

the Debye-Hückel screening length and  $|\Gamma^2|$  is independent of  $\mathbf{k}$  and  $\mathbf{k}'$ . The results will differ from Dumke's nomenclature only in the interchange of  $\alpha_v$  and  $\alpha_c$  to consider hole instead of electron transitions because of the many more states in the valence band.

After some mathematical manipulations

$$\alpha = \frac{1}{(2\pi)^2} \frac{e^2 \langle |P_{vc}|^2 \rangle_{Av} |\Gamma^2| (e^{\theta/T} - 1)^{-1} g}{n \hbar^3 \Delta E k \theta (1 + \alpha_v/\alpha_c)^2 \alpha_v \alpha_c},$$

where the term  $g$  was found to equal

$$g = 4\pi \left( \frac{1-\psi}{1+\psi} \right)^{\frac{1}{2}} (\varphi + \psi) \frac{\partial}{\partial \Phi} \left[ \frac{\Phi - 1}{\Delta} \left\{ \frac{\varphi \Phi + \psi}{(\varphi^2 - 1)^{\frac{1}{2}}} - (\Phi^2 - 1)^{\frac{1}{2}} \right\} \right],$$

the terms  $\psi$ ,  $\varphi$ ,  $\Phi$ , and  $\Delta$  were defined as

$$\psi = \frac{1 - \alpha_v/\alpha_c}{1 + \alpha_v/\alpha_c},$$

$$\varphi + \psi = (1 + \psi) \frac{k\theta}{\hbar\omega + k\theta - \Delta E},$$

and

$$\Delta = (\Phi + \varphi\psi)^2 + (\varphi^2 - 1)(1 - \psi^2).$$

In Fig. 11, the computed shape of  $\alpha$  (in relative units) vs the photon energy  $\hbar\omega$  is shown for the two cases  $b^{-1} = 2 \times 10^6 \text{ cm}^{-1}$  for  $(n_0 + p_0) = 4 \times 10^{16} \text{ cm}^{-3}$  and  $\alpha_v/\alpha_c = 0.1$  and for the case  $|H_{kk'}|^2 = |\beta^2|/(e^{\theta/T} - 1)$ .

## Nordheim's Theory of the Resistivity of Alloys

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Nordheim's theory is extended to account for (1) ionic potentials that extend outside the unit cell, and (2) order of any range. It is shown that the original theory is less approximate than is generally asserted. As an incidental result, it is also shown that Flinn's electronic theory of order can be extended appreciably.

### INTRODUCTION

IT is generally recognized that Nordheim's theory<sup>1</sup> of the resistivity of binary alloys that form continuous solid solutions has only a qualitative significance. Nevertheless there still seems to be an interest<sup>2,3</sup> in this theory, probably because no acceptable theory has been published except for dilute solutions. It therefore should be of interest to prove, as is done in this note, that the usual form of the theory, say Jones',<sup>3</sup> is less approximate than is usually asserted [Jones' equation (25.6) is exact]. The theory is also easily extended: (1) to account for ionic potentials that extend outside the unit cell, and (2) to account for order of any range.

In order to prove these facts, the order parameter of Cowley<sup>4</sup> is introduced using essentially Flinn's notation from his article<sup>5</sup> on the electronic theory of local order. (It is also incidentally proved that three of Flinn's approximations exactly cancel.)

### THEORY: AN EXTENSION OF NORDHEIM'S THEORY OF THE RESISTIVITY OF BINARY ALLOYS

We imagine a disordered lattice of  $A$ - and  $B$ -atoms. Let the rigid potential associated with an  $A$ -atom be

$U_A(\mathbf{r})$  and that associated with a  $B$ -atom be  $U_B(\mathbf{r})$ , where both  $U_A(\mathbf{r})$  and  $U_B(\mathbf{r})$  do not necessarily vanish outside the unit cell. Then the total potential  $U(\mathbf{r})$  is given by

$$U(\mathbf{r}) = \sum_{A\text{-atoms}} U_A(\mathbf{r} - \boldsymbol{\tau}) + \sum_{B\text{-atoms}} U_B(\mathbf{r} - \boldsymbol{\tau}). \quad (1)$$

