

Theory of the Resistivity Change in a Metal due to Multiple Point Imperfections*

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A unified theory is proposed for the resistivity change in a metal due to an arbitrary distribution of point imperfections and to the lattice strain around them. Mott's treatment of the scattering power of an isolated impurity atom in a free-electron metal, using the phase-shift formalism, has been generalized to apply to a complex of interacting point defects. Lattice distortion is approximated in the scattering scheme by a system of charge dipoles. The theory takes a very tractable form when the scattering potential of the assembly is very nearly a superposition of the potentials of discrete imperfections. Empirical data on the scattering power of isolated point defects can then be utilized to yield good estimates for the resistivity change due to aggregates of these defects. For illustration, the scattering power of vacancies, interstitials, divacancies, di-interstitials, Frenkel pairs, and trivacancies in copper have been evaluated.

I. INTRODUCTION

AGGREGATES of point imperfections are formed in metallic specimens after radiation damage, quenching and cold working, and in alloys after solute precipitation. Valuable information can be obtained on their concentration, spatial distribution, interaction, and annealing mechanism by a careful interpretation of data on the resistivity change (in correlation with data on the changes in other physical properties) they bring about in the metal. It is in this interpretation of resistivity data that an accurate theoretical estimate of the resistivity change in the specimen can be an extremely useful parameter. Previous theoretical estimates of these resistivity changes have been rather crude—most of them were restricted to simple systems: specimens with a uniform distribution of point defects^{1,2} or containing defect aggregates with a high degree of symmetry.³ Moreover, except in the case of aggregates with spherical symmetry and of defect pairs,^{4,5} the scattering power has always been worked out in the Born approximation instead of the phase-shift formalism which gives a far more accurate description of the scattering of conduction electrons by point defects. Another source of error in most of the previous treatments was the approximate scattering potential employed in the defect model. The conventional potentials for point defects (i.e., the square-well,^{6,7} the screened Coulomb,⁸ the self-consistent-field,⁹ and others¹⁰) give at best, only an agreement of $\sim 25\%$ with experiment in the

more tractable case of an isolated point defect and they cannot lead to reliable estimates for complex defect systems. Most of the previous estimates of the scattering power of either isolated defects or defect aggregates have also given a poor account of scattering from the lattice strain around them. Lattice distortion is believed to contribute significantly to the resistivity change, particularly in the case of aggregates containing interstitial defects. The most significant approaches to the problem of scattering from lattice strain are the deformation-potential method of Overhauser and Gorman,¹¹ and Jongenburger,¹² and the deformed-atomic-cell treatment of Blatt.¹³ The strain scattering is overestimated with the first method, however, and Blatt's treatment, though leading to better estimates, is limited to isolated point defects.

The present investigation will attempt to remedy some of the short-comings of these previous treatments. In the first place, the more realistic and the more general problem of scattering from an irregular distribution of point defects will be considered, instead of that of scattering from simple geometrical systems. Next, a formulation of the scattering power of an aggregate of point defects in terms of the phase shifts and the position vectors of the individual defects will be presented, as an improvement on the Born approximation. In addition, the scattering power will be expressed in such a form that semiempirical scattering amplitudes of the defects can be employed in the place of amplitudes derived from theoretical models—thus avoiding errors generated by approximate scattering potentials. Finally, a simple prescription, based on the assumption that a displaced ion scatters like a dipole, will be presented to deal, within the proposed phase-shift scheme, with the scattering due to the lattice strain. For illustration, the theory is employed to estimate the resistivity change in copper due to some standard defects and defect complexes, viz: the monovacancy,

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¹ L. Nordheim, *Ann. Physik.* **9**, 607 (1931).

² J. Friedel, *Advan. Phys.* **3**, 446 (1954).

³ M. Asdente and J. Friedel, *J. Phys. Chem. Solids* **11**, 115 (1959).

⁴ C. P. Flynn, *Phys. Rev.* **126**, 533 (1962).

⁵ C. P. Flynn, *J. Phys. Radium* **23**, 654 (1962).

⁶ F. Abeles, *Compt. Rend.* **237**, 796 (1953).

⁷ P. de Faget de Casteljau and J. Friedel, *J. Phys. Radium* **17**, 27 (1956).

⁸ N. F. Mott, *Proc. Cambridge Phil. Soc.* **32**, 281 (1936).

⁹ N. H. March and A. M. Murray, *Proc. Roy. Soc. A* **261**, 119 (1961).

