

## Scattering of Electrons from Point Singularities in Metals\*

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Mott's calculations on the scattering of electrons from substitutional impurity atoms are extended to include the scattering from interstitial atoms and vacancies; the effects of lattice distortions around the singularities are taken into account. It is found that the lattice distortions do not change the order of magnitude of the calculated resistivity in most cases of practical interest, but may in some cases make a difference of a factor of three or more for substitutional atoms of the same valence as the replaced atoms. It is concluded that the resistance change due to a dissociated vacancy-interstitial pair in a monovalent metal of atomic number  $Z$  is about equal to or somewhat larger than that due to two divalent substitutional atoms of atomic number  $Z+1$ . Changes in the temperature-dependent part of the resistivity as a result of lattice distortions are found to be of the same order, at room temperature, as the changes in the residual resistivity due to the lattice distortions.

### I. INTRODUCTION

THE scattering of electrons in solids by isolated point singularities, such as impurity atoms, has received attention in connection with the theory<sup>1,2,2a</sup> of the change in electrical conductivities of metals upon alloying and with the theory<sup>3</sup> of mobilities in semiconductors. Previous theoretical work<sup>1,2</sup> on the scattering of electrons in metals has taken account of the scattering arising from (1) the screened Coulomb potential associated with the substitutional atom of valence differing from that of the replaced atom, and (2) the difference in the average potential within the atomic polyhedron of the substitutional atom from that within the replaced atom, in the case that the impurity atom and the atoms of the mother lattice are of the same valence. Calculations based on these effects lead to semiquantitative agreement with experimental results on the electrical resistance of dilute solid solutions. In cases where one might expect good agreement between theory and experiment, namely, for the monovalent metals, the ratio of the observed resistance change to that calculated by the Thomas-Fermi method for effect (1) above is of the order of 1/7; Mott has attributed this discrepancy to errors inherent in the Thomas-Fermi method.

Interest in the general problem of scattering of electrons by singularities in metals has been revived because of the potentialities<sup>4</sup> of resistance measurements for the study of radiation damage to structural materials. One of the primary problems in the study of radiation damage<sup>5</sup> is the determination of the number of interstitial

atoms and vacancies, produced as a result of irradiation with energetic particles, as a function of temperature, atomic number, crystal structure, and any other experimental parameters. It is clear that resistance measurements represent a powerful tool in such investigations, once the scattering cross sections of the singularities are known.

In the lattice surrounding point singularities there will, in general, exist elastic distortions, i.e., deviations from perfect periodicity, which give rise to scattering potentials in addition to those mentioned above. The scattering arising from this source has previously been neglected, and neither the magnitude nor the sign of the effect on the resistance has been determined. It is intuitively reasonable to assume that the effect of the elastic distortions on the resistance will be small compared with that of the screened Coulomb potential of a substitutional impurity atom of different valence but of about the same size as the atom it replaces; however, in connection with the interest in measurements of radiation damage, it is not obvious that the effect will be negligible for an interstitial atom or vacancy, around which the atomic displacements may be large. The purpose of this note is to examine the effects of the lattice distortions on the electrical resistance for the several interesting cases of vacancies, interstitial atoms, and substitutional impurities, and, in particular, to see if it is possible to explain by distortion effects the existing discrepancies between theoretical and experimental resistivities of substitutional alloys, so that the scattering from vacancies and interstitials can be calculated by the same methods.

### II. CALCULATION OF THE SCATTERING MATRIX ELEMENT

According to Matthiessen's rule, we may treat the scattering from the singularities independently of the purely thermal effects; in the early part of this work, therefore, we shall completely ignore interactions with lattice vibrations, and the resistance we shall calculate is the change in residual resistance of a lattice upon the introduction of point singularities. With the above cus-

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<sup>1</sup> N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).

<sup>2</sup> N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford University Press, London, 1936), Chap. VII.

<sup>2a</sup> K. Huang, Proc. Phys. Soc. (London) **60**, 161 (1948).

<sup>3</sup> E. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1950); G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949) and references contained therein.

<sup>4</sup> Henderson, Cooper, and Marx, Phys. Rev. **86**, 642 (1952) and Marx, Koehler, and Wert, Phys. Rev. **86**, 643 (1952). The writer is indebted to Professor Koehler for discussions of these experiments before publication.

<sup>5</sup> F. Seitz, Disc. Faraday Soc. **5**, 271 (1949).

tomy simplification, our problem reduces to the calculation of the matrix elements of the perturbation Hamiltonian for an electron in a stationary distorted lattice. We shall make the further simplification that the imperfections scatter independently, i.e., that all interference terms vanish; this assumption is certainly valid for sufficiently dilute solid solutions but may lead to small errors in the radiation damage problem if an appreciable fraction of the interstitial atoms are within one or two atomic distances of vacancies.

The perturbation Hamiltonian may be approximated by

$$H(\mathbf{r}) = \sum_j' v_j(\mathbf{r} - \mathbf{R}_j - \mathbf{U}_j) - \sum_j v_j(\mathbf{r} - \mathbf{R}_j), \quad (1)$$

where  $-v_j/e$  is the potential due to the  $j$ th nucleus and its surrounding cloud of electrons.  $\mathbf{R}_j$  is the equilibrium position of the  $j$ th atom in the undistorted crystal, and  $\mathbf{U}_j$  is its displacement as a result of the presence of the singularity. The second summation above represents the potential energy of an electron in the undistorted lattice, and thus all the  $v_j$ 's in this sum are identical. The prime on the first summation symbol serves to remind us that we have added, subtracted, or exchanged an atom in the lattice; in the first or second event the summation is carried out over one extra or one less atom than in the second summation, and in the third event the  $v_j$ 's are no longer all identical. Keeping only the first two terms in the expansion

$$v_j(\mathbf{r} - \mathbf{R}_j - \mathbf{U}_j) = v_j(\mathbf{r} - \mathbf{R}_j) - \mathbf{U}_j \cdot \nabla v_j(\mathbf{r} - \mathbf{R}_j) + \dots, \quad (2)$$

we may write Eq. (1) as

$$H(\mathbf{r}) = W(\mathbf{r}) + w(\mathbf{r}), \quad (3)$$

where

$$W(\mathbf{r}) \cong -\sum_j' \mathbf{U}_j \cdot \nabla v(\mathbf{r} - \mathbf{R}_j), \quad (4)$$

and  $w(\mathbf{r})$  is as defined below. The reason for this separation will immediately become clear. The prime on the summation symbol in Eq. (4) now has the definite meaning that the singularity is excluded from the sum; i.e., the contributions to  $H(\mathbf{r})$  which arise from a region of the crystal of the order of an atomic volume in size centered about the vacancy, interstitial atom or impurity atom, are to be taken account of in  $w(\mathbf{r})$ . In Eq. (4) the potential of the normal lattice atoms of valence  $z$  is denoted simply by  $-v/e$ , and the potential of an impurity atom of valence  $Z$  (which may or may not equal  $z$ ) will be denoted below by  $-V/e$ . With these understandings in mind, we may express the function  $w(\mathbf{r})$  for the four cases of interest as:

1. interstitial lattice atom:  $w_1(\mathbf{r}) = v(\mathbf{r})$ ;
2. vacancy:  $w_2(\mathbf{r}) = -v(\mathbf{r})$ ;
3. substitutional impurity:  $w_3(\mathbf{r}) = V(\mathbf{r}) - v(\mathbf{r})$ ;
4. interstitial impurity:  $w_4(\mathbf{r}) = V(\mathbf{r})$ .

