

the combination energies less than straightforward. With this low dispersion it is perhaps conceivable that the 45.8×10^{-3} -ev and 74.4×10^{-3} -ev peaks could be ascribed to $TO [111] + TO [100]$ and $2TO$ combinations, respectively.

CONCLUSIONS

It is clear that the technique of double differentiation of the current-voltage characteristics of Esaki junctions resolves considerably more structure than can be observed even in conductance plots. In the present paper attention has been focused on multiphonon tunneling process in silicon and germanium junctions. In silicon in particular, the double differentiation has revealed several new multiphonon-tunneling processes all of which can be fitted into a very simple and satisfying assignment scheme. This scheme involves the

transverse acoustic and optical phonons in combinations with intervalley scattering phonons, or in combinations with one or more zone-center optical phonons.

Only three multiphonon combinations have been resolved in germanium junctions and these do not seem to have such a simple assignment as is possible in silicon.

Further work, both theoretical and experimental, will be required before the origin of the peak in the conductance at zero bias is understood.

ACKNOWLEDGMENTS

The authors wish to thank W. L. Feldmann for making all the junctions used in this work, and J. F. Gilbert and J. M. Klein for technical assistance. They are also indebted to Dr. P. A. Wolff and Dr. E. O. Kane for much helpful advice, particularly concerning the assignments of the phonon energies.

Vacancies and Complexes in the Noble Metals*

C. P. FLYNN

Department of Physics, University of Illinois, Urbana, Illinois

(Received August 28, 1961)

In part I, the changes in resistivity of a noble metal on the introduction of vacancies into the lattice are calculated, taking into account the relaxation of the lattice around the defect site. The agreement between calculated and experimental resistivities is satisfactory for a particular model of the scattering power of the vacancy. Using this same model, it is then shown how the calculations of Fumi and Brooks concerning vacancy formation energies can be modified in the light of known surface energy data to yield quite reasonable predictions of formation energies of relaxed vacancies in noble metal lattices. The agreement between calculated and experimental resistivity data implies that the phase shift of electron waves at the Fermi surface are accurate and this in turn permits the prediction of the electron density in the neighborhood of the vacancy. In part II, this electron density is used in a treatment of the interaction energy between vacancies and substitutional impurities in the noble metals. The binding energies deduced in this way from scattering theory exhibit a

strong dependence on the valence of the solute atom and are invariably positive for positive valence solutes at nearest neighboring lattice sites to a vacancy. The computed binding energies are quantitatively compatible with the available experimental data.

The long-range characteristics of interaction between vacancies and both point and extended defects are also investigated in part II. Particular attention is drawn (a) to the oscillatory nature of the interaction as a function of the separation of the defects, and (b) to the different dependence on this separation for interactions concerning the different types of defect. Thus, in every case, the interaction energy oscillates with period k_F/π , k_F being the Fermi energy, while the decay of amplitude with separation takes the form r^{-3} , $r^{-\frac{5}{2}}$, or r^{-2} contingent upon the vacancy interacting with a second point defect, a dislocation, or a crystal boundary, respectively.

Part I: Vacancies in the Noble Metals

I. INTRODUCTION

EXPERIMENTS performed on silver and gold have revealed that defects, trapped in the lattice by quenching, produce changes in the volume, electrical resistivity, and the energy stored in the lattice. The interpretation of these facts is that vacancies, together with a much smaller number of divacancies, cause the observed effects.

In gold, it has been shown that the increase in volume of the lattice is proportional to the increase in

resistivity,¹ with the constant $K = \partial R / \partial V = 340 \pm 50$ $\mu\text{ohm cm.}^2$ Here V is the lattice volume and R the resistivity. By means of resistivity, x-ray, and microcalorimetric techniques, the energy increase of the lattice on formation of a vacancy has been found to be about 0.97 ev in gold,^{1,3} and 1.10 ev in silver.^{4,5} No

¹ J. E. Bauerle and J. S. Koehler, *Phys. Rev.* **107**, 1493 (1957).

² The author is indebted to Professor J. S. Koehler for providing this value of K as the best interpretation of the experimental evidence.

³ W. DeSorbo, *Phys. Rev.* **117**, 444 (1960).

⁴ M. Doyama and J. S. Koehler, *Phys. Rev.* **119**, 939 (1960).

⁵ R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **119**, 600 (1960).

* This work has been supported by the U. S. Atomic Energy Commission.

reliable data have, as yet, become available for copper, owing to the difficulty of keeping the samples pure while quenching, but it appears unlikely that the formation energy is greatly different from that in the other two noble metals. The thermal measurements also permit a determination of the volume change in the lattice on introducing vacancies. The value found in gold is $(0.57 \pm 0.05)\Omega$, with Ω the atomic volume. Thus a significant degree of relaxation exists in the lattice around a vacancy; this fact must be taken into consideration when attempting to predict the properties of vacancies from other data.

The formation energy of vacancies in copper has been treated in considerable detail by studying separately the various contributions due to electron rearrangement and to the interatomic forces.⁶⁻⁸ Not unexpectedly, the total energy change is found as the sum of many terms of differing signs such that a considerable uncertainty exists in the resulting prediction. The lattice relaxation was not accounted for in this treatment, and further, similar calculations are not possible for silver and gold, owing to the unknown nature of the closed shell repulsive energies.

Two other significant calculations of vacancy energies have been made, due respectively to Brooks,⁸ and to Fumi.⁹ These are essentially less complicated treatments not involving separate calculations of each contribution but rather, in the case of Brooks argument, using the properties of the bulk materials in order to take automatic account of many of the cancelling terms found in the previous calculation. Although, superficially, the calculations of Fumi and Brooks appear different in type, and lead to values of the formation energy differing by a factor 3, they are, in fact, linked by the idea of the surface energy of an electron gas around a repulsive potential barrier. It is our objective in the following sections to show how deficiencies in the two approaches can be corrected, and show that the resulting model of vacancies in the noble metals leads to surprisingly accurate predictions of formation energies of vacancies, and of the relaxation and resistivity changes.

II. RESISTIVITY

The presence of a vacancy in a metal lattice results in a decrease of positive charge in the neighborhood of the defect, and in order that the region may preserve the long-range electrical neutrality of the bulk metal, the vacancy then acts as a scattering center. In this way, conduction electrons are rejected from the vacancy location and the defect is screened from the rest of the lattice. To assist in finding a suitable representation of the scattering potential, it is useful to

consider first the electrical resistivity due to vacancies since this gives a direct measure of the phase shifts of electron waves at the Fermi surface. It is readily shown that these same phase shifts also determine the asymptotic form of the electron density disturbance outside the vacancy.

Eshelby¹⁰ has investigated the change in volume of an elastic medium when small sources of dilatation are introduced. His conclusions as applied to the formation of a vacancy are as follows. An ion is removed from the inside of the lattice and placed on the surface, resulting in an increase in the lattice volume of one atomic volume Ω . The lattice around the vacant site then relaxes until the equilibrium volume $\Delta V'$ of the void is reached, at which stage the volume change of the lattice given by linear elastic theory is

$$\Delta V' = \Omega[1 - \gamma(1 - \Delta V'/\Omega)], \quad (1)$$

where

$$\gamma = 3(1 - \sigma)/(1 + \sigma); \quad (2)$$

σ being Poisson's ratio for the lattice.

As stated above, from the point of view of electron scattering, a vacancy represents a localized decrease in the density of positive charge in the lattice. In a monovalent metal, the average positive background charge in an atomic cell is unity, and it follows, at least on a completely free electron picture, that in order for a vacancy of volume ΔV to be electrically screened, $\Delta V/\Omega$ electrons must be displaced from that neighborhood of the lattice.

According to Friedel,¹¹ the charge displaced from a region of an electron gas containing a scattering center may be written down in terms of the phase shifts, $\eta_l(k_F)$ of electrons in l -wave states at the Fermi surface of the gas. Thus for a charge displacement of $-\Delta V/\Omega$, one has

$$-\Delta V/\Omega = (2/\pi) \sum_{l=0}^{\infty} (2l+1) \eta_l(k_F). \quad (3)$$

Moreover, the resistivity change of a metal on introducing scattering centers may also be calculated in terms of these phase shifts. Following Asdente and Friedel¹² who have considered the resistivity due to multiple vacancies without taking account of relaxation effects, one may now use the relation

$$\Delta R = \alpha \sum_{l=0}^{\infty} (l+1) \sin^2[\eta_l(k_F) - \eta_{l-1}(k_F)], \quad (4)$$

to find the increase in resistivity of a bulk sample in terms of the numbers of scattering centers and the phase shifts due to one scatterer. In Eq. (4) α is a numerical constant which has been given by Blatt¹³

⁶ H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942).