¹⁰ L. C. R. Alfred and N. H. March, *Phil. Mag.* **46**, 759 (1955).

¹¹ A. W. Overhauser and R. L. Gorman, *Phys. Rev.* **102**, 676 (1956).

¹² P. Jongenburger, *Nature* **175**, 545 (1955).

¹³ F. J. Blatt, *Phys. Rev.* **108**, 285 (1957); **108**, 1204 (1957).

the interstitial, the divacancy, the trivacancy, the interstitial-vacancy pair, and the di-interstitial, taking into account the lattice strain around them. The values obtained for the resistivity changes are in good agreement with experimental estimates (where available).

II. THEORY

A simplified working model of the scattering system can be obtained by separating the defect population in the metal into complexes of point defects. A complex being defined here as the assembly of all point defects that are close enough to each other (within ~8.0 Å for the common metals) to interact significantly. It follows from this definition that the complexes themselves do not interact with each other and that their respective scattering powers are additive. The resistivity change Δρ in the specimen can therefore be expressed as the sum of the resistivity change Δρ^m due to each complex; leading to the simple relation

$$\Delta\rho = \sum_m \Delta\rho^m. \tag{1}$$

In the more general case of an anisotropic system, the relation is

$$\Delta\rho_{ij} = \sum_m \Delta\rho_{ij}^m, \tag{2}$$

where Δρ_{ij} and Δρ_{ij}^m are changes in the resistivity tensor. The basic problem is now reduced to the determination of the resistivity change Δρ^m or Δρ_{ij}^m for the mth, i.e., the typical defect complex in the specimen.

It will be assumed that this typical defect complex is made up, in general, of interstitial atoms, vacancies, impurity atoms, and charge dipoles distributed at an arbitrary set of points {r_σ} in the lattice and that its effective scattering potential is V(r). Adopting a free-electron model of the host metal and assuming elastic scattering of the conduction electrons and small changes in resistivity, the Boltzmann electron transport equations¹⁴ can be solved for the current density in the metal, giving the expression

$$J = \frac{3n_0\tau}{4\pi k_0^4} \int (\mathbf{E} \cdot \mathbf{k}) \mathbf{k} d\omega + \frac{3n_0\tau^2\mathcal{V}}{4\pi k_0^5} \int [\mathbf{E} \cdot (\mathbf{k}' - \mathbf{k})] P_{k,k'} \mathbf{k} d\omega d\omega', \tag{3}$$

where n₀ is the number of electrons per unit volume, τ is the thermal relaxation time, ℳ is the volume of the metal, ħk₀ is the Fermi momentum in the metal, E is the electric field, P_{k,k'} is the transition probability for scattering from momentum ħk to momentum ħk' by the potential V(r), dω is a surface element on the k

sphere, and dω' is a surface element on the k' sphere. The conductivity in the metal can then be obtained from Ohm's law:

$$J_i = \sum_{j=1}^3 \sigma_{ij}^m E_j, \tag{4}$$

where σ_{ij}^m is the conductivity tensor. On comparing Eqs. (3) and (4) and inverting the σ_{ij}^m matrix, it can be shown that for small resistivity changes in an initially isotropic metal, the resistivity change parameter is given by

$$\Delta\rho_{ij}^m = -\frac{3\mathcal{V}}{4\pi n_0 k_0^5} \int (k_j' - k_j) k_i P_{k,k'} d\omega d\omega'. \tag{5}$$

This expression can be evaluated once P_{k,k'} is known in terms of k and k'.

The transition probability P_{k,k'} can be defined as¹⁴

$$P_{k,k'} = |A(\mathbf{k}, \mathbf{k}')|^2 / \mathcal{V}^2, \tag{6}$$

where A(k, k') is the total scattering amplitude of the conduction electrons for the potential V(r). Formally, A(k, k') is given by the expression¹⁵

$$A(\mathbf{k}, \mathbf{k}') = \lim_{r \rightarrow \infty} r [\Psi - e^{i\mathbf{k} \cdot \mathbf{r}}] / e^{i\mathbf{k}' \cdot \mathbf{r}}, \tag{7}$$

where Ψ is the solution of Schrödinger's equation

$$\nabla^2 \Psi + [k^2 - 2V] \Psi = 0. \tag{8}$$

In the Born approximation, Eq. (7) reduces to the more tractable form¹⁶

$$A(\mathbf{k}, \mathbf{k}') = \int e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} V d\mathbf{r}, \tag{9}$$