Here we have made the assumption that the potential due to an atom in an interstitial position is the same as

for that atom in a normal lattice site. The extent to which this assumption is justified will be considered in Sec. IV.

We now compute the matrix elements of the above perturbation Hamiltonians between two electronic plane wave states characterized by the propagation vectors  $\mathbf{k}$  and  $\mathbf{k}'$ . The matrix elements we require are

$$\langle \mathbf{k}' | H | \mathbf{k} \rangle = \Omega^{-1} \int \exp(-i\mathbf{k}' \cdot \mathbf{r}) [W(\mathbf{r}) + w(\mathbf{r})] \times \exp(i\mathbf{k} \cdot \mathbf{r}) d\tau = M(\boldsymbol{\kappa}) + m(\boldsymbol{\kappa}), \quad (6)$$

where

$$M(\boldsymbol{\kappa}) = -\Omega^{-1} \int \exp(-i\boldsymbol{\kappa} \cdot \mathbf{r}) \sum_j' \mathbf{U}_j \cdot \nabla v(\mathbf{r} - \mathbf{R}_j) d\tau, \quad (7)$$

$$m(\boldsymbol{\kappa}) = \Omega^{-1} \int \exp(-i\boldsymbol{\kappa} \cdot \mathbf{r}) w(\mathbf{r}) d\tau. \quad (8)$$

$\Omega$  is the volume of the metal, and  $\boldsymbol{\kappa} \equiv \mathbf{k}' - \mathbf{k}$ . The matrix element  $m(\boldsymbol{\kappa})$  is the contribution evaluated by Mott,<sup>1</sup> and  $M(\boldsymbol{\kappa})$  is that which takes account of the distortion of the lattice.

We may estimate the value of  $M(\boldsymbol{\kappa})$  in the following way. Let us consider the spherical singularity to be at the center of a large sphere; then according to the theory of elasticity for a homogeneous isotropic medium, the displacement of the lattice at a point  $\mathbf{r}$ , measured from the center of the spherical imperfection, is proportional to  $\mathbf{r}/r^3$  for  $r > r_0$ , where  $r_0$  is the radius of the imperfection.<sup>6</sup> Letting  $\mathbf{U}_j = A\mathbf{R}_j/R_j^3$ , and approximating<sup>2</sup>  $v(\mathbf{r})$  by  $-ze^2 \exp(-qr)/r$ , we obtain

$$M(\boldsymbol{\kappa}) = \frac{4\pi i z e^2 A}{\Omega(\kappa^2 + q^2)} \sum_j' \frac{\mathbf{R}_j \cdot \boldsymbol{\kappa} \exp(-i\boldsymbol{\kappa} \cdot \mathbf{R}_j)}{R_j^3}. \quad (9)$$

The integral in Eq. (7) has been evaluated by interchanging the order of summation and integration, transforming the variable of integration from  $\mathbf{r}$  to  $\mathbf{r} - \mathbf{R}_j$  and integrating by parts.

For purposes of qualitative discussion we may use the approximation of smeared-out positive charge and replace the summation in Eq. (9) by an integration, obtaining

$$M(\boldsymbol{\kappa}) = \frac{16\pi^2 z e^2 A}{\Omega(\kappa^2 + q^2) \Delta} \frac{\sin \kappa r_0}{\kappa r_0}, \quad (9')$$

where  $\Delta$  is the atomic volume, and  $r_0$  has the somewhat ambiguous meaning of the inner cut-off radius for the contribution to the matrix element from the elastic distortions of the smeared-out medium. This approximation is a rather poor one, but it will serve to show in what cases the distortion effects are unimportant. The

<sup>6</sup> We are neglecting a term in the displacement which is proportional to  $\mathbf{r}$ . The effects of this term on the resistance are discussed in Sec. IV.

more accurate expression Eq. (9) can be used in specific cases where Eq. (9') shows the lattice distortion to be significant. The use of Eq. (9) is made more difficult by the fact that the matrix element depends upon the direction of  $\kappa$  in a complicated way, and the Boltzmann transport equation which must be solved for the resistivity has been treated in a simple way<sup>2</sup> only on the assumption that the scattering matrix element is independent of the direction of  $\kappa$ . In a more accurate analysis, therefore, where Eq. (9) is used, it appears necessary, in order to avoid the considerable computational difficulties associated with the solution of the transport equation in its general form, to perform the indicated summation for a number of directions of  $\kappa$  and to replace the resulting complicated function by a function of  $|\kappa|$  alone which represents a suitable average over direction; such a function would be expected to be a better approximation than that indicated by Eq. (9'), but it is not as suitable for a general discussion since it depends on the details of the crystal structure and the type of singularity.

An approximate evaluation of Eq. (7), equivalent to Eq. (9') but exhibiting another feature of the potential, may be performed in the following way. Let us replace the summation in Eq. (4) by an integration before interchanging the order of integration and summation, and obtain

$$W(\mathbf{r}) = \Delta^{-1} \int_{r_0} \mathbf{U}(\mathbf{R}) \cdot \nabla_{\mathbf{R}} v(\mathbf{r} - \mathbf{R}) d\tau_{\mathbf{R}}, \quad (10)$$

where the integration is carried out over all space outside a sphere of radius  $r_0$ , and the subscript  $\mathbf{R}$  on the Nabla operator denotes differentiation with respect to the integration variable. Making use of the vector identity for the divergence of a product  $v\mathbf{U}$ , we transform Eq. (10) into

$$W(\mathbf{r}) = \Delta^{-1} \int_{r_0} \nabla_{\mathbf{R}} \cdot (v\mathbf{U}) - v \nabla_{\mathbf{R}} \cdot \mathbf{U} d\tau_{\mathbf{R}}. \quad (11)$$

According to a well-known theorem of vector calculus, the divergence of  $R^n \mathbf{R}$  is equal to  $(n+3)R^n$ ; thus, since  $\mathbf{U}(\mathbf{R})$  is proportional to  $R^{-3}\mathbf{R}$ , the divergence of  $\mathbf{U}$  vanishes. It should be pointed out that, since  $\nabla \cdot \mathbf{U}$  is proportional to the density change, the density in an infinite, continuous, isotropic medium remains unchanged when a spherically symmetric distortion is introduced. That is, any transfer of material to or from the spherical imperfection is associated with the surface at infinity. In spite of the absence of density changes, however, the potential  $W(\mathbf{r})$  and the matrix element  $M(\kappa)$  do not vanish, as can easily be seen by transforming the first term on the right side of Eq. (11) by the divergence theorem and inserting it in Eq. (7). Interchanging the order of the integrations and evaluating directly, we obtain the result given in Eq. (9').

The above result for the total perturbation Hamiltonian,  $w(\mathbf{r}) + \Delta^{-1} \int \nabla_{\mathbf{R}} \cdot (v\mathbf{U}) d\tau_{\mathbf{R}}$ , should be compared

with the corresponding expression<sup>7</sup> for the scattering of electrons by edge-type dislocations. In the latter case the term  $\nabla \cdot \mathbf{U}$  does not vanish, and the term  $\Delta^{-1} \int \nabla \cdot (v\mathbf{U})$  cancels the term, corresponding to  $w(\mathbf{r})$ , which arises from the missing plane of atoms. The physical difference in the two situations is that, whereas in the present calculation there exists a real discontinuity at the singularity, across the plane of missing atoms, on the other hand, the discontinuity in atomic displacement gives rise only to a fictitious discontinuity in the lattice; that is, the lattice is in register across the missing plane of atoms.