⁷ H. B. Huntington, Phys. Rev. **61**, 325 (1942).

⁸ H. Brooks, *Impurities and Imperfections* (American Society for Metals, Cleveland, Ohio, 1955).

⁹ F. C. Fumi, Phil. Mag. **46**, 1007 (1955).

¹⁰ J. D. Eshelby, J. Appl. Phys. **25**, 255 (1954).

¹¹ J. Friedel, Phil. Mag. **43**, 152 (1952).

¹² M. Asdente and J. Friedel, J. Phys. Chem. Solids **11**, 115 (1959).

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

for an atomic percent of scattering centers in each of the noble metals.

It is now possible to combine Eqs. (1), (3), and (4) and to write down our expression for K in terms of the phase shifts and the Poisson ratio of the lattice:

$$K = V \frac{\partial R}{\partial V} = \alpha \sum_{l=0}^{\infty} (l+1) \sin^2[\eta_l(k_F) - \eta_{l+1}(k_F)] \\ \times \{1 - \gamma[1 - (2/\pi) \sum_{l=0}^{\infty} (2l+1)\eta_l(k_F)]\}^{-1}. \quad (5)$$

While Eq. (5) incorporates the effect of vacancy relaxation on scattering by the core of the vacancy, no direct account has been taken of scattering in the strained lattice outside the vacancy, nor of the effects of possible anharmonic relaxation of the lattice. However, it is easily seen that the effects of anharmonic relaxation may be considered to be included, since the phase shifts used in both Eqs. (3) and (4) can be those resulting from the whole of the region of nonlinear relaxation including the vacancy core, outside which region Eshelby's analysis may be presumed to be correct. Further, the harmonic strain is equivalent to a pure shear superimposed on a bulk compression. Since the shear produces no volume change and therefore little scattering potential, while the compression results only in a negligible increase in the electron wave vector, k , no appreciable resistivity change may be attributed to the lattice strain when using a totally free electron model. When taking into account a realistic lattice potential, some additional scattering may be anticipated owing to the lowered symmetry of the lattice. Several calculations of the magnitude of this type of scattering are available, and while widely different answers have been achieved, the consensus of results appears to indicate that this scattering will be small compared with that caused by the core of the vacancy.^{14,15}

In evaluating K from Eq. (5) one must know the form of the scattering potential in order to find the resulting phase shifts. Since computations involving complex potentials are extremely tedious, it is fortunate that, as has been noted by several workers, results derived from the use of different scattering potentials are remarkably insensitive to the detailed structure of the individual potentials, provided that the comparison is between wells which satisfy the same Friedel sum, i.e., that displace the same amount of charge from the neighborhood of the scatterer.

The most frequently used representation of a defect scattering potential is the square isotropic well adjusted in depth and width to satisfy the Friedel sum. This is the result of the fact that the phase shifts may be derived exactly for the square well potential. From the continuous range of different square well available, one

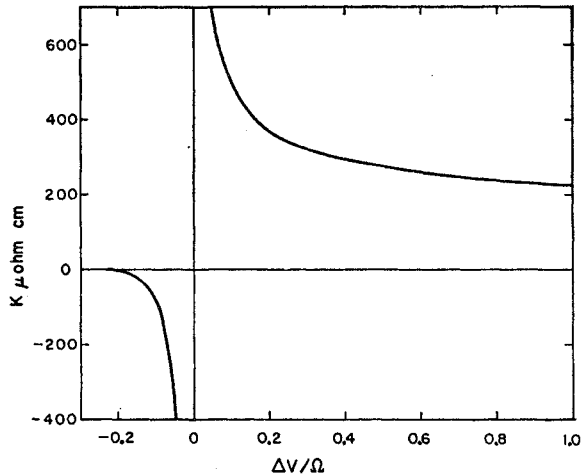


FIG. 1. Values of $K = V(\partial R/\partial V)$ plotted against the crystal volume change ΔV for the case of gold.

chooses by virtue of physical plausibility the most suitable for representing the scattering effect.

In the case of unrelaxed vacancies, the true scattering potential is just the negative of the effective potential due to the presence of the cell which is removed to form the defect. This is altered by the relaxation, but it may nevertheless be observed that the scattering potential is only large with respect to the Fermi energy in that part of the cell where the ionic potential was large; i.e., close to the center of the cell. This suggests that the potential chosen should be rather concentrated at the core of the defect, which is also convenient since the phase shifts then tend to the particularly simple form,

$$\eta_l(k) = \tan^{-1}[j_l(ka)/n_l(ka)], \quad (6)$$

where a is the radius of the region of large potential, and $j_l(ka)$ and $n_l(ka)$ are spherical Bessel and Neuman functions of order l . Using this potential, a may be varied in order to satisfy any desired Friedel sum.

On substituting the phase shifts given by Eq. (5) for various values of a into the expression (4) for k , one obtains the values of K corresponding to different degrees of relaxation of the vacancy. Figure 1 shows these values for gold, K being plotted against ΔV , the volume change of the whole crystal. At the experimentally observed volume change of $\Delta V = 0.57\Omega$, the value found for K is about 270 $\mu\text{ohm cm}$; which is in good agreement with the experimental value of $340 \pm 50 \mu\text{ohm cm}$. Thus only $70 \pm 50 \mu\text{ohm cm}$ of the resistivity change is to be explained by the scattering in the distorted lattice outside the vacancy core. The curves found in the cases of copper and silver are very similar to that for gold, and if, in the absence of further information, one assumes that the relaxation of the lattice round a vacancy is identical with that observed in gold, then the values of K predicted are within 30 $\mu\text{ohm cm}$ of the value obtained for gold.

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

¹⁵ N. H. March and P. M. Lee, Phys. Rev. **118**, 138 (1960).

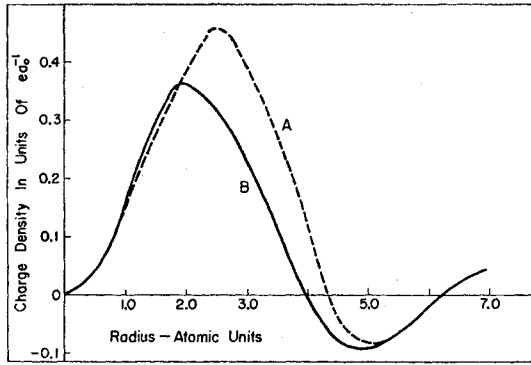


FIG. 2. The radial charge deficit round a vacancy in copper. (A) Hartree-Fock for zero relaxation (Huntington, reference 6). (B) Present treatment for the relaxation observed in gold.

Asdente and Friedel¹² have shown that the resistivity change is reduced if the scattering potential is made more diffuse, the reason lying in the increased ratio of *p*-wave to *s*-wave scattering. Since any such modification impairs the agreement between theoretical and experimental resistivities the choice of scattering potential is confirmed within the limitations of the square-well approximation.

It is important to note that the phase shifts at the Fermi surface are also dominant in determining the form of the electron density disturbance in the lattice surrounding the defect. Daniel¹⁶ has given the expression

$$\Delta\rho(kr)/\rho = \sum_{l=0}^{\infty} (2l+1) \{ [n_l^2(kr) - j_l^2(kr)] \sin^2\eta_l(k) - n_l(kr)j_l(kr) \sin 2\eta_l(k) \}, \quad (7)$$

for the disturbance $\Delta\rho(k, r)$ of the uniform density ρ of an isotropic distribution of plane waves of wave vector k , impinging on an isotropic scattering potential which produces the phase shifts $\eta_l(k)$. On substituting the asymptotic form of the Bessel functions in Eq. (7) he found also the long-range density disturbance in the form

$$\Delta\rho(kr)/\rho = (kr)^{-2} \sum_{l=0}^{\infty} (-1)^l (2l+1) \sin\eta_l(k) \times \sin[2kr + \eta_l(k)]. \quad (8)$$

This expression has been integrated by parts over the available states in k space up to the Fermi limit to yield the asymptotic form of the total density disturbance^{17,18}:

$$\Delta\rho(r)/\rho = (3/2k_F^3 r^3) \sum_{l=0}^{\infty} (-1)^l (2l+1) \sin\eta_l(k_F) \times \sin[2k_F r + \eta_l(k)]. \quad (9)$$

¹⁶ E. Daniel, J. phys. radium **20**, 769 (1959).