which is unfortunately, accurate only for potentials satisfying the condition

$$\left| 2k^{-1} \int_0^\infty V e^{ikr} \sin kr dr \right| \ll 1. \tag{10}$$

The expression (7) is valid, in principle, for all potentials. In practice, difficulties may be encountered in obtaining a good function for Ψ, as the exact solution of Schrödinger's equation for the multipole-type potential of a defect complex can be very tedious. The problem is considerably simplified, however, when V(r) is a superposition of the potentials (which is a very useful approximation when defect interaction is weak) of isolated defects or defect pairs. The effective scattering potential of the complex is then given by

$$V = \sum_\sigma V_\sigma(\mathbf{r} - \mathbf{r}_\sigma), \tag{11}$$

¹⁵ J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley & Sons, Inc., New York, 1956).

¹⁶ P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., 1953).

¹⁴ J. K. Mackenzie and E. H. Sondheimer, *Phys. Rev.* **77**, 264 (1950).

V_g being the potential of the isolated defect or close defect pair centered at \mathbf{r}_g . It can then be shown that¹⁷

$$A(\mathbf{k}, \mathbf{k}') = \sum_g F_g^{-1}(\mathbf{k}, \mathbf{k}') + \frac{1}{2\pi^2} \lim_{\epsilon \rightarrow 0} \sum_{gh} \int \frac{F_g^{-1}(\mathbf{k}, \mathbf{q}) F_h^{-1}(\mathbf{q}, \mathbf{k}')}{k_0^2 - q^2 - i\epsilon} d\mathbf{q} + \text{terms of higher order in } F, \quad (12)$$

where $F_g^{-1}(\mathbf{k}, \mathbf{k}') = e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_g} A_g(\mathbf{k}, \mathbf{k}')$; with $A_g(\mathbf{k}, \mathbf{k}')$ denoting the scattering amplitude corresponding to the potential V_g , and taking the integrals on the energy shell. Substituting for $A(\mathbf{k}, \mathbf{k}')$ in Eq. (6) gives the result

$$P_k^{k'} = \left[\sum_{gh} F_g^{-1} F_h^{-1*} + \left(\sum_g \sum_{uv} F_g^{-1} F_{uv}^{-2*} + \text{c.c.} \right) + \sum_{uv} \sum_{bd} F_{uv}^{-2} F_{bd}^{-2*} + \dots \right] / \mathcal{V}^2, \quad (13)$$

where $\sum_{gh} F_g^{-1} F_h^{-1*}$ is the second term on the r.h.s. of Eq. (12). This expression for $P_k^{k'}$ can now be substituted in Eq. (5) to give a tractable expression for the resistivity change parameter, $\Delta\rho_{ij}^m$. To facilitate the evaluation of $\Delta\rho_{ij}^m$, the exponential phase factor in F_g^{-1} , $F_g^{-1} F_h^{-1*}$, etc. can be expanded in spherical harmonics. It can then be shown that

$$\Delta\rho_{ij}^m = -\frac{3}{4\pi n_0 k_0^5 \mathcal{V}} \int (k_j' - k_j) k_i \times \left\{ \sum_{gh} A_g A_h^* \sum_{\lambda=0}^{\infty} (2\lambda+1) i^\lambda j_\lambda(|\mathbf{k}-\mathbf{k}'|) \times |\mathbf{r}_g - \mathbf{r}_h| \right\} P_\lambda[\cos(\mathbf{k}-\mathbf{k}', \mathbf{r}_g - \mathbf{r}_h)] + \text{terms of higher order in } A_g \} d\omega d\omega', \quad (14)$$

which can be evaluated to the desired order of harmonics and scattering interference terms.

In the case of a complex with a high order of symmetry and weak interacting defects, only the first term of the harmonic expansion has to be considered and the higher order terms in A_g can be neglected. Equation (14) then reduces to a simple relation for the resistivity change due to an isotropic complex with weak defect interaction

$$\Delta\rho^m = \frac{2\pi k_0}{Z\mathcal{N}} \int f(\theta) \sin\theta (1 - \cos\theta) d\theta, \quad (15)$$

where θ is the angle $(\mathbf{k}, \mathbf{k}')$, Z is the valency of the metal, \mathcal{N} the number of atoms in the metal, and

$$f(\theta) = \sum_{gh} A_g A_h^* \frac{\sin[2|\mathbf{r}_g - \mathbf{r}_h| k_0 \sin(\theta/2)]}{2|\mathbf{r}_g - \mathbf{r}_h| k_0 \sin(\theta/2)}.$$

¹⁷ L. H. Schick, Rev. Mod. Phys. 33, 608 (1961).

