the line $Q'K'$,**) which is para-

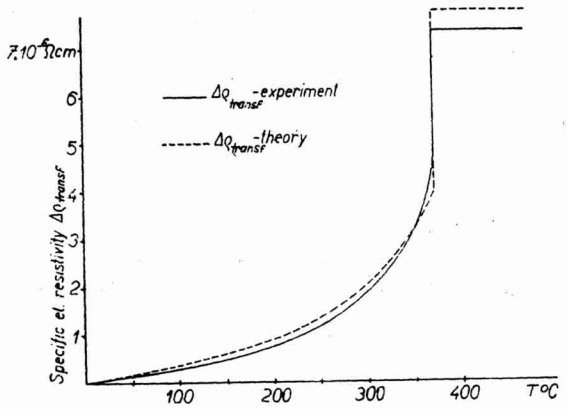

Fig. 3.

llel to QK and the equilibrium curve, mentioned above, give the *anomalous specific resistance* of the alloy due to the order-disorder transformation. The value of this anomalous specific resistivity of Cu_3Au for different temperatures are given in the table I. ($\varrho_{experiment}$!) and in the figure 3.

B. The theory of resistance of alloys.

Following the general quantummacanical theory of electrical resistance as formulated by N. F. Mott,***) we may express the resistivity as follows: the electrical conductivity of metal may be written in the form:

$$\sigma = \frac{Ne^2}{m}\tau,$$

*) Jones, Sykes; Proc. Roy. Soc. A vol. 166 (1938), p. 379.

**) Print Q' denontes the specific resistance of a perfectly ordered alloy at zero temperature.

***) Mott; Theory of the properties of Metals and alloys; Oxford 1936, p. 247.

where τ is the „time of relaxation", equal to half the time between collisions, N is the effective number of free electrons per unit volume, and m, e is mass or charge of the electron respectively; hence for the resistivity we have

$$\varrho = \frac{m}{Ne^2}\frac{1}{\tau}.$$

$\frac{1}{\tau}$ may be also interpreted as the probability per unit time that an electron makes a collision, or is scattered. We know further that according to quantum mechanics, electrons will move through a perfectly *periodic* field without being scattered at all; in a pure metal or perfectly ordered alloy, the only pertubations from the perfect periodic potential in which the conduction electrons move, are due to the thermal vibrations, which give rise to a scattering probability p_t (say), proportional to the temperature. In the solid solution or disordered alloy there will be a further departure of the field from periodicity in the places wihich are occupied by foreign atoms or atoms in wrong positions and hence there will be a further scattering probability p_0 independent of the temperature. It may be shown that these probabilities are independent of one another;*) we thus have

$$\varrho = \frac{m}{Ne^2}(p_t + p_0),$$

and hence for the anomalous resistivity of alloy due to the order-disorder transformation

$$\Delta\varrho_{\text{transf}} = \frac{m}{Ne^2}\, p_0. \tag{1}$$

We know that in pure copper or gold there is one free electron per atom; we can thus suppose, that in the formula for $\Delta\varrho_{\text{transf.}}$ in the case of alloys Cu-Au, the effective number of electrons per unit volume is identical with the number of atoms per unit volume.

On the other hand p_0 is given by the well known formula:**)

$$p_0 = \int_0^{\pi} P(\vartheta)\,(1 - \cos\vartheta)\sin\vartheta\, 2\pi\, \mathrm{d}\vartheta, \tag{2}$$

where $P(\vartheta)$ is the probability per unit time that an electron is scattered through the solid angle $\mathrm{d}\omega$; $P(\vartheta)$ is assumed to be independent of the direction of motion of the electron. Thus we see that we have to calculate the probability $P(\vartheta)$ for any state of disorder of alloy; and to do this we must know the pertubation potential due to the atoms in wrong positions.

*) Mott; loc. cit.; p. 288 and 301.
**) See for exemple Mott, loc. cit., p. 262.

C. The pertubation potential.

In order to determine this pertubation potential we first take pure gold or copper. Following Wigner and Seitz*) we fill up the whole space with polyhedra, one surrounding each atom, in the following way: for the face-centred structure we draw planes bisecting the lines joining each atom to its nearest neigbours and we thus obtain a dodecahedron surrounding each atom. We denote the potential energy of a valence electron in each cell by $V_{Cu}(r)$ in pure copper and by $V_{Au}(r)$ in pure gold and take them equal to the potential energy of the free singly chargend ion of copper and gold respectively.