¹⁷ W. Kohn and S. H. Vosko, Phys. Rev. **119**, 912 (1960).

¹⁸ A. Blandin and J. Friedel, J. phys. radium **21**, 689 (1960).

It will be observed that this expression depends only on the phase shifts at the Fermi surface, in agreement with the statement to this effect made earlier.

The phase shifts given by Eq. (6) converge very rapidly with increasing order so that only $\eta_0(k)$ and $\eta_1(k)$ are really significant. At the observed relaxation, for example, the phase shifts for $l=0, 1$, and 2 at the Fermi surface take values of $0.74, 0.10$, and 0.005 , respectively. Thus two relationships, Eqs. (3) and (5) have been made to agree with experimental data and since each is determined by the phase shifts at the Fermi surface, it follows that $\eta_0(k_F)$ and $\eta_1(k_F)$ are quite good. By virtue of the fact that the disturbance on the electron density may be thrown into the form (9), it follows that the density predicted by means of Eq. (7) with the phase shifts (6) may be treated with some confidence.

The resulting charge density in the neighborhood of a vacancy has been computed for copper, with the degree of vacancy relaxation taken as that observed in gold. These data are exhibited in Fig. 2, together with the charge density for an unrelaxed vacancy found by Huntington from a Hartree-Fock approach. It will be seen that the two computations agree remarkably well at long and very short range, and that in the case of the relaxed vacancy, the principal difference lies in the rejection of less charge from radii α in the region such that $k_F \alpha \approx 2.0$. This is a consequence of the demand of long-range electrical neutrality of the metal. A point of particular importance is that each of the curves shows the oscillatory nature of the density outside the defect site, and unambiguously predicts an increase of negative charge in the lattice in the region occupied by the nearest neighboring ions to the defect. This characteristic will be shown in part II of this paper to be one of the contributing factors to the positive binding energy between vacancies and positive valence solutes in the noble metal lattices.

III. SURFACE ENERGY IN THE NOBLE METALS

Stratton¹⁹ has calculated that part of the surface energy of monovalent metals which is due to the modification of conduction electron energy by the presence of the free surface. The largest contribution is found to be that due to the acceleration of electrons to higher k values by the presence of the potential barriers at the metallic boundary. Other significant contributions are attributed to the electrostatic energy of the dipole layer at the surface, and to the surface free energy of the lattice vibrations. Stratton also found an oscillatory disturbance with asymptotic form,

$$\Delta\rho(z)/\rho = (3/4k_F^2 z^2) \cos 2k_F z, \quad (10)$$

superimposed on the uniform electron density ρ of the interior lattice. In Eq. (10), z is the distance from the

¹⁹ R. Stratton, Phil. Mag. **44**, 1236 (1953).

TABLE I. The surface energy of various liquid metals. References to the sources of experimental and theoretical energies are given in the text.

		Li	Na	K	Cu	Ag	Au	Fe	Ni
Surface energy (erg cm ⁻²)	Expt	398	191	101	1085	785	754	1384	1756
	Theory	400	190	70	740	450	450

boundary to the point at which the density is considered.

Data published after Stratton's work have shown that in the alkali metals, the theory gives excellent agreement with experimentally determined surface energies of liquids.²⁰ Thus, for lithium and sodium agreement is apparently within one percent, although an inadequately explained deficit of about 30% is evident in the case of potassium.

The situation is quite different in the case of the noble metals. Measurements made since the theory was developed have confirmed Stratton's statement that the free electron theory underestimates the actual surface energies by a factor of about $\frac{3}{2}$.²¹ This fact is all the more surprising since one would anticipate that the freedom from closed-shell repulsive energies over the free surface would result in the measurement of surface energies smaller than those predicted from consideration of the conduction electrons only. This discrepancy has been dismissed as due to the failure of free electron theory in the noble metals.

A more likely interpretation of the surface energy data is suggested by Table I, where the measured energies of several liquid metals are shown, together with the theoretical value for the solid at the melting point where available. One observes that the transition metals, iron and nickel, show very large surface energies, as indeed do other metals having unfilled inner shells. The implication that electrons in the d band give rise to surface energy is clear. Moreover, this cannot be considered in any way surprising, for the fact that the d -shell wave functions are sufficiently extended to overlap in the bulk metal indicates that they will also interact with the change in lattice potential at the boundary of the metal. Similarly in the case of the noble metals, a contribution to the surface energy via this mechanism must be anticipated for although the d band is filled, the d shells overlap sufficiently to maintain a bandwidth of about 3 ev. By noting that the interaction between the d band and the potential change in the boundary layer must be repulsive because of the sign of the deviation from the normal lattice potential, one is led to a simple interpretation of the excess surface energy in the noble metals. The experimental data may be taken as an indication that the d shells experience an interaction with the surface potential which is greater than the interaction between

neighboring d shells in the bulk metal, with the consequence that the surface energy is increased, rather than decreased as would be anticipated from considering only the freedom from the interaction between d shells over the free surface. In the case of the alkali metals, the d shell is, of course, empty, and no further contribution to the surface energy occurs.

IV. THE FORMATION ENERGY OF VACANCIES

The computation of the energy of formation of vacancies in copper from detailed consideration of conduction electron rearrangement and closed-shell repulsive energies has been performed and modified successively by Huntington and Seitz,⁶ Huntington,⁷ and Brooks.⁸ At the outset it must be stated that in principle, this is the only good approach to the calculation of formation energies. In practice, however, the addition of the many terms of differing sign which contribute to the formation energy, results in the presence of considerable uncertainty in the final prediction. It is therefore worthwhile to consider simplified treatments in order to obtain a manageable method of predicting the properties of vacancies with reasonable labor and precision.

Brooks has investigated the formation energy in terms of macroscopic ideas, hence eliminating many of the terms of opposing sign evident in the more refined calculation, and also making the treatment easily applicable to all metals. Thus the bulk surface energy and elastic constants are manipulated to find the energy change of the lattice when a hole of atomic dimensions is formed and allowed to relax to its equilibrium configuration. The formation energies found by this treatment are too large by a factor of about two.

A second simplified approach, at first sight apparently unrelated to that of Brooks, was devised by Fumi. In this work the electrons were supposed to occupy a spherical box, of radius R , in which case the wave functions take the radial form of spherical Bessel functions, $j_l(k, r)$, with only those k values permitted which allow the electron waves to satisfy the appropriate boundary conditions at $r=R$. In changing the volume of the box by ΔV , and introducing a scattering center at $r=0$, two contributions to the energy change may be found:

$$E_1 = -(2/5)E_F \Delta V / \Omega \quad (11)$$

and

$$E_2 = -(2\hbar^2/\pi m) \int_0^{k_F} \sum_{l=0}^{\infty} (2l+1) \eta_l(k) k dk. \quad (12)$$

²⁰ J. W. Taylor, Phil. Mag. 46, 867 (1955).

²¹ V. E. Smirnova and F. B. Ormont, Doklady Akad. Nauk. SSSR 82, 751 (1952).

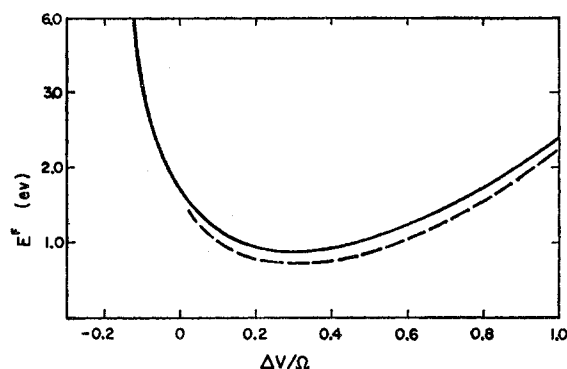


FIG. 3. Vacancy formation energy E^F as a function of crystal volume change ΔV .

The first term is simply the energy change of the conduction electrons due to the expansion of the box. What must be noted is that in the case of a strong repulsive scattering potential, the second term is predominantly a calculation of surface energy of the electron gas round the potential barrier. The situation is quite analogous to that treated by Stratton; in passing from the plane surface barrier to the spherical barrier, one still finds the drop in electron density outside the barrier (see Fig. 2) and the oscillatory modification found by Stratton on the conduction electron density in the bulk metal gives way, in the case of the spherical defect, to the familiar "long-range oscillations" given by Eq. (9).