The only quantity remaining to be defined explicitly in the final expression for $\Delta\rho_{ij}^m$ or $\Delta\rho^m$ is the scattering amplitude A_g corresponding to the scattering potential V_g . Expressions for A_g of interest to the present problem are obtainable in the Born approximation and the phase-shift formalism. In the Born approximation, the scattering amplitude is given by Eq. (9) with V_g replacing V . As it was pointed out earlier, Eq. (9) is exact only when the Born condition (Eq. 10) is satisfied. It has been common practice, however, to employ the Born approximation for potentials well outside that range, simply because analytical expressions for A_g can be obtained for most of the conventional defect potentials; thus simplifying considerably further mathematical operations. One should bear in mind that resistivity estimates obtained with the Born approximation could be off by a factor of 3 or more and are not reliable parameters in the interpretation of experimental data.

In the phase-shift formalism, A_g is obtained from Eq. (7) after replacing V by V_g . As opposed to the Born approximation, there is, in this case, no simple expression for the scattering amplitude for a general potential; the form and the complexities of A_g will depend largely on the number of poles and on the anisotropy in V_g . For several potentials of interest in defect problems, explicit phase-shift expressions for A_g can be derived without difficulty. For example:

(1) *Central Field*. The scattering amplitude due to the spherically symmetric field of an isolated point defect is given by the familiar Faxén and Holtmark¹⁸ expression

$$A_g = (ik_0^{-1}) \sum_{l=0}^{\infty} (2l+1) e^{i\eta_{lg}} \sin\eta_{lg} P_l[\cos(\mathbf{k}, \mathbf{k}')], \quad (16)$$

where η_{lg} is the phase shift of the l th-order partial wave for the central potential V_g .

(2) *Homopole*. In the case of a pair of like defects at close range, the scattering amplitude can be obtained for a spheroidal well-type potential. Bross and Seeger¹⁹ have shown that

$$A_g = (2ik_0)^{-1} \sum_{l=0}^{\infty} \sum_{m=-l}^l (-1)^m (2l+1) (e^{2i\eta_{lg}^m} - 1) \times \text{Ps}_l^{-m}(\cos\varphi_s', \gamma^2) \text{Ps}_l^m(\cos\varphi_s, \gamma^2) e^{im(\phi_s - \phi_s')}, \quad (17)$$

where γ is a parameter related to the potential well and the interdefect separation, φ_s, ϕ_s and φ_s', ϕ_s' are the angular coordinates of \mathbf{k} and \mathbf{k}' , respectively, referred to a prolate spheroidal coordinate system, Ps_l^m and Ps_l^{-m} are spheroidal wave functions, and η_{lm}^g is the phase shift of Ps_l^m for the potential V_g .

(3) *Dipole*. Although the dipole is not a regular defect in metals as it is in semiconductors, it can still be a

¹⁸ M. Faxén and G. Holtmark, Z. Physik. 45, 307 (1927).

¹⁹ A. Seeger and H. Bross, Z. Physik. 145, 161 (1956); J. Phys. Chem. Solids 6, 324 (1958).

useful concept in the construction of mathematically tractable models of certain defect configurations, particularly in the treatment of lattice distortion. The potential of a dipole is weak enough to be treated in the Born approximation.²⁰ It can be shown that for a screened-Coulomb-type dipole potential, i.e.,

$$V_{\sigma} = \frac{M_{\sigma}}{|\mathbf{r}-\mathbf{r}_{\sigma}|^2} \cos(\mathbf{M}_{\sigma}, \mathbf{r}-\mathbf{r}_{\sigma}) [1+q|\mathbf{r}-\mathbf{r}_{\sigma}|] \times \exp[-q|\mathbf{r}-\mathbf{r}_{\sigma}|], \quad (18)$$

where M_{σ} is the dipole strength, and q the screening constant, the scattering amplitude is given by

$$A_{\sigma} = 2i \exp[i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_{\sigma}] \sin[(\mathbf{k}-\mathbf{k}') \cdot \mathbf{a}] A_{\sigma}^1, \quad (19)$$

where the charges of the dipole are at $\mathbf{r}_{\sigma}+\mathbf{a}$ and $\mathbf{r}_{\sigma}-\mathbf{a}$, and A_{σ}^1 is the scattering amplitude due to one of the charges of the dipole when isolated. In the phase-shift representation, A_{σ}^1 can be taken formally to be expression (16), the scattering amplitude for a central field.