Mott has approximated<sup>1</sup>  $w(\mathbf{r})$  for case 3 by

$$\begin{aligned} w_3(\mathbf{r}) &= -(Z-z)e^2 \exp(-qr)/r + (E_Z - E_z) \delta_{zz}, & r < R_0 \\ &= -(Z-z)e^2 \exp(-qr)/r, & r > R_0 \end{aligned} \quad (12)$$

where  $\delta_{zz}$  is the Kronecker delta, and  $R_0$  the radius of the equivalent sphere of the lattice atoms.  $E_z$  is the energy of the lowest electronic state in the conduction band of the pure lattice, and  $E_Z$  is the lowest energy for an electron about the impurity atom, which is compressed or distended to fill a volume corresponding to its present position in the foreign lattice. A term proportional to  $(E_Z - E_z)$  should also be included for substitutional atoms of different valence, of course, although its contribution will be small for atoms of about the same atomic number because of the similarity of the electronic wave functions. For a pair such as Hg in Ag the effect of this term may be as large as the valence term, so we shall use Eq. (12) without the Kronecker delta in order to allow for the effect, at least formally, in all cases. For the other three cases, (1), (2), and (4),  $w(\mathbf{r})$  is taken to be  $-e^2 \exp(-qr)/r$  multiplied by the appropriate quantity  $z$ ,  $-z$  and  $Z$ , respectively, plus a term corresponding to that just discussed which takes account of the change in average potential in the region of the singularity. The matrix elements  $m(\kappa)$  [Eq. (8)] are readily evaluated, and the following results are obtained:

$$\begin{aligned} m_1(\kappa) &= \frac{-4\pi z e^2}{\Omega(\kappa^2 + q^2)} + \frac{\Delta_1 E}{\Omega} 4\pi R_0^3 f(\kappa R_0), \\ m_2(\kappa) &= \frac{4\pi z e^2}{\Omega(\kappa^2 + q^2)} + \frac{\Delta_2 E}{\Omega} 4\pi R_0^3 f(\kappa R_0), \\ m_3(\kappa) &= \frac{-4\pi(Z-z)e^2}{\Omega(\kappa^2 + q^2)} + \frac{(E_Z - E_z)}{\Omega} 4\pi R_0^3 f(\kappa R_0), \\ m_4(\kappa) &= \frac{-4\pi Z e^2}{\Omega(\kappa^2 + q^2)} + \frac{\Delta_4 E}{\Omega} 4\pi R_0^3 f(\kappa R_0), \end{aligned} \quad (13)$$

where  $f(y) = (\sin y - y \cos y)/y^3$ .

<sup>7</sup> D. L. Dexter, Phys. Rev. 86, 447 (1952).

## III. CALCULATION OF RESIDUAL RESISTANCE

The calculation of the resistivity from the Boltzmann transport equation proceeds in the manner described in reference 2; the change in the residual resistivity upon the introduction of  $N$  randomly spaced identical point singularities is found to be

$$\Delta\rho = \frac{z^2 e^2 m^* N}{6\pi \hbar^3 n^2} \int_0^\pi d\theta (1 - \cos\theta) \times \sin\theta \frac{\Omega^2 k^4}{\pi^2 z^2 e^4} |M(\boldsymbol{\kappa}) + m(\boldsymbol{\kappa})|^2, \quad (14)$$

where the matrix elements are assumed to depend only on  $\theta$ , the angle between  $\mathbf{k}$  and  $\mathbf{k}'$ , and  $n$  is the density of free electrons in the pure lattice. We have now to consider only those values for  $\mathbf{k}$  and  $\mathbf{k}'$  which lie along the Fermi surface, so that  $|\mathbf{k}| = |\mathbf{k}'|$  and  $\boldsymbol{\kappa} = |\mathbf{k}'| - \mathbf{k} = 2k \sin \frac{1}{2}\theta$ . After making the substitution  $x = \sin \frac{1}{2}\theta$ , we insert the expressions for  $m_1(\boldsymbol{\kappa})$  and  $M(\boldsymbol{\kappa})$ , Eqs. (13) and (9'), and obtain for the resistivity change associated with the addition of  $N$  interstitial lattice atoms the value

$$\Delta\rho_1 = \frac{4z^2 e^2 m^* N}{3\pi \hbar^3 n^2} \int_0^1 x^3 dx \left[ \frac{-1}{a^2 + x^2} + \Delta_1 E \frac{(2kR_0)^2 f(2kR_0 x)}{(ze^2/R_0)} + \frac{4\pi A_1}{\Delta(a^2 + x^2)} \frac{\sin 2kr_0 x}{2kr_0 x} \right]^2. \quad (15)$$

The parameter  $a$  is defined as  $q/2k$  and is of the order unity for the monovalent metals. To obtain the resistivity change associated with the presence of vacancies, substitutional atoms, and interstitial impurity atoms, it is necessary to replace the square-bracketed quantity above by the expressions

$$\left[ \frac{1}{a^2 + x^2} + \Delta_2 E \frac{(2kR_0)^2 f(2kR_0 x)}{(ze^2/R_0)} + \frac{4\pi A_2}{\Delta(a^2 + x^2)} \frac{\sin 2kr_0 x}{2kr_0 x} \right]^2,$$

$$\left[ -\left(\frac{Z}{z} - 1\right) / (a^2 + x^2) + (E_z - E_z)(2kR_0)^2 \frac{f(2kR_0 x)}{(ze^2/R_0)} + \frac{4\pi A_3}{\Delta(a^2 + x^2)} \frac{\sin 2kr_0 x}{2kr_0 x} \right]^2,$$

$$\left[ -\frac{Z}{z(a^2 + x^2)} + \Delta_4 E \frac{(2kR_0)^2 f(2kR_0 x)}{(ze^2/R_0)} + \frac{4\pi A_4}{\Delta(a^2 + x^2)} \frac{\sin 2kr_0 x}{2kr_0 x} \right]^2,$$

respectively.

Before evaluating Eq. (15) let us investigate the magnitudes of the dimensionless parameters  $a^2$ ,  $2kR_0$ , and  $2kr_0$ . According to the Thomas-Fermi approximation,<sup>8</sup>  $q^2$  is equal to  $(4m^*e^2/\hbar^2)(3n/\pi)^{\frac{1}{3}}$ , so that  $a^2 = q^2/4k^2$  is

$m^*e^2/[\pi\hbar^2(3\pi^2n)^{\frac{1}{3}}]$ , where we have made use of the relation  $k^3 = 3\pi^2n$ . Evaluating  $a^2$  for copper with the use of specific heat data,<sup>9</sup> we set  $m^* = 1.47m_e$  and  $n = 0.85 \times 10^{23} \text{ cm}^{-3}$ , so that  $a^2$  becomes 0.65. Experimental resistance measurements indicate, however, that  $a^2$  is of the order 1.5 for the monovalent metals. Such a discrepancy is to be expected from the Thomas-Fermi approximation.<sup>2</sup>

We now recall that  $r_0$  is the inner cut-off radius for the contribution from the lattice distortions; thus  $r_0$  must be determined in any particular case from the sizes of the atoms and the cavities available to them, and from the elastic constants of the medium. However, in most cases of practical interest  $r_0$  will be of the order of  $R_0$ , the radius of the equivalent sphere for the lattice atoms. Using this value for  $r_0$  in the present qualitative discussion, we find  $2kr_0$  is equal to  $2(3\pi^2n)^{\frac{1}{3}}(3n_{\text{eff}}/4\pi n)^{\frac{1}{3}} = 3.84(n_{\text{eff}})^{\frac{1}{3}}$ , where  $n_{\text{eff}}$  is the effective number of free electrons per atom, or about unity for the monovalent metals.