Using Eqs. (11) and (12) Fumi found a formation energy of about 0.9 eV in copper, and on subtracting an uncertain contribution of ~ 0.3 eV from the closed-shell energies, obtained the low estimate of 0.6 eV even before allowing for the effects of vacancy relaxation. However, the remarks made in Sec. III suggest that the reason for the low predicted energies lies in the treatment of the d -shell contribution to the formation energy, for, just as in the case of surface energy calculations, no account has been taken of the interaction of the d shell with the modified lattice potential near the defect. By analogy with the surface effects, one might anticipate that this interaction is considerably larger than the 0.3 eV included in Fumi's calculation, so that the estimated formation energy must be increased substantially.

While no pretense at precise calculation of vacancy energies can be made, it is interesting to observe the effect of the considerations outlined above on the theoretical predictions. In what follows we will take the most rudimentary account of the fact that free electron theory underestimates the energy associated with repulsive barriers in the noble metals. The free electron surface energy deduced by means of Eq. (12) will be increased by the factor $\frac{3}{2}$, and, as suggested by the experimental surface energies, the resulting contribution to the formation energy will be considered to include all contributions from d -shell interactions. Thus

TABLE II. Vacancy formation energies in the noble metals. The subscripts 1, 2, and expt signify the following: 1—values derived at the calculated minimum energy; 2—values derived at the relaxation found experimentally in gold; expt—experimental probable value of formation energy.

	E_1	E_2	E_{expt}
Cu	1.0	1.5	...
Ag	1.0	1.2	1.10
Au	0.9	1.2	0.97

while it has been observed that the deficiencies of Fumi's calculation may well lie in his treatment of the d -shell disturbances, the present treatment is not committed to this hypothesis, but rather, constitutes a speculation as to the manner in which the additional surface energy actually observed in the noble metals, will vary on altering the geometries of the barrier provoking the surface effects.

The formation of vacancies will be considered in the following way. An ion is removed to the surface of the lattice with a consequent decrease in electron energy given by Eq. (11) with $\Delta V = \Omega$. The surface energy given by Eq. (12) is now invoked with phase shifts corresponding to the values used in the earlier treatment of resistivity. This energy is increased by a factor $\frac{3}{2}$ such that in the limit when the scattering center becomes large with respect to the electron wavelength, the surface energy is in rough agreement with experiment.

The effects of lattice relaxation are now included by permitting the change in electron energy to distort the lattice around the defect. The stored energy will be taken as the value given by Brooks:

$$E_s = 8\pi r_s^3 G \epsilon^2, \quad (13)$$

with r_s the radius of the atomic sphere, ϵ the fractional change in the radius of the vacancy cell due to relaxation, and G an elastic modulus derived and tabulated by Brooks. The surface energy changes in a manner described by the changing phase shifts, with correspondence between the values of the phase shifts and of ϵ established by the usual criterion of long-range electrical neutrality of the defect neighborhood, as is ensured by the use of the Friedel sum rule. It must be noted that no change in the energy E_1 may be admitted during the relaxation, since energy changes due to modification of the crystal volume by relaxation are now included in Eq. (13).

With this model one obtains the data for gold shown in Fig. 3 as a plot of vacancy energy against change of lattice volume. While the relaxation is exaggerated, the energy at the rather flat minimum will be seen to be in fair agreement with the experimental value. Table II shows the minimum energies for the three noble metals; the predictions are reasonable in the cases of copper and silver also, with the effects of different Fermi energies and elastic constants cancelling out to

a large extent in the vacancy formation energy. Also given in Table II are the formation energies found at the relaxation observed in gold. These values are, of course, larger than the previous minimum set, and it will be seen from the table in which the experimental formation energies are also given, that the two sets of predicted data straddle the observed energy in the case of each of the noble metals.

In passing, one may also note that the model throws some light on the mechanism of divacancy binding. Let us suppose that a divacancy may be represented as a single isotropic scattering center, and that relaxation takes place as before against the lattice strain. The broken line in Fig. 3 represents the half-divacancy energy plotted against the half-volume change of the lattice in gold. The broken line falls below the monovacancy curve, indicating that for equal fractional relaxation of vacancy and divacancy, the divacancy exhibits a binding energy of about 0.3 ev. Physically this binding energy may be considered as due to the sharing of part of the surface of the constituent vacancies, with a consequent decrease in the surface energy of the electron gas. This tendency towards positive binding energy appears to be well established in gold, where quenching experiments have been interpreted as indicating a divacancy binding energy of ~ 0.1 ev.²²

V. DISCUSSION

The model presented here has been seen to predict with surprising facility and accuracy the energies of formation, the relaxation, and the resistivity effects

associated with vacancies in the noble metals. While the model is plausible and probably contains many of the physical phenomena occurring near a vacancy site, the situation has been considerably oversimplified. That this is so becomes increasingly evident on applying the above treatment to the alkali metals with the obvious difference that the free electron surface energies are satisfactory in this case. In the case of sodium, the elastic modulus given by Brooks is so small that an extreme relaxation of the vacancy is predicted, together with a negative value of the formation energy.

A probable reason for this discrepancy is not too difficult to find, for Bridgman's²³ data show that the bulk compressibility of sodium decreases by a factor ~ 10 on compressing the metal to 0.7 of its former volume. It appears most likely that the elastic modulus tabulated by Brooks will also show a large increase, and in this way the excessive relaxation will be inhibited and reasonable values for the formation energy of vacancies may follow. However, further treatment on the present model is clearly out of place. One may conclude that it is impossible to go further without a more detailed treatment of the lattice forces.

While the situation is not satisfactory in the case of the alkali metals, the model may nevertheless be helpful in estimating other properties of vacancies in the noble metals, particularly in the case of interactions concerning the electron density in the lattice surrounding the vacancy. In this respect, agreement with resistivity data leads to confidence in the phase shifts found here, and consequently also in the nature of the predicted disturbance of the electron gas in the surrounding lattice.

Part II: Interaction of Vacancies with Other Defects in the Noble Metals

I. INTRODUCTION

The magnitude of the energy change in a noble metal lattice, caused by the association of a vacancy with a substitutional impurity, is known from direct experimental evidence only to the extent of order of magnitude estimates of ~ 0.1 ev. However, indirect evidence is available in the form of the activation energy for self-diffusion of the impurity in the solvent lattice. This is primarily a consequence of the precision with which diffusion phenomena may be studied using radio tracer techniques.²⁴

If, following Lazarus,²⁵ one assumes a vacancy mechanism for self-diffusion in the noble metals, and

also makes allowance for possible differences in the energy of motion of various types of ion, then the difference of activation energy between solvent and solute atoms depends directly on the difference of formation energy of a vacancy, firstly in the pure solvent metal and, secondly, in the first neighboring lattice site to an impurity ion. In this way the change in activation energy in passing from solute to solvent atoms in the solvent lattice may be related to the association energy of the vacancy-impurity pair.

However, interpretation of the self-diffusion data is by no means unambiguous owing to the fact that estimating changes in the energy of motion is, if anything, even more difficult than estimating association energies. Moreover, the radio tracer technique measures the mass flow of ions through the lattice rather than the actual ionic jump frequencies uncomplicated by the effects of correlated exchanges of vacancy and impurity sites. Thus, before using the diffusion data, the activation energy must be multiplied by a "correlation factor" which is known only approximately from

²² J. S. Koehler, F. Seitz, and J. E. Bauerle, *Phys. Rev.* **107**, 1499 (1957).

²³ P. W. Bridgman, *The Physics of High Pressures* (G. Bell and Sons, London, 1931).

²⁴ For a complete discussion of diffusion phenomenon, the reader is referred to the review article by D. Lazarus, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10.

²⁵ D. Lazarus, *Phys. Rev.* **93**, 973 (1954).

simplified theoretical arguments.^{26,27} The correlation effect has never been observed experimentally owing to the inherent difficulty of measuring the actual jump frequencies.

Previous theoretical treatments of the vacancy-impurity interaction are open to a great deal of criticism both on account of the models used, and also because of the interpretation of the models. For example, the Thomas-Fermi approximation has been used to estimate the potential in the neighborhood of an impurity ion due to the screening of the ion by conduction electrons, whereas it is now well established that the predictions of the Thomas-Fermi model are not at all reliable under these circumstances. A discussion of the deficiencies of the existing work is deferred until Sec. II, but it may be noted that despite the agreement between the prediction of theory and the experimental diffusion constants, the approximations made in these treatments do not seem to be substantially justified by other experimental evidence.