In order to decompose this into a more workable form, we introduce a function  $C_\tau$  defined at the lattice points as follows:

$$C_\tau = m_B, \text{ if an } A\text{-atom is at } \boldsymbol{\tau} \\ = -m_A, \text{ if a } B\text{-atom is at } \boldsymbol{\tau},$$

where  $m_i$  is the concentration of the  $i$ th component. Further, we define an average potential

$$U_1(\mathbf{r}) = \sum_{\boldsymbol{\tau}} \{ m_A U_A(\mathbf{r} - \boldsymbol{\tau}) + m_B U_B(\mathbf{r} - \boldsymbol{\tau}) \}, \quad (2)$$

which is periodic, and a "difference potential"

$$U_2(\mathbf{r}) = \sum_{\boldsymbol{\tau}} C_\tau \{ U_A(\mathbf{r} - \boldsymbol{\tau}) - U_B(\mathbf{r} - \boldsymbol{\tau}) \} \\ = \sum_{\boldsymbol{\tau}} C_\tau \Delta U(\mathbf{r} - \boldsymbol{\tau}), \quad (3)$$

which is disordered. Clearly, we have that

$$U(\mathbf{r}) = U_1(\mathbf{r}) + U_2(\mathbf{r}). \quad (4)$$

We next imagine we have the exact Bloch functions for the average potential (2) and then perturb these

<sup>1</sup> L. Nordheim, *Ann. Physik* **9**, 607 (1931).

<sup>2</sup> N. V. Grum-Grzhimailo, *Fiz. Metal. i Metalloved. Akad. Nauk S.S.S.R. Ural. Filial* **5**, 23-29 (1957).

<sup>3</sup> H. Jones, *Handbuch der Physik* edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 19, p. 269.

<sup>4</sup> J. M. Cowley, *Phys. Rev.* **77**, 669 (1950).

<sup>5</sup> P. A. Flinn, *Phys. Rev.* **104**, 350 (1956).

Bloch functions with the difference potential (3). The matrix element for the  $\mathbf{k}'$  to  $\mathbf{k}$  scattering is

$$\begin{aligned} \langle \mathbf{k}' | U_2(\mathbf{r}) | \mathbf{k} \rangle &= \frac{1}{N\Omega} \int_{\text{vol}} \psi_{\mathbf{k}'}^* \sum_{\mathbf{s}} C_s \Delta U(\mathbf{r}-\mathbf{s}) \psi_{\mathbf{k}}(\mathbf{r}) d\mathbf{r} \\ &= \frac{1}{N\Omega} \sum_{\mathbf{s}} C_s \int_{\text{vol}} e^{+i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} \Phi(\mathbf{r}-\mathbf{s}) d\mathbf{r}, \end{aligned} \quad (5)$$

where,

$$\Phi(\mathbf{x}) \equiv u_{\mathbf{k}'}^*(\mathbf{x}) \Delta U(\mathbf{x}) u_{\mathbf{k}}(\mathbf{x}). \quad (6)$$

Since we apply periodic boundary conditions to the perturbed as well as to the unperturbed problem,  $\Phi(\mathbf{x})$  is periodic with the period of total crystal. Thus we have,

$$\begin{aligned} |\langle \mathbf{k}' | U_2(\mathbf{r}) | \mathbf{k} \rangle|^2 &= \frac{1}{(N\Omega)^2} \sum_{\mathbf{s}} \sum_{\mathbf{n}} C_s C_n \iint e^{i\Delta\mathbf{k} \cdot (\mathbf{r}-\mathbf{z})} \\ &\quad \times \Phi(\mathbf{r}-\mathbf{s}) \Phi^*(\mathbf{z}-\mathbf{n}) d\mathbf{r} d\mathbf{z}. \end{aligned} \quad (7)$$