We know that the wave function for the lowest electronic state $u(r)$ or $u'(r)$, in the two pure metals, satisfies the Schrödinger equation:

$$\nabla^2 u + \frac{8\pi^2 m}{h^2}(E - V_{Cu})\, u = 0,$$

and (3)

$$\nabla^2 u' + \frac{8\pi^2 m}{h^2}(E' - V_{Au})\, u' = 0$$

and also fulfiles the following conditions on the boundary of the polyhedron

$$\frac{\partial u}{\partial n} = 0 \quad \text{or} \quad \frac{\partial u'}{\partial n} = 0, \tag{4}$$

where $\frac{\partial}{\partial n}$ denotes differentiation normal to the bounding plane.

For any other occupied electronic state with wave number $\mathfrak{k}$ in pure copper we shall assume the wave function to have the form:

$$\Psi_{\mathfrak{k}} = u(r)\, e^{i(\mathfrak{k},\mathfrak{r})}, \tag{5}$$

where $u(r)$ is independent of $\mathfrak{k}$. For the energy of the $\mathfrak{k}$-state we obtain for pure copper:

$$E_k = \int \Psi_{\mathfrak{k}}^* \left[-\frac{h^2}{8\pi^2 m} \nabla^2 + V_{Cu}(r) \right] \Psi_{\mathfrak{k}}\, d\tau, \tag{5a}$$

which reduces to $E_{\mathfrak{k}} = E_0 + h^2k^2/8\pi^2 m$. In the case of pure gold we have similar relations:

$$E_{k'} = \int \Psi_{\mathfrak{k}'}^* \left[-\frac{h^2}{8\pi^2 m} \nabla^2 + V_{Au}(r) \right] \Psi_{\mathfrak{k}'}\, d\tau = E'_0 + h^2k'^2/8\pi^2 m, \tag{6}$$

where we assume, for the wave function $\psi_{\mathfrak{k}'}$ the following form

$$\Psi_{\mathfrak{k}'} = u'(r)\, e^{i(\mathfrak{k}',\mathfrak{r})}. \tag{6a}$$

*) Phys. Rev. vol. 43, (1933), p. 804.

The velocity of an electron in both cases is given by the formula:

$$\mathfrak{v} = \frac{2\pi}{h} \operatorname{grad}_{\mathfrak{k}} E_{\mathfrak{k}} = \frac{h\mathfrak{k}}{2\pi m}.$$

The electrons behave, therefore, as though they are free.

In the crystal of pure copper or gold as a whole we may write

$$\Psi_{\mathfrak{k}} = e^{i(\mathfrak{k}',\mathfrak{r})}\, U(x, y, z)$$

or (7)

$$\Psi_{\mathfrak{k}'} = e^{i(\mathfrak{k}',\mathfrak{r})}\, U'(x, y, z),$$

where U is equal to $u(r)$ within each polyhedron in pure copper, and U' equal to $u'(r)$ inside each polyhedron in pure gold.

In the case of alloy Cu_3Au we can proceede in a similar way. To obtain the wave function of the lowest state, we have to solve Schrödinger's equation for each polyhedron with corresponding potential energy of the free singly charged positive ion of copper or gold and join these wave functions smoothly at the boundaries of the cells.

Naturally it is difficult to find the exact solution, but we can show, shat it is easy give a solution for slightly different case. We suppose that within the polyhedron occupied by the copper atom the potential energy of an electron is given by: $V_{Cu}(r) - -\frac{1}{4}(E_0 - E'_0)$ and inside the cell with gold atom the potential energy is: $V_{Au}(r) + \frac{3}{4}(E_0 - E'_0)$; the meaning of V_{Cu}, V_{Au}, E_0 and E'_0 being the same as before. We see now that the solution of Schrödinger's equations with the boundary conditions (4), corresponding to the lowest state in such a alloy, is composed of the wave functions $u(r)$ or $u'(r)$ respectively, which are identical with the wave functions in the case of pure gold or copper.*) In crystal of the alloy as a whole we may assume, that the wave function of any occupied state with the wave number $\mathfrak{k}$ has the form

$$e^{i(\mathfrak{k},\mathfrak{r})} U(\mathfrak{r}), \tag{8}$$

where $U(\mathfrak{r})$ is equal to $u(r)$ within each cell with copper atom and equal to $u'(r)$ inside each polyhedron with gold atom. The energy of the lowest state inside the cell with copper atom is now: $E_0 - -\frac{1}{4}(E_0 - E'_0)$. The energy of the same state inside the cell with gold atom has the same value and may be expressed by the formula: $E'_0 + \frac{3}{4}(E_0 - E'_0)$. The energy of any other occupied state is given by formula:

*) We suppose that the values of the wave functions $u(r)$ or $u'(r)$, which satisfy the boundary conditions (4) and are normalised to unity for the cell in the alloy Cu_3Au, are practically equal on the boundaries of polyhedra. This condition as can be easily seen from numerical calculations is fulfilled.

$$\left.\begin{matrix} E_0 - \frac{1}{4}(E_0 - E'_0) \\ E'_0 + \frac{3}{4}(E_0 - E'_0) \end{matrix}\right\rangle + \frac{h^2k^2}{8\pi^2 m}. \qquad (9)$$

In our exact problem we must find the solution for the case when the potential in the cells is equal to V_{Cu} or V_{Au} respectively. We therefore have to apply the ordinary pertubation method and determine the exact energy and wave function of the lowest state. The pertubing energy (ΔV) in a alloy is $-\frac{3}{4}|(E_0 - E'_0)|$ within the cells with gold atoms and $+\frac{1}{4}|E_0 - E'_0|$ within the cells with copper atoms. It is well known that the first-order energy correction is equal to the mean value of the pertubing energy operator averaged over the unpertubed, or zero-order, wave function. If we normalize the wave functions $u(r)$ or $u'(r)$ so that the integrals: $\int u^* u \, d\tau$ or $\int u'^* u \, d\tau$ over each cells is equal to unity, than we see that the first order energy correction δE of the lowest state is zero in the alloy Cu_3Au for any state of disorder:

$$\delta E = \frac{\int U^* \triangle V U \, d\tau'}{\int U^* U \, d\tau'} = \frac{N\frac{3}{4} \cdot \frac{1}{4}|E_0 - E'_0| - N\frac{1}{4} \cdot \frac{3}{4}|E_0 - E'_0|}{\int U^* U \, d\tau} = 0,$$

where N denotes the number of atoms in the alloy and $\int d\tau'$ is taken over the space occupied by the alloy.

We may now suppose that we have solved with sufficent accuracy this pertubation problem in the case of the *perfect* ordered alloy and we thus know the exact wave functions of any occupied state. But for our purposes it is sufficient to take the wave functions in the approximate form (8). Let us now calculate the *change* of energy of the electron in the ground state when two neighbouring atoms interchange their places. The change of this energy in the cell which was former occupied by the copper atom is now:

$$\int u^*(r) \left(-\tfrac{1}{4}|E_0 - E'_0| - \tfrac{3}{4}|E_0 - E'_0|\right) u(r) \, d\tau^* = \\ = -|E_0 - E'_0| \cdot \int u^*(r) \, u(r) \, d\tau = -|E_0 - E'_0|,$$

where $\int d\tau$ denotes the integration over the polyhedron corresponding to the copper atom. We obtain the energy with the same absolute value but opposite sign for the cell occupied formerly by a gold atom. We see thus that by interchanging two atoms in the right positions, we are introducing at each polyhedron the pertubating potential $+|E_0 - E'_0|$ or $-|E_0 - E'_0|$ respectively, which gives rise to a scattering of the conducting electrons. Accordingly to our simplified assumptions (8) and (9), we suppose, that these conducting electrons behave as though they were free and thus the calculation of the probability $P(\vartheta)$ is reduced to the problem of the scattering of free electrons by the constant field $\pm|E_0 - E'_0|$ within each polyhedron occupied by an atom in wrong position.

D. The scattering probability in the case of nearly ordered alloy.

When the alloy is nearly perfectly ordered the scattering centres have very simple form. The interchange of the positions of two neighbour-atoms gives rise to a perturbing potential which is constant in both corresponding polyhedra and its value is $+ |E_0 - E'_0|$ or $- |E_0 - E'_0|$ respectively. We can thus say, that in the case of nearly perfectly ordered alloy the scattering centres are formed by scattering dipoles, which are formed by two kind of constant pertubing potential, filling up two adjacent cells. These dipoles are distributed at randon in the alloy.