While crystal boundaries and dislocations are well known to be the major sources and sinks of vacancies, little is known about the interactions between the point and extended defects. It is clear that there will be contributions to the interaction energy from both the lattice distortion and the modification of the conduction electron states resulting from the proximity of the two defects. Attempts have been made to calculate that part of the energy due to the overlapping of the elastic strain fields,^{28,29} but as yet, no theory has been proposed which permits the calculation of the contribution to the energy due to the free electrons. This is all the more surprising since, in the case of the interaction with other point defects, the change in electronic energy has been assumed to dominate the interaction.

The scattering of electrons by anomalies in a metal lattice has been re-investigated recently owing mainly to the work of Friedel.^{30,31} The theory has been applied to the interpretation of resistivity¹³ and nuclear resonance data^{16-18,32} in dilute alloys and a most encouraging quantitative agreement between experiment and theory is found in each case. In the following sections the scattering theory together with the model used in part I will be used to study the interaction of vacancies with other defects in noble metal lattices. A discussion of interactions involving extended defects will be deferred until Sec. VIII. In Secs. II through VII, the interactions of vacancies with point defects will be considered, and

it will be seen that the association energy of pairs of defects predicted in this way is in good agreement with the available experimental data.

II. PREVIOUS THEORETICAL TREATMENTS

The vacancy-impurity interaction in monovalent metals has been considered by Lazarus,²⁵ who assumed that a vacancy in the metal lattice could be represented by a unit negative charge corresponding to the removal of an ion having one net positive charge. A neighboring impurity ion having valence $Z+1$ was then supposed to be screened from the bulk of the metal according to the linearized Thomas-Fermi potential,

$$V(r) = -(Ze/r) \exp(-\lambda r), \quad (14)$$

where the screening parameter λ was found in terms of free electron theory. The energy of association of the two defects then follows as

$$E = (Ze^2/a) \exp(-\lambda a), \quad (15)$$

where a is the separation of the defects. On taking account of the change in energy of motion of the impurity ion, the resulting activation energy for self-diffusion proved to be in remarkably good agreement with experiment.

Recently, the same scheme has been extended by Le Claire,²⁷ who uses the more elaborate Thomas-Fermi potential of Alfred and March,³³ in order to obtain the energy change of the lattice when a solvent ion in the saddlepoint configuration is exchanged for an impurity ion. By considering this situation, Le Claire includes any effect of valence on the energy of motion of ions in the lattice. The energies obtained from this treatment are larger than those found by Lazarus, but on allowing for correlation effects, the predictions once more fall into agreement with experiment. However, in the following discussion, it will be shown that several assumptions in this treatment are invalid so that the apparent agreement may not be taken as a vindication of the theory.

Equations (7)–(9) show clearly that the electron density in the lattice around a defect does not exhibit the monotonic decay predicted by the Thomas-Fermi theory. Rather one finds the “long-range oscillation” phenomena whose existence appears amply well established by experiment. The r^{-3} dependence of the electron density disturbance, for example, is known to be quite accurate from measurements of nuclear quadrupole coupling with the screening charge in dilute alloys.¹⁷

In defense of the use of the Thomas-Fermi model, Le Claire has noted that the charge density at the half-vacancy sites of the saddlepoint configuration is roughly the same whether scattering theory or the statistical treatment is used. However, this is not sufficient to ensure that the potential also is in agree-

²⁶ A. B. Lidiard, *Phil. Mag.* **5**, 1171 (1960).

²⁷ A. D. Le Claire (to be published).

²⁸ J. D. Eshelby, *Acta Met.* **3**, 487 (1955); *Ann. Physik* **465**, 118 (1958).

²⁹ R. A. Swalin, *Acta. Met.* **5**, 443 (1958).

³⁰ J. Friedel, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 446.

³¹ J. Friedel, *Nuovo cimento* **7**, 287 (1958).

³² C. P. Flynn and E. F. W. Seymour, *Proc. Phys. Soc. (London)* **76**, 526 (1960).

³³ L. C. R. Alfred and N. H. March, *Phys. Rev.* **103**, 877 (1956).

ment. Moreover, this potential is supposed to interact with the charge in the half-vacancies, with the charge assumed to maintain the density to be anticipated in the undisturbed metal. This is not consistent with the fact that scattering theory shows that the vacancy suffers short-range screening owing to the expulsion of electrons from the regions of low ion density in the lattice. The consequence of this effect is that little charge exists in the vacancy sites, so that irrespective of the potential used, one would anticipate a considerable reduction in the predicted saddlepoint energies.

One ought also to take adequate account of the lattice strain in the neighborhood of the defects. As was noted in part I, the requirement of long-range electrical neutrality of the lattice must be used when considering the electron distribution around a defect. In the same way that the relaxation of the lattice surrounding a vacancy is needed in order to study the distribution of screening charge, so also is it necessary to know the lattice strains associated with the saddlepoint configuration in order to predict the electron scattering. In the face of an inadequate supply of such information, one can only conclude that calculation of the electron energy associated with the saddlepoint configuration is at present impossible.

Finally, it is clear that a completely reciprocal relationship exists between the impurity atom and the vacancy. Not only does the vacancy scatter electrons towards the impurity, but the reverse also occurs, both processes leading to fluctuations of electron density at neighboring lattice sites. Thus, in computing the energy of association of the defect pair, one must consider the effects of the disturbance both at the vacancy and the impurity sites. In the following treatment it will be seen that roughly equal contributions to the energy change may be attributed to the disturbances caused by the two different point defects.

III. ENERGIES FROM SCATTERING THEORY

For reasons given earlier, the disturbed electron density, $\Delta\rho(\mathbf{r})$, outside a vacancy in a noble metal lattice should be given fairly accurately by the expressions used in part I. In the pure metal, this disturbance occurs in the normal lattice potential, but on the association of a substitutional impurity with the vacancy, part of the density disturbance falls in the modified lattice potential in the neighborhood of the impurity. Calling this disturbance of the lattice potential $\mathcal{V}(\mathbf{r})$, the first-order contribution to the lattice energy caused by the proximity of the defects is given by the volume integral

$$E_i = \int_{\text{lattice}} \Delta\rho(\mathbf{r})\mathcal{V}(\mathbf{r})d\mathbf{v}. \quad (16)$$

This energy is derived quite differently from that

found from the Thomas-Fermi treatment. In the latter case, the charge was assumed to exist at the vacancy site, and the potential produced by the impurity outside its own cell gave rise to the interaction energy. Here the potential outside the cell is assumed to be small because of the short-range screening [which effectively reduces the domain of the integral in Eq. (16) to the impurity cell], and the potential difference inside the cell interacts with a charge which is not present *a priori*, but rather, is a direct consequence of electron scattering by the vacancy.

A second contribution, E_v , to the energy of association, is a consequence of scattering by the impurity atom. A first order treatment of the modification of vacancy energy, caused by an electron density disturbance in the surrounding lattice, is given in Sec. V on the basis of the previous treatment of vacancy formation energies.

Since both vacancies and impurities produce changes in lattice volume, and in this way give evidence of strain fields in the lattice, it is not surprising that an interaction between the defects may result from overlapping elastic strains. While the interaction in an isotropic material is of extreme short range, Eshelby²⁸ has shown that significantly longer range interactions occur when the anisotropy of the lattice is taken into account. In the notation used in part I, Eshelby finds for the interaction of two defects separated by a distance r in a cubic lattice the relationship

$$E = (15/8\pi\gamma^2r^3)\Delta V_1\Delta V_2\Gamma d, \quad (17)$$

with the subscript on ΔV distinguishing between the isolated defects, Γ being given in the terms of the directional cosines of \mathbf{r} with respect to the cubic axes, and the modulus d equal to $C_{11}-C_{12}-2C_{44}$. On substituting appropriate constants for the noble metals in Eq. (17), together with the value -0.1 given by Eshelby for Γ in the $[110]$ direction and the typical $\Delta V/\Omega$ of 0.2 and 0.5 for the impurity and vacancy, respectively, one finds the contribution to the association energy from strain effects to be $\sim 10^{-2}$ ev. This value is an order of magnitude less than the typical contribution from the electronic energy as computed in the present paper, and so that one is justified in ignoring the strain energy. This conclusion is born out, at least in so far as the noble metals are concerned, by the results of calculations by Swalin,²⁹ who has computed strain energy changes appropriate to the saddlepoint configuration and has found very little correlation between the strain energy and the charge difference of activation energy between solvent and impurity ions in silver.