Letting  $\mathbf{y}=\mathbf{r}-\mathbf{z}$  and  $\mathbf{s}=\mathbf{n}+\boldsymbol{\tau}$ , we find that (7) reduces to

$$\begin{aligned} &\frac{1}{(N\Omega)^2} \sum_{\boldsymbol{\tau}} \left( \sum_{\mathbf{n}} C_n C_{\mathbf{n}+\boldsymbol{\tau}} \right) \\ &\quad \times \int_{\text{vol}} e^{i\Delta\mathbf{k} \cdot \mathbf{y}} d\mathbf{y} \int_{\text{vol}} \Phi(\mathbf{z}-\mathbf{n}+\mathbf{y}-\boldsymbol{\tau}) \Phi^*(\mathbf{z}-\mathbf{n}) d\mathbf{z} \\ &= \frac{1}{(N\Omega)^2} \sum_{\boldsymbol{\tau}} \alpha_{\boldsymbol{\tau}} \int_{\text{vol}} e^{i\Delta\mathbf{k} \cdot \mathbf{r}} Q(\mathbf{r}-\boldsymbol{\tau}) d\mathbf{r}, \end{aligned} \quad (8)$$

where

$$Q(\mathbf{r}) \equiv \int_{\text{vol}} \Phi(\mathbf{x}+\mathbf{r}) \Phi^*(\mathbf{x}) d\mathbf{x}, \quad (9)$$

and

$$\alpha_{\boldsymbol{\tau}} \equiv \sum_{\mathbf{n}} C_n C_{\mathbf{n}+\boldsymbol{\tau}}. \quad (10)$$

[It will be noted that  $Q(\mathbf{r})$  is an autocorrelation function which has a particularly simple interpretation in the free electron case where  $u_{\mathbf{k}}(\mathbf{r})=1$ .] We denote the integral in (8) by  $I(\mathbf{k}',\mathbf{k},\boldsymbol{\tau})$ , so that

$$|\langle \mathbf{k}' | U_2(\mathbf{r}) | \mathbf{k} \rangle|^2 = \frac{1}{(N\Omega)^2} \sum_{\boldsymbol{\tau}} \alpha_{\boldsymbol{\tau}} I(\mathbf{k}',\mathbf{k},\boldsymbol{\tau}), \quad (11)$$

which is equivalent to Jones' equation (25.5). The  $\alpha_{\boldsymbol{\tau}}$  is an order parameter differing from that used by Flinn only by a normalizing constant  $Nm_{AMB}$ . We refer to Flinn for a discussion of it, but we need to point out Flinn's article contains a small error which is important to us here. He states that for random solutions,  $\alpha_{\boldsymbol{\tau}}$  is zero for all  $\boldsymbol{\tau}$ ; we correct it to read "for random solutions,  $\alpha_{\boldsymbol{\tau}}$  is zero for all nonzero  $\boldsymbol{\tau}$ ." This is simply verified. Thus, we have for random solutions,

$$|\langle \mathbf{k}' | U_2(\mathbf{r}) | \mathbf{k} \rangle|^2 = \frac{1}{(N\Omega)^2} \alpha_0 I(\mathbf{k}',\mathbf{k},0), \quad (12)$$

$$\alpha_0 = Nm_{AMB}, \quad (13)$$

which proves that the *second sum in Jones' equation (25.5) is identically zero for random solutions even if the rigid atomic potentials extend over more than one cell.* It is further seen from (11) how order of any range enters to modify Nordheim's theory. Contrary to what one might gather from Seitz's statement,<sup>6</sup> short-range order can invalidate Eq. (12); i.e., Seitz's Eq. (9) or Jones' Eq. (25.6).

Note that if (11) is used in an energy calculation, it yields only pair interactions with  $\alpha_{\boldsymbol{\tau}}$  giving the number of pairs separated by a distance  $\boldsymbol{\tau}$ , where  $A-A$ ,  $A-B$ , and  $B-B$  have the weighting determined by the definition of  $C_{\boldsymbol{\tau}}$ . Thus we see that  $\alpha_0$  corresponds to a self-energy. In the case of random solutions, pair interactions (or double scattering) are accounted for, but the negative weighting of the  $A-B$  and  $B-A$  pairs just cancel the contribution of the  $A-A$  and  $B-B$  pairs except for  $\boldsymbol{\tau}=0$ .

Finally, it should be pointed out that Flinn<sup>5</sup> unnecessarily restricts himself to potentials that go to zero at the cell boundaries, and then arrives at an integral over the unit cell [his Eq. (36)]. He then inserts potentials which are not zero outside the cell and replaces the integration over the unit cell by an integration over all space. From the development above, it is clear that these three approximations exactly cancel.

<sup>6</sup> F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 543.