Before we start with the calculation of the scattering probability we express it in terms of the area $J(\vartheta)\,\mathrm{d}\omega$ which an electron must hit in order to be scattered into solid angle $\mathrm{d}\omega$. If we denote by $J_D(\vartheta)$ this probability calculated for a single scattering dipole, then clearly

$$P(\vartheta) = xNavJ_D(\vartheta), \tag{10}$$

where x is a fraction giving the proportion of the scattering dipoles present, Na number of atoms per unit volume and v is the velocity of the electron.

Now it is easy to calculate the scattering probability $J_D(\vartheta)$. First it will be convenient to replace our polyhedra by the sphere with the same volume, since the polyhedra approximate closely to spheres. Our scattering dipoles thus consists of two identical spheres, with radius a, in contact and inside one of these spheres the scattering potential is $+ |E_0 - E'_0|$, within the other one is $- |E_0 - E'_0|$. For the incident, unpertubed wave of a conducting electron we may take with good approximation the plane wave: $e^{i(\mathfrak{k}, \mathfrak{r})}$, as we are only interested in the electrons on the Fermi' surface.

In order to obtain the scattering probability $J_D(\vartheta)$, we have to find the wave function which consists of an incident wave and scattered wave, so that, at large distances from the scattering dipole, which is assumed to be at the origin,

$$\Psi_{\mathfrak{k}} \sim e^{i(\mathfrak{k}, \mathfrak{r})} + \frac{e^{ikr}}{r} f(\vartheta). \tag{11}$$

We then have $J_D(\vartheta) = |f(\vartheta)|^2$.

If, moreover, $|E_0 - E'_0| \ll \frac{1}{2}mv^2$ (v is the velocity of the conducting electron, i. e. on the Fermi' surface), as is the case in the applications considered, the problem may be solved by Born's approximation, and we have*)

$$J_D(\vartheta) = \left| \frac{2\pi m}{h^2} \int e^{i(\mathfrak{k}-\mathfrak{k}', \mathfrak{r})}\, \Delta V\, \mathrm{d}\tau \right|^2, \tag{12}$$

*) Mott: loc. cit.; p. 87 and 88, eq. (3) and (5).

where $\mathfrak{k}$ and $\mathfrak{k}'$ ($|\mathfrak{k}| = |\mathfrak{k}'|$) means are respectively the wave vector of a colliding electron before and after the collision, ΔV is the perbating potential of the scattering dipole and the integration is over the space of the dipole.

We split now the pertubation potential in two parts: $\Delta V = \Delta V_1 + \Delta V_2$; ΔV_1 is equal to $+ |E_0 - E'_0|$ inside the sphere with the center at the origin and the radius a and equal to zero outside this sphere, whereas ΔV_2 is different from zero only in the second sphere of equal volume, whose centre is at distance of $\vec{l}$ ($|\vec{l}| = 2a$) from the origin and ΔV_2 is equal there to $- |E_0 - E'_0|$. Accordingly, we can split our integral in (12) in two parts: a) A first integral over the first sphere has the form

$$|E_0 - E'_0| \int e^{i(\mathfrak{k}-\mathfrak{k}', \mathfrak{r})}\, d\tau;$$

we introduce the polar coordinates r, Θ, φ, with the polar axis along with $\mathfrak{k} - \mathfrak{k}'$, and after carrying out the intergration we obtain

$$4\pi a^3 \mid E_0 - E'_0 \mid f(2ka \sin \tfrac{1}{2}\vartheta),$$

where (13)

$$f(x) = x^{-3} (\sin x - x \cos x).$$

b) In the second integral we carry out the translation of the origin of the coordinate system into the centre of the second sphere $\mathfrak{r} = \mathfrak{r}' + \vec{l}$. This integral has then a form:

$$- |E_0 - E'_0|\, e^{i(\mathfrak{k}-\mathfrak{k}', \vec{l})} \int e^{i(\mathfrak{k}-\mathfrak{k}', \mathfrak{r}')}\, d\tau =$$

$$= - |E_0 - E'_0|\, 4\pi a^3 f(2ka \sin \tfrac{1}{2}\vartheta)\, .\, e^{i(\mathfrak{k}-\mathfrak{k}', \vec{l})}.$$