III. APPLICATIONS

The basic procedure in utilizing the present theory to estimate the resistivity change in a specimen consists in: (1) breaking down the defect population into complexes of known atomic configuration and scattering potential, (2) determining the resistivity change due to each complex from Eqs. (5) or (14), and (3) adding up these resistivity changes in accordance with Eq. (2). When solutions of Eq. (8) are not immediately available, the superposition potential expression, Eq. (11), can be employed. Errors due to this approximation can be minimized by a judicious choice of the defect units within the complex, i.e., which to treat as isolated point defects, homopoles, or dipoles. The scattering amplitudes for the three types of potentials given in Eqs. (16), (17), and (18), should cover the common defect complexes except dense defect zones like the "displacement spikes" resulting from high-energy bombardment. The homopole will apply to pairs of like atoms or of vacancies at close range. The dipole can be used in the treatment of lattice distortion when it is assumed that a displaced ion leaves an equal point charge of opposite sign at the vacated lattice site. As it was pointed out earlier, none of the theoretical defect potentials consistent with the free-electron model lead to satisfactory values for the resistivity change. Good estimates can be obtained, however, with the simple expressions of the present model by employing scattering potentials or scattering amplitudes derived from a more accurate theory or constructed from empirical data.

For illustration, the results of the previous section

have been employed to evaluate the resistivity change in copper due to 1 at. % of some standard defects and small defect complexes taking into account the lattice strain around them. The specific cases considered are those of the monovacancy, the interstitial, the divacancy, the trivacancy, the interstitial vacancy or Frenkel pair, and the di-interstitial. The atomic configurations considered for these calculations are: those of Tewordt²¹ for the monovacancy, of Benneman²² for the interstitial, of Oli and March²³ for the divacancy, and of Damask and Ors.²⁴ for the trivacancy. In the case of the interstitial-vacancy pair and the di-interstitial, a superposition of the single defect configurations at nearest-neighbor distance has been adopted, as suggested by Johnson and Brown.²⁵ The basic scattering unit for this set of defects is the vacancy (as displaced ions, following from Eq. (19), can be taken to have the same scattering amplitude as a vacancy with a change of sign). In the present calculations, two different scattering amplitudes were employed for the vacancy: one was derived from a square-well-type potential for a vacancy in copper²⁶ and the other was obtained semiempirically, by a method suggested by Kohn and Vosko.²⁷ The results for these two cases are presented in Table I and compared with experimental estimates (where available).

It is found that the semiempirical phase shifts give a better over-all agreement with experimental estimates than the square well. This indicates that semiempirical scattering amplitudes should lead to more reliable estimates of the resistivity change for large defect aggregates. The more striking features of the results for the semiempirical phase shifts are: (1) there is agreement with the findings of previous authors^{5,28} that the resistivity of the divacancy is $\sim 5\%$ less than the combined resistivities of two isolated vacancies, (2) the scattering power of the di-interstitial is $\sim 2\%$ less than the combined scattering of two isolated interstitials, (3) the contribution to the resistivity change from the lattice strain is $\sim 0.5\%$ for the vacancy and $\sim 25\%$ for the interstitial, and (4) there is agreement with the observation of Flynn⁴ that the residual resistivity due to a defect complex can be approximated within 5% by adding up the resistivity change due to each defect unit in the complex. This is found to be true, however, only when the configuration of the complex is roughly a superposition of the configuration of the isolated defect

²¹ L. Tewordt, *Phys. Rev.* **109**, 61 (1958).

²² K. H. Benneman, *Z. Physik.* **165**, 445 (1961).

²³ B. Oli and N. H. March (private communication).

²⁴ A. C. Damask, G. J. Dienes, and V. G. Weizer, *Phys. Rev.* **113**, 781 (1959).

²⁵ R. A. Johnson and E. Brown, *Phys. Rev.* **127**, 446 (1962).

²⁶ C. Budin, F. Denayrou, A. Lucasson, and P. Lucasson, *Compt. Rend.* **256**, 1518 (1963).