Equation (15) and the corresponding expressions for the other types of singularities can easily be integrated numerically in any particular case, once the values of the parameters are known. Since we are at the moment primarily interested in the corrections to the resistivity due to the effects of the lattice distortions, let us perform the following approximate evaluation of Eq. (15) in order to compare the contribution from the lattice distortions with the largest contribution from the other sources. In most cases where the shielded Coulomb effect exists, it represents the largest contribution to the resistance; consequently we shall compare the distortion scattering with the shielded Coulomb scattering in all cases but that of the substitutional atom of valence  $Z=z$ . Thus the following Eqs. (16-1), (16-2), and (16-3) are not to be considered evaluations of the resistance, but rather as expressions to indicate the relative importance of the lattice distortions. Leaving out the term proportional to  $\Delta_1 E$ , an approximate evaluation of Eq. (15), valid only for  $4\pi A_1/\Delta$  less than unity, is found to be

$$\Delta\rho_1 = \frac{2z^2 e^2 m^* N}{3\pi \hbar^3 n^2} \left( \ln \frac{a^2 + 1}{a^2} - \frac{1}{a^2 + 1} \right) [1 - \eta(r_0) 4\pi A_1/\Delta]. \quad (16-1)$$

The first term in the square brackets arises from the shielded Coulomb potential of the interstitial lattice atom, and the second from the lattice distortions. The corresponding expressions for vacancies and interstitial foreign atoms are

$$\Delta\rho_2 = \rho_N [1 + \eta(r_0) 4\pi A_2/\Delta], \quad (16-2)$$

$$\Delta\rho_4 = \rho_N [(Z/z)^2 - (Z/z)\eta(r_0) 4\pi A_4/\Delta],$$

<sup>9</sup> F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. IV.

<sup>8</sup> Reference 2, p. 87.

respectively, where we have written  $\rho_N$  for the quantity

$$\rho_N = \frac{2z^2 e^2 m^{*2} N}{3\pi \hbar^3 n^2} \left( \ln \frac{a^2 + 1}{a^2} - \frac{1}{a^2 + 1} \right). \quad (17)$$

$\eta$  is unfortunately a rapidly varying function of  $r_0$ , being about 0.1 for  $2kr_0$  equal to 3.84, i.e., for  $r_0 = R_0$ , about 0.5 for  $r_0$  equal to  $4/5 R_0$ , and about  $-0.1$  for  $r_0 = 1.15R_0$ . Because of this rapid variation of  $\eta$  with  $r_0$ , it is necessary to attempt to fix the proper value for  $r_0$  from comparison with the summation in Eq. (9). It appears that for the vacancy or substitutional atom  $r_0$  should be chosen somewhat larger than  $R_0$ , so that  $\eta$  is in the range 0.1 to  $-0.2$ . For the interstitial atom  $r_0$  should be about  $R_0$ , so that  $\eta$  is of the order 0 to 0.2.

For the case of the substitutional atom of valence different from that of the lattice atoms the comparable resistivity change is

$$\Delta\rho_3 = \rho_N [(Z/z-1)^2 - (Z/z-1)\eta(r_0)4\pi A_3/\Delta]; \quad (16-3)$$

if the valences are the same, however,  $\Delta\rho_3'$  becomes

$$\Delta\rho_3' = \frac{2z^2 e^2 m^{*2} N}{3\pi \hbar^3 n^2} \left\{ \frac{2(E_Z - E_z)^2 (2kR_0)^4}{(ze^2/R_0)^2} \times \left[ \int_0^1 f^2(2kR_0 x) x^3 dx + 2 \frac{(ze^2/R_0)(4\pi A_3'/\Delta)}{(E_Z - E_z)(2kR_0)^2} \times \int_0^1 f(2kR_0 x) \frac{\sin 2kr_0 x}{2kr_0 x} \frac{x^3 dx}{a^2 + x^2} \right] \right\}, \quad (18)$$

on the assumption that the coefficient of the second integral is small in comparison with unity. The first integral has been evaluated numerically by Mott<sup>1</sup> for  $r_0$  equal to the radius of the equivalent sphere of the lattice atoms, i.e., for  $2kr_0$  equal to 3.84; he found the value of the first integral to be  $4.0 \times 10^{-3}$ . Using this same value for  $r_0$  and evaluating the second integral numerically also, we find that it is equal to  $3 \times 10^{-3}$  for  $a^2$  equal to 1.5. The above values for these integrals are typical of those for the monovalent metals; if  $a^2$  is larger than 1.5, the second integral is somewhat smaller than the value quoted [by approximately the ratio  $2/(a^2 + 0.5)$ ], and if  $r_0$  is larger than the radius of the equivalent sphere for the lattice atoms, the second integral, corresponding to the lattice distortions, is reduced in about the same way as is  $\eta$ .

Equation (18) becomes, on inserting the above numerical results for the integrals,

$$\Delta\rho_3' = \frac{2z^2 e^2 m^{*2} N}{3\pi \hbar^3 n^2} \left\{ \frac{1.74(E_Z - E_z)^2}{(ze^2/R_0)^2} \times \left[ 1 + \frac{0.10(4\pi A_3'/\Delta)(ze^2/R_0)}{(E_Z - E_z)} \right] \right\}. \quad (16-3')$$

From the Eqs. (16) we can now see the sign of the effects of the lattice distortions on the calculated re-

sistance. In the expressions for  $\Delta\rho_1$ ,  $\Delta\rho_2$ , and  $\Delta\rho_4$  the signs of the  $A$ 's are positive, negative, and positive, respectively; that is, the lattice is pushed out around an interstitial atom and relaxes around a vacancy. In these three cases, therefore [see Eqs. (16-1), (16-2), and (16-4)], the resistance is reduced by the inclusion of the effects of the lattice distortions, as long as  $\eta$  is positive. This conclusion is reasonable physically on the basis that in each case the relaxation of the lattice around the singularity tends to smooth out the perturbing potential. When  $\eta$  is negative, on the other hand, the scattering is increased by the distortion. This situation corresponds to a reinforcement of the scattered wave, even though the potential is of the opposite sign from the shielded Coulomb potential, because of the difference in phase of the electron wave in the regions where the two potentials are most effective.