The changes in scattering power of the defects due to volume changes caused by the association will also be ignored in the present work. Since the impurities considered will have the same d -shell structure as the

solvent ions, it does not appear likely that the presence of an impurity next to a vacancy will grossly affect the volume of either defects, although in the event of such a change occurring, considerable error could be introduced into the theory. It will be noted that one can ignore the effects of strain on scattering much more confidently in the case of two defects associating at neighboring sites than is possible in the case of the saddlepoint configuration. What one is assuming is that from the point of view of strain, the impurity atom acts precisely like a solvent atom, an assumption which is untrue, but which is likely to be harmless. In the case of the saddlepoint energy even granted this assumption, one still cannot perform a reasonable calculation since the strain is large and relatively unknown even for the solvent ion, so that the magnitude of the scattering is very uncertain.

An exception to the remarks made above may be noted in the association of two vacancies to form a divacancy. Since the scattering power and energy of a vacancy are fundamentally concerned with the relaxation of the lattice it is evident that a divacancy may not be considered using so simple a model as that proposed when simply exchanging solvent and solute atoms. For this reason, only the asymptotic form of the vacancy-vacancy interaction at large separations will be considered, so that the volumes of the vacancies may be assumed to be relatively undisturbed by the strain interaction.

It is also interesting to inquire as to the contribution of d electrons to interaction of vacancies with solutes of the same period as the solvent ions. One may note with Kohn and Vosko¹⁷ that the long-range oscillations evident in the s band round a defect are essentially a product of the sharp Fermi surface of the electron gas. It is easily shown that in the case of a filled d band there can be no oscillations of electron density having the long-range character of those in the s band. Moreover, returning to the picture of the electrons satisfying boundary conditions on a potential barrier, one notes that as opposed to the s -band density which is large at the cell boundaries, the d -band density is low so that smaller deviations are required in satisfying the boundary conditions. These considerations tend to indicate that d -shell effects should be small, and it is gratifying to note that experimental evidence is not in contradiction with this conclusion. Thus, the activation energies for self-diffusion of impurities depend much more on valence than on the period from which the solute is taken, a clear indication that the substitution of a different filled shell in the core of the impurity does not greatly affect the interaction energies. This observation may not hold in the case of impurities of negative valence, for the d shell of the impurity is then incomplete and the local properties of the d band could be modified considerably. Some explanation of the behavior of negative-valence solutes may be available from this viewpoint.

IV. SCATTERING BY THE VACANCY

In part I, the scattering of electrons was considered purely in terms of the free electron approximation. The conduction electron wave functions were taken to have the form,

$$\psi_{lm}(k, \mathbf{r}) = \alpha_{lm} j_l(kr) Y_l^m(\theta, \varphi), \quad (18)$$

with Y_l^m a spherical harmonic, and no account was taken of the effects of the periodic lattice potential on the form of the electron waves in the crystal. In this section where interaction energies are to be considered, it is necessary to use a more detailed description of both the lattice potential and the electronic wave functions.

In this respect one is fortunate, since it has been shown by Daniel¹⁶ that the results of free electron scattering theory hold good when the electron waves are considered to be modulated by a factor $\psi_k(\mathbf{r})$, corresponding more nearly to the form of the wave functions in the metal lattice. The theory has been redeveloped by Kohn and Vosko,¹⁷ who reach roughly the same conclusions. Thus, Eq. (7) for the electron density in the neighborhood of a spherically symmetric scattering in the presence of an isotropic distribution of incident plane waves, may be approximated in the case of Bloch waves $\psi_k(\mathbf{r})e^{ik \cdot \mathbf{r}}$ by the form

$$\Delta\rho(k, \mathbf{r}) = \psi_k^*(\mathbf{r})\psi_k(\mathbf{r}) \sum_{l=0}^{\infty} (2l+1) \{ [n_l^2(kr) - j_l^2(kr)] \times \sin^2\eta_l(k) - n_l(kr)j_l(kr) \sin 2\eta_l(k) \}. \quad (19)$$

In the absence of other defects in the neighborhood of a vacancy, the electron density disturbance given by Eq. (19) falls in the undisturbed lattice potential $V(\mathbf{r})$. On moving an impurity atom into this density change from a remote point in the lattice, a disturbance of the energy occurs given by

$$E_v = (e/\pi^2) \int_0^{k_F} k^2 \int_{\text{lattice}} \Delta\rho(k, \mathbf{r}) [U(\mathbf{r}) - V(\mathbf{r})] d\mathbf{r} dk, \quad (20)$$

where $U(\mathbf{r})$ is the lattice potential in the presence of the impurity, and the total charge density fluctuation has been found by integrating over the filled states in k space.

The energy E_v is known to be positive since $U(\mathbf{r}) - V(\mathbf{r}) = \mathcal{V}(\mathbf{r})$ is positive for positive-valence solutes, and as seen in part I, $\Delta\rho(\mathbf{r})$ shows an increase in electron density at nearest lattice sites to a vacancy.

The potential difference $\mathcal{V}(\mathbf{r})$ is now needed in order to obtain the energy E_v . This potential is not, of course, well known since the distribution of screening charge within the impurity cell is required before it is possible to compute the potential. However, in the case of solvent and solute atoms belonging to the same period, adequate and relatively simple approximations can be found. We will assume that the potential difference inside solvent and impurity cells is the difference in

potentials due to the nuclear charges in the ions, together with the potential due to the different conduction electron distributions in the two types of atomic cells. This effectively assumes that the electrons forming the core of the atoms are distributed in an identical manner in solvent and solute ions. The resulting potential then has one contribution of the form Z/r_1 , where r_1 is the distance from the impurity nucleus, and the impurity ion has once more been assumed to have valence of $Z+1$. The second and more uncertain part of the potential is due to the s electrons but although this contribution is important in reducing the potential to zero in the neighborhood of the cell boundary, and so restricting the volume over which the integration in Eq. (20) must be performed, the interaction energy proves to be quite insensitive to the details of the screening distribution.

In order to demonstrate this insensitivity clearly, E_v has been computed for two different and rather extreme charge density distributions. Firstly, the $Z+1$ conduction electrons will be assumed to be spread uniformly through the impurity cell, with the result that the potential difference $\mathcal{V}_1(r_1)$ is given by

$$\mathcal{V}_1(r_1) = Z[(1/r_1) - (3/2a) + (r_1^2/2a^3)]. \quad (21)$$

It is obvious that this potential is too slowly screened to be realistic, since the screening charge may be expected to concentrate in the region of large potential near the center of the cell. To contrast with this calculation, the energy has also been computed with all the screening charge concentrated into the central quarter of the cell volume. Thus, the second potential used takes the form

$$\mathcal{V}_2(r_1) = Z[(1/r_1) - (3/2b) + (r_1^2/2b^3)], \quad (22)$$

with $b = (a^3/4)^{1/3}$. No virtue other than simplicity is claimed for these potentials, but they almost certainly err from the true distribution in opposing senses, and in this way emphasize the adequacy of the approximation. In Sec. VI the values of E_v found from this treatment will be presented, and it will be seen that the effect of using the different potentials causes a change of less than 20% in the value of E_v . This is a consequence of the fact that the bulk of the energy may be attributed to the central parts of the impurity cell where the effect of different nuclear potential is dominant.

V. SCATTERING BY THE IMPURITY ATOM

We will now compute the energy change of the lattice which occurs because of electron scattering by the impurity ion and the consequent modification of the electron states in the neighborhood of the vacancy. In order to achieve this result, use will be made of the analysis given by Fumi of s -band energy in the presence of a point defect.

Fumi analyzed the electron gas into the usual spherical eigenstates and found the energy changes

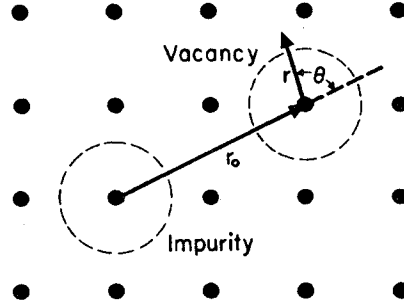


FIG. 4. Geometry for analysis of disturbed electron density.

(11) and (12) on introducing the vacancy scattering. In the present case, the electron gas is disturbed, and the crux of the problem is re-analyzing the electron gas into eigenstates around the vacancy site. Having these states, one may then make use of the same distribution of energy change against states found by Fumi, only taking account of the different occupation of the states.