²⁷ W. Kohn and S. H. Vosko, *Phys. Rev.* **119**, 912 (1960).

²⁸ R. O. Simmonds, J. S. Koehler, and R. W. Baluffi, *Radiation Damage in Solids* (International Atomic Energy Agency, Vienna, 1962), Vol. I, p. 155.

²⁰ R. Stratton, *J. Phys. Chem. Solids* **23**, 1011 (1962); A. G. Samoilovich and M. V. Nitsovich, *Fiz. Tverd. Tela* **5**, 2981 (1963) [English transl.; *Soviet Phys.—Solid State* **5**, 2182 (1963)].

TABLE I. Change in resistivity for Cu in $\mu\Omega\text{-cm/at.}\%$ due to several types of defects.

Type of defect	Vacancy	Interstitial	Di-vacancy	Di-interstitial	Frenkel pair	Tri-vacancy
calculated with square-well phase shifts	1.504	2.40	3.07	4.70	3.61	5.81
calculated with semi-empirical phase shifts	1.1	1.43	2.12	2.81	2.61	3.45
experimental or semi-empirical estimates	1.1 ^a	$\sim 1.5^b$	$\sim 2.0^c$	$\sim 2.9^b$	2.5 ^d	...

^a Reference 26.^b Estimated by addition rule for defect pairs.^c Reference 28.^d A. Seeger, E. Mann, and R. V. Jan, *J. Phys. Chem. Solids* **23**, 639 (1962).

units; the rule does not apply when there is a major redistribution of atoms on aggregation.

It should be pointed out that the results presented above apply to a random distribution of defects or defect complexes and do not include the anisotropic contribution from the second and higher harmonics of Eq. (14). Anisotropy in the scattering power is important in the case of extended defect clusters, defect discs and loops; it is not very significant for defect pairs unless they occur in a preferred crystal orientation,^{5,19} nor for the trivacancy which has tetrahedral symmetry.

IV. DISCUSSION

The theory presented in this report gives a simple and quite efficient method of estimating the resistivity change in a metal due to multiple point imperfections and to the lattice strain around them. It is applicable to most defect containing systems of interest; namely: radiation damaged, quenched and cold-worked metallic specimens, ordered and disordered alloys, and alloys with precipitation zones. The mathematical operations are clear-cut and the labor involved depends generally on the intricacies of the defect configurations and on the accuracy desired. The problem is in its most tractable form when the scattering potential of the defect system can be approximated by a superposition potential. In that case, it is possible to utilize arbitrary potentials and scattering amplitudes for the individual defects in the cluster—thus ensuring good estimates for the resistivity change due to large defect complexes.

To make a proper assessment of the potentialities of the theory, it should be compared with relevant previous work, in particular, with the treatment of the resistivity of alloys by Nordheim,¹ and Asch and Hall,²⁹ and with the recent work of Flynn,^{4,5} and Keller³⁰ on the scatter-

ing power of pairs of (like and unlike) defects. The present treatment can be considered as a generalization of these theories. In the first place, the work of Nordheim, and Asch and Hall has been extended beyond the Born approximation to the phase-shift formalism which is far more accurate. It has also been extended to apply to a completely anisotropic scattering system rather than to a random or ordered distribution of scattering centers. The work of Flynn and of Keller has been extended to apply to complexes made up of more than two defects. As a matter of interest, it can be verified that Eqs. (13) and (14) of Flynn⁵ and Eq. (9) of Keller for the relaxation time can be obtained from Eq. (14) of this report when g and h are set equal to 2, and $\mathbf{r}_g = (a, \pi/2, 0)$, or \mathbf{r}_1 ; and $\mathbf{r}_h = (a, \pi/2, \pi)$, or \mathbf{r}_2 , and using the appropriate multiplying factor. It should also be pointed out that the interference terms in the scattering amplitude [see Eq. (12)] for a superposition potential were neglected by Keller, while Flynn⁵ only referred to them formally. These terms are presented here in a tractable form, as they can contribute significantly to the scattering when defects are at close range.