In the calculation of  $\Delta\rho_3$  [see Eq. (16-3)], the lattice distortions may either reduce or increase the resistance. For example, if a relatively small, light atom of valence higher than that of the lattice atoms is in a substitutional position, the distortions will further increase the magnitude of the scattering potential near the singularity and thus increase the resistance (for  $\eta > 0$ ). Similarly, for  $\Delta\rho_3'$  [see Eq. (16-3')] the distortions may either increase or decrease the calculated resistance; the effect of a heavier atom of the same valence will be to expand the lattice, but the electronic energy difference depends on the details of the wave functions, and  $E_Z - E_z$  may be negative, as for Au in Cu, or positive, as for Ag in Cu. In addition to these effects the sign of  $\eta$  may result either in a reduction or increase in the calculated resistance as a result of the distortions.

We have now to discuss the magnitudes of the parameters  $A$ ; we shall first consider  $A_2$ , which characterizes the displacements around a vacancy. The relaxation around a vacancy has been estimated by Huntington and Seitz,<sup>10</sup> and by Huntington,<sup>11</sup> for the f.c.c. lattice of copper, and by Dienes<sup>12</sup> for copper and for the b.c.c. lattice of sodium. Huntington and Seitz<sup>10</sup> found that the nearest neighbors in Cu are displaced inward by an amount  $\sim 2 \times 10^{-2} \lambda$ , where  $\lambda$  is the nearest neighbor distance. Thus  $A_2$  is  $-2 \times 10^{-2} \lambda^3$ , and, since  $1/\Delta = \sqrt{2}/\lambda^3$  in a f.c.c. crystal,  $4\pi A_2/\Delta = -0.35$ . In the accompanying more accurate treatment Huntington<sup>11</sup> estimated the inward displacement in Cu to be less than or equal to about  $1 \times 10^{-2} \lambda$ , and Dienes calculated  $2 \times 10^{-2} \lambda$  for Cu and something less than this for the b.c.c. lattice of Na. For a displacement of  $\sim 2 \times 10^{-2} \lambda$  the correction to the resistance [see Eq. (16-2)] is of the order 5 percent.

It seems reasonable to assume, with regard to the estimates of the corrections to  $\Delta\rho_3$  and  $\Delta\rho_3'$ , that the inward displacements are somewhat less around any

<sup>10</sup> H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942).

<sup>11</sup> H. B. Huntington, Phys. Rev. **61**, 325 (1942).

<sup>12</sup> J. Dienes, AEC Report NAA-SR-144 (1951).

small substitutional impurity atom than they are around a vacancy. The relative correction to  $\Delta\rho_3$  for the substitution of a smaller atom is thus, less than or of the order,  $0.05/(-1+Z/z)$ . The magnitude of the relative correction to  $\Delta\rho_3'$  is  $\cong 0.02(z\epsilon^2/R_0)/(E_Z-E_z)$ . For  $E_Z-E_z \sim 2$  ev ( $E_Z-E_z \sim 2$  ev for the case of copper in gold<sup>2</sup>),  $z=1$ , and  $r_0=1.59\text{\AA}$  (for gold), the correction is about 0.1.

The remaining situations, those of interstitial atoms and of substitutional atoms which are larger than the lattice atoms they replace, are all associated with a distension of the lattice. We can immediately restrict ourselves further, in the case of interstitial impurity atoms, to those which are smaller than the lattice atoms, since larger ones will not go into solid solution in interstitial positions; in the event that a large impurity is knocked from a normal lattice site into an interstitial position in the course, say, of nuclear bombardment, the lattice will tend to rearrange itself to exchange the positions of the large interstitial impurity and of a lattice atom.

Let us consider on the basis of the theory of elasticity for a continuous isotropic medium the problem of a spherical cavity, initially of radius  $R_1$ , into which we forcibly insert a sphere of material, initially of radius  $R_2$ , too large for the cavity.<sup>13</sup> We may obtain two values for  $A$ , depending on the two sets of boundary conditions we may impose at the periphery of the cavity. If we assume that the sphere is compressible, with about the same elastic constants as those of the medium, we obtain

$$A_c = \frac{R_1^3(R_2-R_1)}{R_1+2R_2/[1+3\nu/(1-2\nu)]} \sim \frac{R_1^3(R_2-R_1)}{R_1+R_2/2}, \quad (19)$$

where  $\nu$  is Poisson's ratio. If we assume that the sphere is incompressible, on the other hand, we obtain

$$A_i = R_1^2(R_2-R_1). \quad (20)$$

In the case of the large, heavy substitutional atom the second boundary condition is probably the better, whereas for an interstitial lattice atom it is probably correct to consider the atom as being partially compressible. The two expressions (19) and (20) differ by about a factor of two for several of the interesting cases.

We shall associate with  $R_2$  the radius of the atom, that is, one half of the nearest neighbor spacing  $\lambda$  in a pure crystal of that material, not the radius of the equivalent sphere. Discussing first the case of the substitutional atom, we see that it is not clear what length should be used for the radius  $R_1$ .  $R_1$  cannot properly be taken to be the radius of the equivalent sphere for the displaced lattice atom, since such an assumption would allow no lattice distortion unless the impurity atom were at least 10 percent larger in diameter than the lattice atom it replaces. However, if we take  $R_1$  to be half the nearest neighbor separation of the

lattice, we are exaggerating the distortion inasmuch as we are not allowing the impurity atom to take advantage of the effectively larger radius of the cavity in directions other than directly toward the nearest neighbors. Nevertheless, we shall use  $\lambda/2$  as the cavity radius for an approximate evaluation of  $4\pi A_i/\Delta$  (thus exaggerating the distortion effects); we find for the f.c.c. lattice the value  $4\pi A_i/\Delta = 2.2(-1+\lambda'/\lambda)$ , and for the b.c.c. lattice  $4\pi A_i/\Delta = 2.0(-1+\lambda'/\lambda)$ . Thus [see Eq. (16-3)], the lattice distortions associated with the presence of a substitutional atom of 50 percent larger radius than that of the replaced atom would give rise to scattering of about 1/10 the magnitude of that from the shielded Coulomb potential from an atom of twice as high a valence as the lattice atoms. However, according to the Hume-Rothery rule, it is difficult experimentally to put an appreciable amount of impurity into a metal if the radius of the impurity atom is more than about 15 percent larger than that of the lattice atoms. For a divalent impurity in a monovalent lattice, consequently, the maximum correction to the shielded Coulomb scattering is of the order of or less than 5 percent. For a monovalent atom in a divalent lattice, though, the correction can become 10 percent, and for a divalent impurity in a trivalent lattice about 15 percent. These last corrections are too large to be ignored in careful interpretations of experimental results. Unfortunately, the separation of the effects of distortions is made difficult by the circumstance that as the impurity atom increases in size, thus increasing the effects of lattice distortions, so also increases the effects associated with the difference in the cores, about which relatively little is known theoretically; we have so far ignored these effects except for substitutional impurities of the same valence as the lattice atoms, but they are in fact sizable for atoms of much different atomic number, and furthermore are in some cases of opposite sign from those of lattice distortions. This point will be discussed further in the next section.

The distortion correction arising from a substitutional atom of the same valence as the lattice atoms likewise shows a dependence on the valence. For example, a gold atom has a radius 13 percent larger than that of a copper atom, and, according to the above model, i.e., Eq. (20), produces displacements in a copper lattice characterized by  $4\pi A_3'/\Delta = 0.28$ . Taking  $r_0(\text{Cu}) = 1.41 \times 10^{-8}$  cm and  $E_Z-E_z = -3$  ev,<sup>1</sup> we find [see Eq. (16-3')] that the resistance may be changed about 5 percent by the lattice distortions from the value calculated on the basis of the inner potential alone. Divalent atoms with these relative sizes and with the same value for  $E_Z-E_z$  would result in a correction of 10 percent.