It is clear at the outset that the gas cannot be analyzed into pure s , p , d , \dots etc., states, for the presence of gradients in the electron density automatically implies that mixed states are present. Thus, in principle, one must find for each k value the orthogonal states

$$\Psi_n(k, \mathbf{r}) = \sum_{l, m} \alpha_{lmn}(k) \psi_{lm}(k, \mathbf{r}), \quad (23)$$

which result from the mixing with coefficients $\alpha_{lmn}(k)$ of the undisturbed eigenstates. The quantity of l , m , wave present at that k value then follows as

$$\beta_{lm}(k) = \sum_n |\alpha_{lmn}(k)|^2, \quad (24)$$

and according to Fumi's arguments, the change in energy of formation of the vacancy, and hence also the change in association energy, follows as

$$E_v = (2\hbar^2/\pi m) \int_0^{k_F} \sum_{l, m} \delta_{lm}(k) \eta_l(k) k dk, \quad (25)$$

with $\delta_{lm}(k) = \beta_{lm}(k) - 1$. However, the amount of labor involved in this complete treatment proves unnecessary because of the rapid convergence of the phase shifts $\eta_l(k)$ and the consequent negligibility of terms of higher order than $l=1$ in Eq. (25). Thus, in order to trap a satisfactory answer, we need only find the four coefficients $\delta_{00}(k)$, $\delta_{10}(k)$, $\delta_{11}(k)$, and $\delta_{1-1}(k)$.

The coefficient $\delta_{00}(k)$ is easily seen to be equal to $\Delta\rho(k, r_0)/\rho$, for in the expansion of the density of the disturbed gas around the point r_0 ,

$$\rho(k, \mathbf{r}) = \sum_n \Psi_n^*(k, \mathbf{r}) \Psi_n(k, \mathbf{r}), \quad (26)$$

only the s -wave terms contribute to the density at r_0 , owing to the fact that $j_l(0)=0$; $l>0$. Figure 4 shows the geometry of this situation including the choice of the angle θ for the analysis of the angular factors in the wave functions.

TABLE III. Vacancy-impurity coupling energies due to vacancy scattering in copper and silver. The two different impurity potentials \mathcal{V}_1 and \mathcal{V}_2 are described in the text.

Potential	Energy per charge difference (ev)	
	\mathcal{V}_1	\mathcal{V}_2
Cu	2.6×10^{-2}	2.2×10^{-2}
Ag	3.1×10^{-2}	2.6×10^{-2}

The p -wave coefficients may also be dealt with in a simple fashion. Since the $l=1$ phase shift for a vacancy is invariably less than about 15% of that for the s wave, the energy changes produced by the p waves and the association of the two defects may be expected to be small also. We are therefore prepared to estimate this correction to the s -wave term from the asymptotic form of the electron density disturbance. From Eq. (8) the density is seen to take the form

$$\rho(k, r_0) = \rho \{ 1 + (kr_0)^{-2} \sum_l \gamma_l(k) \sin[2kr_0 + \xi_l(k)] \}, \quad (27)$$

where $\xi_l(k)$ is the phase shift produced by the impurity atom, and

$$\gamma_l(k) = (-1)^l (2l+1) \sin \xi_l(k). \quad (28)$$

This density must tend to the form given in Eq. (26).

If in Eq. (26) one ignores s - d mixing, then from the form of the spherical Bessel functions as r tends to zero, viz.:

$$j_l(x) = [(2l+1)(2l-1) \cdots 3 \cdot 1]^{-1} x^l, \quad (29)$$

it is clear that the coefficient of $(kr)^2$ in the expansion of $\rho(k, r)$ is simply a linear combination of the $\delta_{00}(k)$ and $\delta_{10}(k)$. Thus, the second derivative of the density with respect to kr_0 , may be seen to have the value $(2/3)[\delta_{10}(k) - \delta_{00}(k)]$. Similarly the second derivative normal to r_0 takes the value $(2/3)[\delta_{1\pm 1}(k) - \delta_{00}(k)]$. Now from Eq. (27), the second derivative along r_0 takes the asymptotic form,

$$\begin{aligned} \partial^2 \rho(k, r) / \partial (kr)^2 &= - (2/kr_0)^2 \sum_l \gamma_l \sin[2kr_0 + \xi(k)] \\ &= 4\Delta\rho(k, r) / \rho, \end{aligned} \quad (30)$$

by virtue of Eq. (8). The second derivative normal to r_0 can be seen to have no term having the long-range character of Eq. (30) (i.e., of order r_0^{-2}) so that one finds a zero asymptotic value for this derivative. Finally then, by comparing the derivatives deduced from the different expansions (26) and (27) of the electron density, one obtains the values of the coefficients δ_{lm} for $l=0$ and 1 in the form

$$\delta_{00}(k) = -\delta_{10}(k)/5 = \delta_{1\pm 1}(k) = \Delta\rho(k, r) / \rho. \quad (31)$$

These expressions may now be substituted into Eq. (25) for the interaction energy to yield the final

expression

$$E_i \simeq (2\hbar^2/\pi m) \int_0^{k_F} \frac{\Delta\rho(k, r)}{\rho} [\eta_0(k) - 3\eta_1(k)] k dk. \quad (32)$$

The values of $\Delta\rho(k, r)/\rho$ produced at the vacancy site by various substitutional impurities are now needed in order to predict the energy, E_i . These have been computed for impurities in the same period as the solvent atoms according to the predictions of the square-well potentials introduced by Blatt.¹³ Since this approach has been justified by its success in the interpretation of resistivity,¹³ Knight shift,¹⁶ and quadrupole coupling data³² in dilute alloys, it does not appear worthwhile to depart from precedent and derive the electron density changes from arduous computations concerning more sophisticated scattering potentials. The results of this treatment are presented in the next section.

VI. ENERGIES OF ASSOCIATION

The ground-state wave functions $\psi_k(r)$ given by Mott and Jones³⁴ for copper and silver, have been used as the modulating factor on the plane electron waves in order to allow the computation of E_v in these metals. The contribution to the defect pair formation energy per excess valence of the solute ion in these metals is given in Table III for each of the solute potentials described in Sec. IV. It will be seen that the values lie in the neighborhood of 2.6×10^{-2} ev/charge difference, which may be compared with the prediction of $\sim 3.7 \times 10^{-2}$ ev/charge predicted from the Thomas-Fermi approximation. The reason for the insensitivity of this part of the interaction energy to the distribution of screening charge in the solute cell has been noted previously.

Using the analysis given in Sec. V, the energy has also been computed for square wells of various strengths

TABLE IV. Theoretical binding energies B for vacancy-impurity pairs in copper and silver. The contributions E_v and E_i , due respectively to scattering by the vacancy and by the impurity, are given, and also the experimental change in ΔE_{diff} in activation energy for self-diffusion in passing from solvent to solute ion. For references to the source of experimental data see reference 27, where details of the derivation of the correlation factors will also be found.

Solute	Energies in ev				Correlation factor
	E_v	E_i	$B = E_v + E_i$	ΔE_{diff}	
Solutes in copper					
Zn	0.02 ₅	0.00	0.02 ₅	0.16	0.55
Ga	0.05	0.06	0.11	0.15	0.27
Ge	0.07 ₅	0.12	0.19 ₅
As	0.10	0.17	0.27	0.31	0.37
Solutes in silver					
Cd	0.03	0.00	0.03	0.11	0.52
In	0.06	0.03	0.09	0.15	0.40
Sn	0.09	0.08	0.17	0.21	0.41
Sb	0.11 ₅	0.12	0.23 ₅	0.25	0.40

³⁴ N. F. Mott and H. Jones, *Metals and Alloys* (Oxford University Press, New York, 1936).

corresponding to different impurities in the noble metals. The energies were found for various depths of the potential well and the values for particular impurities obtained by interpolation to the appropriate Friedel sum as given by Blatt. The vacancy phase shifts are also needed in order to obtain E_i , and have been taken throughout as those found in part I for the relaxed vacancy in gold.

The resulting values of E_v and E_i , and of their sum B , the energy of association (binding energy) of the defects, are displayed in Table IV for solutes from the same period of the solvents copper and silver. The values of E_i quoted are the mean of the values predicted from use of the two different forms of $\psi(r)$. For comparison, the difference of activation energy for self-diffusion between the solvent and solute ions is given together with the approximate correlation factors according to Le Claire.

The theoretical association energies predicted by the present treatment appear quantitatively satisfactory when compared with the diffusion data, though perhaps too large in the case of higher valence solutes. While one might hope that the theory is capable of predicting the energy to within a factor of say 50%, it is difficult to set bounds on the certainty of the theoretical data. Moreover the lack of direct experimental evidence concerning the interaction only serves to emphasize the fruitlessness of a protracted discussion of these predictions; for the present, it is sufficient to note that a theory taking reasonably faithful account of physical processes in the neighborhood of a double defect in a metal lattice can produce sensible values for the formation energy of the defect.