Neither Nordheim nor Flynn or Keller discussed the resistivity change due to lattice distortion. The treatment of this problem by the deformation potential and the deformed-atomic-cell methods is not as flexible or as accurate as it is by the present theory. The deformation-potential method tends to be clumsy for systems with a nongeometrical configuration and it leads, moreover, to unrealistic estimates of the residual resistivity. The deformed-atomic-cell approach, on the other hand, is restricted to isolated point defects or central force fields. It is of interest to point out, however, that the distorted-atomic-cell treatment could be extended to apply to arbitrary aggregates of defects if it is assumed that the deformation of the atomic cell due to an isolated defect or impurity does not change when these imperfections are brought together to form a complex. One could then utilize Eq. (14) to estimate the resistivity change, treating each individual defect and the lattice distortion around it as a single scattering center. The scattering amplitudes to be utilized can be derived from Blatt's prescription or semiempirically, with the modified Freidel's sum rule.¹³

Although the present theory is a net improvement on previous work, it can still be criticized on several important points. The most serious shortcomings and some suggestions for their corrections are discussed below:

The Mott Model. The metal model employed in this investigation is essentially that used by Mott⁸ in an early theory of residual resistivity in alloys. There are some drastic approximations in that model, like the use of plane waves, spherical Fermi surfaces, and the neglect of electron interaction, which can lead to significant errors in the resistivity estimates. It is only quite recently that investigators have concerned them-

²⁹ A. E. Asch and G. L. Hall, *Phys. Rev.* **132**, 1047 (1963).³⁰ J. M. Keller, *J. Phys. Chem. Solids* **24**, 1121 (1963).

selves with improving the Mott model. Harrison³¹ and Goodings and Mozer³² have considered the scattering of Bloch waves from point imperfections, Gautier³³ and Huebener³⁴ have treated nonspherical Fermi surfaces, and Langer³⁵ and Suris³⁶ have dealt with the problem of scattering for an interacting electron gas. These modifications, although quite elaborate, can, in principle, be incorporated with the present theory.

Electronic structure and interaction of defects. Treating atomic defects as point charges is another approximation of the Mott model. It is a very convenient concept in a mathematical theory but it can lead to inaccurate results due to neglecting the structure of the ionic core. The appropriate corrections can be made by replacing the point charge by a Wigner-Seitz cell or by some other cellular model.³⁷ Another source of error associated with the electronic structure of the defects is in the determination of the scattering potential and scattered wave function for a defect aggregate. In principle, this corresponds to the extremely difficult problem of calculating the electronic structure of a large polyatomic molecule. Utilizing a superposition potential in the place of the correct self-consistent field amounts to neglecting interaction between the defects and this can be a serious omission for defects at close range. Since a rigorous solution of the potential problem for a cluster of five or more defects is so difficult, an interesting alternative would be to solve the problem in

steps, by a perturbation method, starting with the superposition potential as the first approximation.

Lattice distortion. The treatment of lattice distortion in the present investigation is extremely simple-minded; it is based entirely on the shaky assumption that an atomic defect can be equated to a point charge. The errors due to neglecting the ionic core are even more serious here, since one is concerned with changes within a fraction of an Å from the nucleus. The displacement potential approach, in spite of the fact that it overestimates the resistivity change, seems a more realistic treatment of lattice strain. It should give more useful results if it were modified to incorporate a phase-shift formalism, or if semiempirical parameters were introduced in the scheme.

Phase shifts. The semiempirical phase shifts obtained by the method of Kohn and Vosko are not very realistic, as phase shifts of order greater than 1 are neglected. It may not be a serious error for vacancies or divalent impurities in a monovalent metal but in the case of a large residual defect charge, the inclusion of phase shifts of higher order could alter significantly the resistivity change due to large defect complexes.

V. CONCLUSION

In conclusion, it is quite clear that a great deal of research has still to be done on the problem of the resistivity change due to multiple point defects before reliable estimates can be obtained from a theory which does not employ empirical parameters. In the meantime, it makes sense to employ the experimental scattering power of point defects, which are now available for most metals, in attempts to estimate the resistivity change due to their aggregates. In that context, the present theory, with some slight modifications perhaps, is a most useful approach to the problem, as far as expediency and accuracy are concerned.

³¹ W. A. Harrison, *Phys. Rev.* **110**, 14 (1958).

³² D. A. Goodings and B. Mozer, *Phys. Rev.* **136**, A1093 (1964).

³³ F. Gautier, *J. Phys. Radium* **23**, 105 (1962).

³⁴ R. P. Huebener, *Phys. Rev.* **138**, A803 (1965).

³⁵ J. S. Langer, *Phys. Rev.* **120**, 714 (1960); **124**, 1033 (1961).

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