From our preceeding analysis we then obtain for the scattering probability $J_D(\vartheta)$ the following expression:

$$\left| \frac{8\pi^2 m}{h^2} |E_0 - E'_0|\, a^3 f(2ka \sin \tfrac{1}{2}\vartheta)\, (1 - e^{i(\mathfrak{k}-\mathfrak{k}', \vec{l})}) \right|^2.$$

As the orientation of the dipoles are random in the alloy we can take for $|1 - e^{i(\mathfrak{k}-\mathfrak{k}', \vec{l})}|^2$ in the last formula its avarage value over all possible orientations. If we introduce the polar coordinates with polar axis in the $(\mathfrak{k} - \mathfrak{k}')$-direction, we have:

$$\overline{|1 - e^{i(\mathfrak{k}-\mathfrak{k}', \vec{l})}|^2} = \frac{\int_0^{2\pi} \int_0^{\pi} 2[1 - \cos(4ka \sin \tfrac{1}{2}\vartheta \cos x)] \sin x\, dx\, d\varphi}{\int_0^{2\pi} \int_0^{\pi} \sin x\, dx\, d\varphi} =$$

$$= 2 \left(1 - \frac{\sin(4ka \sin \tfrac{1}{2}\vartheta)}{4ka \sin \tfrac{1}{2}\vartheta}\right).$$

We can thus write $J_D(\vartheta)$ in the form:

$$J_D(\vartheta) = \left\{\frac{8\pi^2 m}{h^2} |E_0 - E'_0| a^3\right\}^2 f^2(2ka \sin \tfrac{1}{2}\vartheta)\left(2 - 2\frac{\sin(4ka \sin \tfrac{1}{2}\vartheta)}{4ka \sin \tfrac{1}{2}\vartheta}\right). \tag{14}$$

E. Scattering probability in the case of perfectly disordered alloy.

In the case of a perfectly disordered alloy we can proceede in a similar manner.

In the perfectly ordered alloy each gold atom is surrounded by 12 copper atoms and among the 12 nearest neighbours of each copper atom there are 4 gold atoms and 8 copper atoms. When the alloy is perfectly disordered, we may say, that in the average each „wrong" atom of copper is surrounded by 3 gold atoms in wrong positions and similary each „wrong" gold atom has as its nearest neighbours 3 copper and 2 gold atoms in wrong positions.

If we denote now by $J_{\Phi=0}(\vartheta)\,\mathrm{d}\omega$ the area per unit volume which an electron must hit in order to be scattered into solid angle $\mathrm{d}\omega$, than for $P(\vartheta)$ we have similar expression as before; that is

$$P(\vartheta) = v\, J_{\Phi=0}(\vartheta)\,\mathrm{d}\omega.$$

In order to calculate the probability $J_{\Phi=0}(\vartheta)$ in this case, we may use the Born's formula (12) again. We split the pertubation potential ΔV into parts; each one is equal to $+|E_0 - E'_0|$ or $-|E_0 - E'_0|$ in the sphere corresponding to the atom in the wrong position. The integral in the expression (12) is then given by the following sum:

$$\int e^{i(\mathfrak{k}-\mathfrak{k}',\mathfrak{r})}\,\Delta V\,\mathrm{d}\tau = \sum_{\vec{l}} \int e^{i(\mathfrak{k}-\mathfrak{k}',\mathfrak{r})}\,\Delta V_l\,\mathrm{d}\tau_l,$$

where $\int \mathrm{d}\tau_l$ is taken over the sphere with the wrong atom in the position given by the latice vector $\vec{l}$ and ΔV_l is the corresponding pertubation potential.