For discussion of the displacements of the lattice surrounding an interstitial atom we could, if necessary, use Eq. (19) and attempt to fix the radius of the interstitial hole from geometric arguments; however, our result would be extremely dependent on our assumptions because of the smallness of the cavity in compari-

<sup>13</sup> N. F. Mott and F. R. N. Nabarro, Proc. Phys. Soc. (London) 52, 86 (1940).

son with the interstitial atom. Fortunately we need not rely on the elastic theory of a continuous medium for the solution of this atomic problem, since the displacements of the nearest atoms have been estimated on an atomistic basis. Huntington and Seitz<sup>10</sup> have found a displacement of about  $0.10 a/2$  for the face-centered atoms in Cu ( $a$ =cube edge length), and Dienes<sup>12</sup> calculated  $0.09 a/2$  in Cu, and  $0.30 a/2$  for the displacement of the nearest atoms, those in body-centered positions, in sodium, on the assumption that the center of the cavity is located in the center of one face of the unit cell. These displacements lead to values for  $A$  of  $0.1 (a/2)^3$  in Cu and  $0.3 (a/2)^3$  in Na, so that  $4\pi A_1/\Delta \sim 0.6$  in Cu and  $\sim 0.9$  in Na. Thus, the scattering from the lattice distortions around interstitial atoms is of the order  $1/10$  that from the shielded Coulomb potential for a divalent impurity in Cu or Na.

#### IV. DISCUSSION OF RESULTS

In reviewing the above calculations with the intent of examining their validity, we recall that we have assumed potentials of the form  $e \exp(-qr)/r$  for the various nuclei and their surrounding electrons (except for the substitutional atom of the same valence as the lattice atoms, in which case we added a square-well potential to take account of the difference in average potential throughout the atomic volume). Let us examine this assumption more closely to see what effect it has had on our results. We can be fairly confident of its approximate validity as applied to the evaluation of the Hamiltonian  $W(\mathbf{r})$  [Eq. (4)] and the matrix element  $M(\mathbf{k})$  [Eq. (9)], which are both related to the effects of the lattice distortions, since the primary effect of the small displacement of a lattice atom can be described in terms of the motion of its shielded nuclear charge alone.<sup>14</sup> That this is so can be understood from the fact that the density of the lattice outside the imperfection is unchanged, so that no change occurs in the average potential of the unit cell. Of course, if the volume of the inner core is not small as compared with that of the equivalent atomic sphere, the "effective nuclear charge" may be larger than  $e$  times the valence of the atom; we shall ignore this possible effect, temporarily, and shall consider the only serious error in our evaluation of  $M(\mathbf{k})$  to arise from our value of the shielding constant  $q$  as calculated from the Thomas-Fermi approximation. We may evaluate the shielding constant experimentally from the resistance change associated with the addition of small amounts of substitutional impurity atoms of adjacent atomic number, for which the effects of lattice distortions and different electronic energies should be small. In the following it will be assumed that this has been done, so that for every metal our shielded Coulomb potential is correct. Thus we expect the relative magnitudes of the distortion effects as calculated above to be qualitatively correct, namely, of the order of or

less than 10 percent; hence it is not possible to explain by these distortion effects the relatively large discrepancies between calculated and measured resistivities for solid solutions.

We have, however, introduced serious errors in our choices of potentials associated with the singularities themselves, whenever we have neglected the electronic energy difference,  $E_Z - E_z$ , throughout the region occupied by the singularity. That is, as pointed out earlier, Eqs. (16-1), (16-2), and (16-3) are not even approximately valid in absolute value. It is clear from the experimental data<sup>15</sup> that the effect of the  $\Delta E$  term is large, and in some cases, e.g., for the substitution of Ag in Au, as large as the shielded Coulomb scattering from an atom of one higher valence (see Table I.) Terms of the above type, i.e., the  $\Delta E$  terms, can easily be carried along in the scattering matrix elements, as was done up until the approximate evaluations of Eqs. (16). They have not been included in Eqs. (16) for the purpose of exhibiting explicitly the magnitude of the effects associated with lattice distortions.

In the remaining discussion we shall explicitly restrict ourselves to consideration of those metals to which the application of free-electron theory may be expected to be semiquantitatively correct, that is, to the alkali and noble metals. Let us now consider to what extent we are able to make quantitative predictions of resistance measurements. We have found that the lattice distortions around all the types of singularities treated give rise to corrections in the calculated resistance of the order of 5 or 10 percent. Experimentally we can measure the shielding constant  $q$  with much higher accuracy than we can calculate it, but it seems unlikely that even with adjacent metals in the periodic table we can eliminate all the effects but valence with an accuracy better than 5 or 10 percent. That is, even using experimentally determined values for  $q$  it is improbable that we can calculate resistances to within 10 percent, and it thus appears that distortion effects are of secondary importance.

It is interesting to note, however, that the lattice distortions play another role which in some cases is a very important one and may even lead to a difference of a factor of three or more in the calculated resistance. Consider, for example, the resistance associated with the additions of Cu to Ag. Mott<sup>1</sup> has estimated the term  $E_Z - E_z$  for Cu in Ag from Wigner-Seitz calculations of the energy of the lowest electronic state as a function of the radius of the equivalent sphere and has calculated, neglecting all distortion effects, a resistance about one third that observed experimentally. Mott assumed, for the equivalent sphere radius of the Cu atom, the normal radius of the equivalent sphere for a silver atom in a pure silver lattice and obtained an energy difference  $E_{Cu} - E_{Ag} = -0.5$  ev. Since the Cu atom is 13 percent smaller in radius than the Ag atom it replaces,

<sup>14</sup> J. Bardeen, Phys. Rev. **52**, 688 (1937), Table I; J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

<sup>15</sup> References to most of the pertinent data can be found in reference 2 and in E. Grüneisen, *Ergeb. exakt. Naturwiss.* **21**, 50 (1945).



we would expect some relaxation of the lattice, leading to an effective radius for the equivalent sphere for Cu somewhat smaller than that assumed by Mott. A displacement of the nearest neighbors equal to one fourth that calculated<sup>10-12</sup> around a vacancy, that is,  $5 \times 10^{-3} \lambda$ , would lead to a reduction of 3 percent for the radius of the equivalent sphere. Using this reduced radius, we find an energy difference  $-0.8$  ev from the Wigner-Seitz energy calculations, thus leading to agreement with experiment. The displacement of  $5 \times 10^{-3} \lambda$  was of course chosen *ad hoc*, but it is not an unreasonably large value, and the above example demonstrates how lattice distortions may have a large effect in cases where the energy curve for the impurity has a steep slope at the equivalent sphere radius of the lattice atoms, and where the energy difference is small. For Ag in Cu, on the other hand, the above effect is a small one, since the energy curve for Ag has a broad minimum between the sphere radii for Cu and Ag. When a shielded Coulomb term is present, as for a divalent impurity, the above effect likewise will be a relatively small one if the square well adds to the valence effect (as for Hg in Cu), since a square well of the order 2 ev deep is required to give rise to the resistance associated with a single charge, and the energy shifts according to the above mechanism can be only of the order of a few tenths of an ev. If the square well tends to cancel the valence term, as is the case, for example, with Cd in Cu, the above distortion effect could in principle be important, although in practice the writer does not know of an alloy for which it makes a significant contribution.