To carry out the intergrations we transform the origin of the coordinates into the centre of each spehre and we thus obtain:

$$\sum_{\vec{l}} \int e^{i(\mathfrak{k}-\mathfrak{k}',\mathfrak{r})}\,\Delta V_l\,\mathrm{d}\tau_l = \sum_{\vec{l}} \int e^{i(\mathfrak{k}-\mathfrak{k}',\vec{l}+\mathfrak{r}')}\,\Delta V_l\,\mathrm{d}\tau'_l =$$

$$= \sum_{\vec{l}} e^{i(\mathfrak{k}-\mathfrak{k}',\vec{l})} \int e^{i(\mathfrak{k}-\mathfrak{k}',\mathfrak{r}')}\,\Delta V_l\,\mathrm{d}\tau'_l,$$

where the integration $\int \mathrm{d}\tau'_l$ is over each sphere in the new coordinale system.

For the square of this integral we than have

$$\left|\int e^{i(\mathfrak{k}-\mathfrak{k}',\,\mathfrak{r})}\,\Delta V\,d\tau\right|^2 = (E_0 - E'_0)^2\,\left|\int e^{i(\mathfrak{k}-\mathfrak{k}',\,\mathfrak{r}')}\,d\tau'_l\right|^2 \sum_{\vec{l}}\sum_{\vec{l}'}{}' \pm e^{i(\mathfrak{k}-\mathfrak{k}',\,\vec{l}-\vec{l}')}, \tag{15}$$

where the double summation extends over all the latice points corresponding to the atoms in the wrong positions and the sign + or — before the exponential term is to be taken according as the distance $\vec{l}-\vec{l}'$ between two atoms corresponds to like or to unlike atoms respectively. We thus see that the integral in (15) has the same form as in the preceding paragraph and its value is then given by the formula (13).

In order to carry out the duble summation in (15) it will be sufficient to take into account only two sets of terms:

a) The terms which correspond to $\vec{l}-\vec{l}'=0$ and the number of which is equal to the total number of atoms in the wrong positions, i. e. to $2\,.\,\frac{1}{4}\,.\,\frac{3}{4}\,Na$, where Na is the number of atoms per unit volume.

b) The terms which correspond to two adjacent atoms. When in this case we draw lines connecting each wrong atom with its nearest neighbours in wrong positions; we see that these lines are oriented at random in the alloy as a whole. According to what we said at the begining of this paragraph, we can see at once, that from each copper atom in the wrong position there diverge on the average 3 lines to its three nearest gold atoms also in the wrong position; similarly from each wrong atom of gold 3 lines diverge to the three nearest copper atoms and 2 lines to the two nearest gold atoms also in the wrong position. Thus the total number of such dublets is equal to:

$Na\,F_AF_B\,.\,(3+3) = Na\,\frac{3}{4}\,.\,\frac{1}{4}\,.\,6$ in the case of two odjacent unlike atoms and to $Na\,F_AF_B\,.\,2 = Na\,\frac{3}{4}\,.\,\frac{1}{4}\,.\,2$ in the case of two like atoms.

Now we can easely carry out the summation in (15) for the terms corresponding to $|\vec{l}-\vec{l}'| = 2a$. This sum is equal to

$$\overline{NaF_AF_B\,(2-6)\,e^{i(\mathfrak{k}-\mathfrak{k}',\,\vec{l}-\vec{l}')}}$$

where $\overline{e^{i(\mathfrak{k}-\mathfrak{k}',\,\vec{l}-\vec{l}')}}$ means the average value taken over all possible orientations of $(\vec{l}-\vec{l}')$ in the space, i. e. it is thus equal to*)

*) The polar coordinates are introduced in the same way as before; e. i. with polar axis in $(\mathfrak{k}-\mathfrak{k}')$-direction.

$$\frac{\int_0^{2\pi}\int_0^{\pi} e^{i(\mathfrak{k}-\mathfrak{k}',\vec{l}-\vec{l}')}\sin x\,\mathrm{d}x\,\mathrm{d}\varphi}{\int_0^{2\pi}\int_0^{\pi}\sin x\,\mathrm{d}x\,\mathrm{d}\varphi} = \frac{\sin(4ka\sin\frac{1}{2}\vartheta)}{4ka\sin\frac{1}{2}\vartheta}.$$

It is not necessary to take into account the set of the terms in the double series (15) corresponding to the interaction of the next nearest neighbours, as these terms lead in the final formula for electrical resistivity, to integrals, whose values are practically zero.

If now we put expressions obtained above into the integral (15) we have:

$$|\int e^{i(\mathfrak{k}-\mathfrak{k}',\,v)}\,\Delta V\,\mathrm{d}\tau|^2 = (E_0 - E'_0)^2\,|\int e^{i(\mathfrak{k}-\mathfrak{k}',\,v')}\,\mathrm{d}\tau'|^2\,Na\,\tfrac{3}{4}\,\tfrac{1}{4}\,\cdot$$
$$\cdot\left[2 - 4\frac{\sin(4ka\sin\frac{1}{2}\vartheta)}{4ka\sin\frac{1}{2}\vartheta}\right].$$

For the square of the integral in the last equation we take the expression (13) and can thus write:

$$|\int e^{i(\mathfrak{k}-\mathfrak{k}',\,v)}\,\Delta V\,\mathrm{d}\tau|^2 =$$
$$= (E_0 - E'_0)^2\,(4\pi\,a^3)^2\,f^2(2ka\sin\tfrac{1}{2}\vartheta)\,Na\,\tfrac{1}{4}\,\tfrac{3}{4}\left[2 - 4\frac{\sin(4ka\sin\frac{1}{2}\vartheta)}{4ka\sin\frac{1}{2}\vartheta}\right].$$

It is now possible to calculate probability $J_{\Phi=0}(\vartheta)$ by means of Born's formula (12):

$$J_{\Phi=0}(\vartheta) = \left\{\frac{8\pi^2 m\,a^3}{h^2}\right\}^2 (E_0 - E'_0)^2\,f^2(2ka\sin\tfrac{1}{2}\vartheta)\,Na\,\tfrac{1}{4}\,\tfrac{3}{4}\,\cdot$$
$$\cdot\left[2 - 4\frac{\sin(4ka\sin\frac{1}{2}\vartheta)}{4ka\sin\frac{1}{2}\vartheta}\right]. \qquad (16)$$

F. Scattering probability in the disordered alloy.

If we compare the formulae (14) and (16) for scattering probability in the two limiting cases, we can immediately sec, that the average scattering probability *per atom* in the nearly perfectly ordered alloy is:

$$\left\{\frac{8\pi^2 ma^3}{h^2}(E_0 - E'_0)\right\}^2 f^2(2ka\sin\tfrac{1}{2}\vartheta)\left(1 - \frac{\sin(4ka\sin\frac{1}{2}\vartheta)}{4ka\sin\frac{1}{2}\vartheta)}\right)$$

and in the perfectly disordered alloy is (number of atoms in the wrong positions $= 2\,Na\,F_A F_B = 2\,Na\,\frac{1}{4}\,\frac{3}{4}$)

$$\left\{\frac{8\pi^2 ma^3}{h^2}(E_0 - E_0')\right\}^2 f^2(2ka\sin\tfrac{1}{2}\vartheta)\left(1 - 2\frac{\sin(4ka\sin\frac{1}{2}\vartheta)}{4ka\sin\vartheta}\right).$$

During the order-disorder transformations one of these expressions changes continuously into the other one. We will not investigate this change in details; for our purposes it will be sufficient to suppose, that this transition is proportional to the change of Bragg's order parameter Φ, defined by eq. (1) in the first chapter. We thus assume, that the average scattering probability $J_\Phi(\vartheta)$ *per atom* corresponding to the Bragg's order Φ is equal to

$$J_\Phi(\vartheta) = \left\{\frac{8\pi^2 ma^3}{h^2}(E_0 - E'_0)\right\}^2 f^2(2ka\sin\tfrac{1}{2}\vartheta)\left(1 - (2-\Phi)\cdot\frac{\sin(4ka\sin\tfrac{1}{2}\vartheta)}{4ka\sin\tfrac{1}{2}\vartheta}\right). \tag{17}$$

Any more detailed calculation does not practically change the electrical resistivity; the integrals, which contain $\frac{\sin(4ka\sin\frac{1}{2}\vartheta)}{4ka\sin\frac{1}{2}\vartheta}$ as a factor in the integrand, have very small values.

§ 3. Final expression for resistivity and comparison with the experimental results.