Throughout the foregoing discussion it has been assumed that the effective nuclear charge for all the monovalent metals is  $e$ . That this is a valid assumption for resistance calculations is indicated by the goodness of the agreement of Bardeen's calculations of resistance in the monovalent metals with the measured values, and in particular by the circumstance that his results for Au are no worse than for Cu although an effective nuclear charge of  $e$  was assumed for both metals. Another argument supporting this conclusion derives from measurements of the resistivity of solid solutions of the monovalent metals, such as Cu in Ag. If the effective nuclear charges of any of these metals were different from  $e$ , certainly gold would be expected to have one of the largest because of its large inner core, and conversely, copper would be expected to have the smallest (of the noble metals) because of its relatively small core; furthermore, one would expect to find a relatively large difference in their effective charges because of the large difference in their core sizes. Stating this again in a slightly different way, unless the effective charges are all close to  $e$ , it seems difficult to understand how they can all be equal. But the smallness of the experimental resistivities of dilute monovalent alloys and the close agreement<sup>1</sup> with experiment of most of these resistivities calculated with the square well potentials as described above show that the differences in the effective nuclear

TABLE I. Measured resistivity change (see reference 16) in micro-ohm cm of the metal  $z$  upon the addition of one atomic percent of the element  $Z$ .

$z$ in $z$	Au		Cu	
Percent of $Z$	Measured value	Ag Measured value	Measured value	Reduced value
Hg	0.41	0.79	1.00	1.13
Cd	0.64	0.38	0.21	0.24
Zn	0.96	0.62	0.34	0.38
Au	...	0.38	0.55	
Ag	0.38	...	0.14	
Cu	0.48	0.07	...	

charges must be small compared with  $e$ ; therefore, we conclude that they are all closely equal to  $e$ . A third argument in support of this conclusion is based on the measured resistivities of Cu, Ag, and Au containing divalent, trivalent, and tetravalent impurities.<sup>16</sup> These measurements show that the scattering from the impurities of valence  $Z$  is approximately proportional to  $(Z-1)^2$ . If the effective nuclear charge of Au were appreciably larger than that for Cu, for example, one would expect large discrepancies in this proportionality, and in particular, one would expect to find a negative slope in a plot of resistivity change in Au versus  $(Z-1)^2$  for the impurity series Cu, Zn, Ga, Ge. The consistency of these data with the interpretation on the basis of the valence effect is a strong indication that the effective nuclear charges for the noble metals are all very close to  $e$ .

The measurements of Linde<sup>16</sup> shown in Table I provide an excellent test for our understanding of the resistivities of dilute substitutional alloy; if these data can be interpreted on the basis of the electronic energy difference, the valence, and the distortion effects, one might hope to be able to compute in the same way the resistance change in a monovalent metal upon the introduction of vacancies and interstitials. The resistivity changes in Cu, Ag, and Au (in micro-ohm cm) upon the introduction of one atomic percent of monovalent or divalent impurities are shown in the first three columns. According to Eqs. (16-3) and (17) the resistivity change is approximately proportional to  $n^{-\frac{1}{2}}$ , as may be seen by expanding the logarithm in Eq. (17). Thus in the fourth column we have multiplied the value for Cu by the ratio of the atomic radii for Ag and Au to that for Cu, in order to make the values for Cu directly comparable with those for Ag and Au. The most striking feature to notice is that for the addition of those elements for which we expect only valence effects to be important, i.e., for Hg in Au, Cd in Ag, and Zn in Cu, the resistivity changes are indeed very similar, 0.41, 0.38, and  $0.38 \mu\Omega$  cm, respectively. This result indicates that the dependence of the Thomas-Fermi shielding constant  $q$  on density is correct, and also indicates that such effects as the association of vacancies with the

<sup>16</sup> J. O. Linde, Ann. Physik (5) 15, 239 (1932).



divalent impurity atoms are unimportant for an interpretation of these data.

Most of these data for Cu, Ag, Au in Cu, Ag, and Au can be interpreted on the basis of the square well potential, as Mott has shown.<sup>1</sup> It should be pointed out, however, that the resistivity changes of Cu in Au and of Ag in Au are not consistent with the square well potential. That is, if the electronic energy for Cu is 0.8 eV lower than that for Ag, as indicated by the Wigner-Seitz calculations and by the measured resistivity change for Cu in Ag, then the height of the square well for Cu in Au should be 0.8 eV less than for Ag in Au (1.9 eV as measured by resistivity change), or should be 1.1 eV instead of the measured 2.1 eV; stating this again in a slightly different way, accepting the measured resistivities for Cu in Ag and for Ag in Au, we would predict a resistivity change of  $0.126 \mu\Omega \text{ cm}$  rather than the observed change of  $0.485 \mu\Omega \text{ cm}$  for Cu in Au. Distortion effects cannot significantly improve this discrepancy, nor is it possible to construct a reasonable, internally consistent set of effective nuclear charges and square wells that will explain all of these results, even if we wished to change the effective nuclear charges. Thus it appears that the details of the wave functions and potentials are important for interpreting some of these resistance data.

Similarly the data for Hg, Cd, and Zn in Cu, Ag, and Au cannot be satisfactorily understood on the basis of valence, square well, and distortion effects. For example, one can explain Zn in Ag giving rise to a larger resistivity change than Zn in Cu, but one cannot explain the even larger change for Zn in Au; the result for Cd in Cu is understandable, but not that for Cd in Au. Again it is not possible to interpret all of the data in a reasonable way by assigning different effective nuclear charges to the various atoms.

Our conclusions from all of the above arguments are that the valence and effective nuclear charge effects alone are fairly well understood, and that the rough approximation of a square-well potential is not sufficient to account for the specific potentials and wave functions in most of these simple systems. Consequently, we do not believe that it is reasonable to expect to be able to compute the scattering from vacancies and interstitials on the same approximations. Nevertheless, since the valence effect does seem to be constant from one metal to the next and since there is relatively little spread in the measured resistivity changes for divalent impurities, it seems safe to choose a value in this range for the addition of vacancies and interstitials to the lattice. The writer's estimate of the resistivity change in Cu, Ag, and Au per atomic percent of imperfection is  $\sim 0.4 \mu\Omega \text{ cm}$  for vacancies and  $\sim 0.6 \mu\Omega \text{ cm}$  for interstitials. These values are probably good to within a factor of two.

To make more precise statements than the above concerning the scattering from interstitials and vacancies seems a formidable problem involving a self-

consistent calculation for the potential and displacements near the singularity, a calculation in which modifications to the  $d$  shell probably are important. Until better approximations are likewise made for the electronic wave functions and for the solution of the Boltzmann transport equation and until more is known about the "effective number of free electrons per atom" and the electronic effective mass, it is questionable if such a calculation is warranted.