After these calculations it is possible to write the final expression for the anomalous resistivity $\varrho_{\text{transf.}}$ of alloy Cu_3Au in the different states of disorder. If we denote by y the number of atoms in the wrong positions (i. e. $y = 2\,Na\,F_A F_B(1-\Phi)$), then according the formula (10) $P(\vartheta)$ is clearly equal to: $P(\vartheta) = y\,v\,J_\Phi(\vartheta) = 2\,Na\,F_A F_B(1-\Phi)\,vJ_\Phi(\vartheta)$. If we assume $Na = N$ (one electron per atom) we may write the expression for anomalous resistivity (1) in the form:

$$\Delta\varrho_{\text{transf.}} = \frac{mv}{e^2 N}\,y\,.\,B,$$

where (18)

$$B = \int_0^\pi J_\Phi(\vartheta)\,2\pi\,(1-\cos\vartheta)\sin\vartheta\,\mathrm{d}\vartheta.$$

If we put for $J_\Phi(\vartheta)$ the expression from (18) we can thus write the formula for specific resistivity in the final form.

$$\Delta\varrho_{\text{transf.}} = \frac{mv}{e^2}\,2\,(\tfrac{1}{4}\cdot\tfrac{3}{4})\,(1-\Phi)\left\{\frac{8\pi^2 ma^3}{h^2}(E_0 - E'_0)\right\}^2 \cdot \int_0^\pi f^2(2ka\sin\tfrac{1}{2}\vartheta)\left(1-(2-\Phi)\frac{\sin(4ka\sin\tfrac{1}{2}\vartheta)}{4ka\sin\tfrac{1}{2}\vartheta}\right)2\pi\,(1-\cos\vartheta)\sin\vartheta\,\mathrm{d}\vartheta. \tag{19}$$

To compare this theoretical formula with experiment we are accepting the following data:

1. It is well known that the lattice constant of the alloy Cu_3Au is $3{,}7 \cdot 10^{-8}$ cm and hence for the radius of atomic sphere we obtain: $a = 1{,}46 \cdot 10^{-8}$ cm.

2. From the paper of N. F. Mott (The electrical resistance of dilute solid solutions; Proc. of Camb. Phil. Soc., Vol. 32, p. 287, 1936) we choose for the value $|E_0 - E'_0| = 2{,}1 \quad eV = 3{,}34 \cdot 10^{-12}$ erg as corresponding to $a = 1{,}46 \cdot 10^{-8}$ cm.

3. The maximum kinetic energy of the conducting electrons may be taken from the meassurements on the soft X-ray spectra of pure copper carried out by Skinner*) and has the following value: $E_m \doteq 8{,}5$ eV; the corresponding value of the wave vector k is then: $1{,}5 \cdot 10^8$ cm^{-1} and the product $2ka$ is equal $\doteq 4{,}5$. The velocity v can, of course, be calculated from E_m by the formula: $E_m = \frac{1}{2} mv^2$.

4. The integrals in the expression (19) were calculated numerically and the following values and obtained

$$\int_0^{\pi} f^2(2ka \sin \tfrac{1}{2}\vartheta)\,(1 - \cos\vartheta) \sin\vartheta \, d\vartheta = 0{,}014,$$

$$\int_0^{\pi} f^2(2ka \sin \tfrac{1}{2}\vartheta) \frac{\sin(4ka \sin \frac{1}{2}\vartheta)}{4ka \sin \frac{1}{2}\vartheta} (1 - \cos\vartheta) \sin\vartheta \, d\vartheta = -0{,}0006.$$

The values of the integrals which are contained in the integrand factors corresponding to the interaction of nex-nearest neighbours are so small, that we can neglect them.

If we put these constants into (19), we obtain for the anomalous specific resistivity $\Delta\varrho_{\text{transf.}}$ the values, which are tabulated in the colum $\Delta\varrho_{\text{transf.-theory}}$ in the table I and shown in the fig. 3.

Table I.

$T°$ C	Φ	$\Delta\varrho_{\text{transf.-experim.}}$	$\Delta\varrho_{\text{transf.-theory.}}$
		Ω . cm	Ω . cm
372°	0	$7{,}1 \cdot 10^{-6}$	$7{,}6 \cdot 10^{-6}$
372°	0,46	4,5	4,1
342°	0,64	2,8	2,7
313°	0,69	2,0	2,3
240°	0,83	1,0	1,3
166°	0,91	0,6	0,68
93°	0,96	0,33	0,30
20°	0,98	0,19	0,15
0°	1	0	0

*) Nature, vol. 140 (1937), p. 508.