We have now to discuss the previously neglected effects arising from the uniform dilation of the lattice. In Sec. II we assumed displacements of the form  $\mathbf{U} = A\mathbf{r}/r^3$  instead of the general form  $A\mathbf{r}/r^3 + B\mathbf{r}$ . The second term is responsible for a uniform density change throughout the metal, and will lead to a change in resistivity just as does the application of a hydrostatic pressure. The latter effect can be qualitatively accounted for<sup>17</sup> in most cases on the basis of the change in amplitudes of the lattice vibrations associated with the strengthened atomic forces in the compressed metal. Thus the density change gives rise to a temperature dependent resistance change which should not be treated on the same basis as the changes in the residual resistance discussed above. At constant temperature, however, the change in the measured resistivity of a sample after the introduction of point singularities will depend not only on the factors discussed in Secs. II-IV, but also on the density change of the material associated with the parameter  $B$ . Furthermore, in an interpretation of experimental resistance measurements, it must be borne in mind that the dimensions of the sample also change, both because of the  $B$  term and also the  $A$  term, and thus the resistivity of the material would have changed even if the measured resistance remained constant. The correction to the resistivity because of this last effect is in all cases small compared with those previously discussed.

We may obtain an estimate of the magnitude of the density change effect from the following considerations. Suppose that a metallic sphere, initially of radius  $R$ , has introduced into it a number  $N$  identical singularities. Then the density  $D$  is changed by an amount

$$\delta D \cong -DN \nabla \cdot \mathbf{U} = -3BDN, \quad (21)$$

where  $B$  is given by  $2A(1-2\nu)/R^3(1+\nu)$ . Now the change in resistivity  $\delta\rho$  is given by

$$\begin{aligned} \frac{\delta\rho}{\rho} &= \frac{d(\log\rho)}{d(\log D)} \frac{\delta D}{D} \\ &= -\frac{d(\log\rho)}{d(\log D)} \frac{2N\Delta}{\Omega} \left( \frac{1-2\nu}{1+\nu} \right) \left( \frac{4\pi A}{\Delta} \right), \quad (22) \end{aligned}$$

or about  $(3/2)(4\pi A/\Delta)f$ , where  $f$  is the number of singularities per lattice atom, and where we have made use of the observed<sup>17</sup> resistivity dependence on density,

<sup>17</sup> See, for example, reference 2, p. 271.

namely,  $d(\log\rho)/d(\log D) \sim -3$  for most metals. Since we found above that  $4\pi A/\Delta$  is of the order of or less than  $2/3$ , the fractional resistivity change associated with the change in density is of the order of or less than one percent in the presence of one percent singularities. This change is small ( $\sim 1/10$ ) compared with the residual resistance change arising from the shielded Coulomb term or the electronic energy difference term discussed above, and of about the same magnitude as that associated with the lattice distortions, i.e., the  $A$  term.

In conclusion, mention should be made of the implications of the foregoing to studies of densities of imperfections in metals. For example, in Seitz's<sup>18</sup> discussion of the generation of vacancies by moving dislocations, he used a scattering cross section of vacancies for electrons 25 times larger than the estimate given above and obtained a very conservative value for the density of vacancies in Cu at liquid air temperatures. His estimate was based on the measured<sup>19</sup> resistivity change in Cu after straining by about 10 percent at liquid air temperatures, namely,  $0.019 \mu\Omega \text{ cm}$ , and on the assumption that all or most of the resistivity change is associated with the presence of vacancies. His result for the concentration of vacancies under these conditions of  $1.6 \times 10^{18} \text{ cm}^{-3}$  would become, if the present estimate for the vacancy cross section is correct, equal to  $4 \times 10^{19} \text{ cm}^{-3}$ . Since the energy required to create a vacancy is about 1 eV, this concentration of vacancies represents a storage of about  $4 \times 10^{19} \text{ eV/cm}^3$  and since the energy expended in straining the lattice by 10 percent is  $7.5 \times 10^{19} \text{ eV/cm}^3$ , these arguments would suggest that at least half of the energy of cold work is stored at liquid air temperatures.<sup>20</sup>

It is of interest to inquire if the low temperature data are consistent with the hypothesis that dislocations are predominantly responsible for the resistivity change in Cu. If the resistivity change per line cm of edge-type dislocation<sup>7</sup> is  $1.7 \times 10^{-14} \mu\Omega \text{ cm}$  and the energy stored<sup>21</sup> per cm is  $1.6 \times 10^8 \text{ eV}$ , the resistivity change per unit stored energy is  $1.06 \times 10^{-22} \mu\Omega \text{ cm per eV}$ . This value is to be compared with  $4.7 \times 10^{-22} \mu\Omega \text{ cm per eV}$  for vacancies. That is, for a given amount of stored energy, vacancies have about 4 times as large an effect on the

resistivity as do edge-type dislocations. Thus even if all the energy expended in cold work at low temperatures were stored in the form of dislocations, the resistivity change would be only about half of that observed. A similar result is found for the room temperature data, namely, that it does not seem possible to explain all of the observed resistivity change associated with cold-working on the basis of scattering from dislocations alone.<sup>7</sup> If many vacancies are produced by moving dislocations, as suggested by Seitz,<sup>18</sup> it seems possible that at room temperatures they are able to clump together into cavities of the type recently proposed by Blin and Guinier<sup>22</sup> as a result of small-angle x-ray scattering experiments, and that an interpretation of room temperature data on cold-worked specimens also may be based on vacancy effects.

## V. SUMMARY

We have estimated the contributions to the electrical resistance arising from distortions of the lattice around vacancies, interstitials, and substitutional impurity atoms, and have shown that the scattering associated with distortion of the lattice outside of the imperfection itself leads to a correction sufficiently small, of the order 5 or 10 percent, to be neglected in all practical calculations capable of being performed at present. The reasons for the smallness of the correction are: (1) the smallness of  $4\pi A/\Delta$ , that is, the smallness of the distortion, and (2) the smallness of  $\eta$  because of the effective cancellation of the scattered wave associated with the rapid variation of its phase in the regions where the distortion is sizeable. We conclude that accurate interpretations of resistance measurements cannot be expected on the basis of the effects discussed by Mott for substitutional impurities, i.e., the valence and the energy difference effects, and that in many cases a difficult self-consistent calculation is required for both the displacements and potential near the singularity. The resistivity change in Au, Ag, and Cu associated with one atomic percent of vacancy-interstitial pairs is estimated to be about 1 micro-ohm cm. A brief discussion of deviations from Matthiessen's rule shows that such effects are small ( $\approx 1/10$ ) compared with valence effects.

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<sup>18</sup> F. Seitz, *Phil. Mag. Supplement* **1**, 43 (1952).

<sup>19</sup> J. Molenaar and W. H. Aarts, *Nature* **166**, 690 (1950).

<sup>20</sup> Energy storage measurements by G. I. Taylor and H. Quinney [*Proc. Roy. Soc. (London)* **143**, 307 (1934); **163**, 157 (1937)]; B. Welber [*Phys. Rev.* **87**, 211 (1952)]; and H. Kanzaki [*J. Phys. Soc. Japan* **6**, 456 (1951)] indicate that the energy stored during cold-working at room temperature is only about 3 percent of the expended energy, thus suggesting considerable annealing below room temperature, in agreement with the experiments of Molenaar and Aarts (see reference 19), Koehler (see reference 4) and others.

<sup>21</sup> J. S. Koehler, *Phys. Rev.* **60**, 397 (1941).

<sup>22</sup> J. Blin and A. Guinier, *Compt. rend.* **233**, 1288 (1951).