Before proceeding to the discussion of the long-range interaction between vacancies and other defects having various symmetry properties, it may be advantageous to comment briefly on the possibility of extending the treatment given above to the case of the interaction of vacancies with positive-valence impurities from a different row of the periodic table. At first it may be speculated that since the potential near the center of the impurity cell is dominated by the nuclear charge, the contribution of E_v to the binding energy would be strongly dependent on the period from which the impurity is taken. This conclusion would, of course, be in disagreement with experimental evidence.

The fallacy in this argument becomes evident on considering the wave functions inside the impurity cell, for the perturbation treatment used here cannot be used without modification in the evaluation of energies for impurities from a different period. The reason is that the conduction electron waves inside the impurity cell must take up the number of radical nodes appropriate to the period from which the solute is taken, so that inside this cell, the wave functions resemble much more closely those in the monovalent metal starting the period containing the solute atom, than the wave function characteristic of the solvent

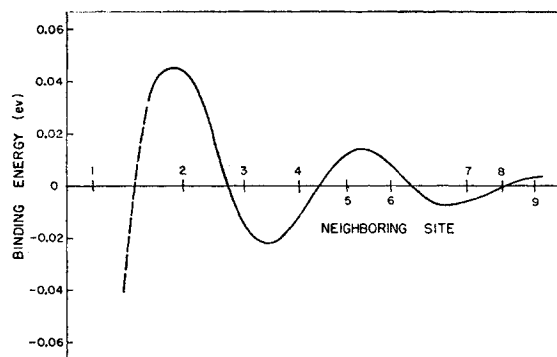


FIG. 5. Asymptotic form of vacancy-vacancy interaction energy in gold.

atom. In this event, the contribution to the association energy will also tend to that found when solvent and solute atoms are from the same period, and since, as seen in the case of impurities in copper and silver above, the predicted energies are not sensitive to the row of the periodic table considered, it will be seen that the apparent discrepancy has been resolved. In all, the reason for the insensitivity of the binding energy to the period from which the solute is taken, bears a close resemblance to the explanation of the fact that similar Fermi energies are found in the noble metals despite the differing nuclear charges.

VII. THE LONG-RANGE VACANCY—VACANCY INTERACTION

It will be evident at this stage that, since the interaction energy of two point defects depends on the disturbance of electron density at the defect sites, the interaction energy will exhibit a variation with separation of the defects similar in form to the long-range characteristics of the density disturbance. In the particular case of the vacancy—vacancy interaction, the direct factor of $\Delta\rho(k,r)/\rho$ apparent in Eq. (32) indicates a direct proportionality between the two effects. Thus the binding energy will not show a monotonic decrease with increasing defect separation, but will have a long-range oscillatory nature.

The problem of computing the interaction energy between a vacancy and the density fluctuations caused by a second vacancy is little different from the case considered earlier in which an impurity atom produces the disturbance. However, it is to be anticipated that this treatment will be unsatisfactory in the case of two vacancies in close proximity, because the relaxation of the lattice will be modified. We will therefore be content to derive only the asymptotic form of the interaction energy for large vacancy separation.

To achieve this result one need only substitute Eq. (8) for the asymptotic form of the density oscillations due to a vacancy into Eq. (32) for the interaction energy. Noting that a factor of two must be inserted to take account of the equivalence of the two vacancies, and integrating by parts up to the Fermi limit, one

finds for asymptotic value of the interaction energy

$$E_{vv} = [4E_F/\pi(k_F r)^3][\eta_0(k_F) - 3\eta_1(k_F)] \quad (33)$$

$$\times \sum_{l=0}^{\infty} \gamma_l(k_F) \cos[2k_F r + \eta_l(k_F)],$$

where, as before, $\gamma_l(k) = (-1)^l(2l+1) \sin \eta_l(k)$, and E_F is the Fermi energy.

The interaction energy found in this way is shown in Fig. 5 for the case of gold. Owing to the near equality of the Fermi energies in silver and gold, this diagram also applies to silver, but the energies shown must be increased by about 25% in order to obtain values appropriate to copper. It will be seen from the figure that at the nearest neighboring site where the approximations made in the derivation are certainly not valid Eq. (33) predicts a negative binding energy corresponding to mutual repulsion of the defects. At longer range where the approximations are adequate, the amplitude of the energy oscillations is seen to fall off below 10^{-2} ev when the vacancies are at about the sixth neighboring lattice sites.

VIII. INTERACTION OF VACANCIES WITH EXTENDED DEFECTS

It is possible to comment more generally on the interaction between defects caused by their associated long-range disturbances of the electron gas, for it is clear that the coupling between pairs of impurity atoms will take a form quite analogous to that found in the case of pairs of vacancies. However, a phenomenon more pertinent to the present discussion of vacancies is in interaction of vacancies with extended defects in the noble metal lattices.

We will deal first with the dislocation, which will be considered in a simplified fashion as infinitely long cylindrical scattering regions in the crystal. By setting up Schroedinger's equation in cylindrical coordinates, one can obtain the form of the density oscillations due to a cylindrically symmetric distribution of plane waves of wave vector k , approaching the dislocation at an angle θ to its axis:

$$\Delta \rho(kr)/\rho = \sum_{n=0}^{\infty} \epsilon_n \{ [N_n^2(kr) - J_n^2(kr)] \sin^2 \xi_n(k) - N_n(kr) J_n(kr) \sin 2\xi_n(k) \}. \quad (34)$$

Here $N_n(kr)$ and $J_n(kr)$ are cylindrical Bessel functions of order n , r is the distance from the dislocation core, $\xi_n(k)$ is the radial phase shift of the n th partial wave, $\kappa = k \cos \theta$, and ϵ_n takes the values

$$\epsilon_n = 1, \quad n=0;$$

$$= 2, \quad n>0.$$

The asymptotic form of Eq. (34) may be obtained

from the limiting form of the Bessel functions, namely

$$J_n(x) \underset{x \rightarrow \infty}{=} (2/\pi x)^{1/2} \cos[x - (n + \frac{1}{2})\pi/2];$$

$$N_n(x) \underset{x \rightarrow \infty}{=} (2/\pi x)^{1/2} \sin[x - (n + \frac{1}{2})\pi/2]. \quad (35)$$

On substituting Eqs. (35) into (34) and averaging over θ to find the disturbance due to an isotropic distribution of incident plane waves, one finds the form of the oscillations to be

$$\Delta \rho(k, r)/\rho = (2/\pi k^3 r^3)^{1/2} \sum_{n=0}^{\infty} (-1)^n \epsilon_n$$

$$\times \{ [\cos 2\xi_n(k) - 1] \sin 2kr + \sin 2\xi_n(k) \cos 2kr \}, \quad (36)$$

where the Bessel function invoked by the averaging process has again been approximated according to Eq. (35). Equation (36) may be integrated over k space to give the asymptotic form of the total density oscillations as

$$\Delta \rho(r)/\rho = 3(2\pi k_F^5 r^5)^{-1/2} \sum_{n=0}^{\infty} (-1)^n \epsilon_n \sin \xi_n(k_F)$$

$$\times \sin[2k_F r + \xi_n(k_F) - \pi/4]. \quad (37)$$

In order to find the interaction energy between a vacancy and this charge disturbance, we need only note that Eq. (32) remains valid in the long-range limit despite the change of symmetry of the density fluctuation; the only difference between the two cases is that the relation $\delta_{00}(k) = \delta_{1\pm 1}(k)$ is now exact rather than asymptotic for one of the p states. Thus, one finds for the interaction between vacancies and dislocations the limiting form

$$E_{vd} = 6E_F(2\pi k_F^5 r^5)^{-1/2} [\eta_0(k_F) - 3\eta_1(k_F)]$$

$$\times \sum_{n=0}^{\infty} (-1)^n \epsilon_n \sin \xi_n(k_F) \sin[2k_F r + \xi_n(k_F) - \pi/4]. \quad (38)$$

Owing to the longer range nature of the disturbance produced by the dislocation, one is justified in neglecting that contribution to the interaction energy due to the disturbance of the electron density at the dislocation site provoked by the presence of the vacancy.

The interaction energy between a vacancy and a crystal boundary may be derived by means of a similar argument. If we assume that the boundary acts as an infinitely repulsive barrier, the wave functions must vanish on the boundary, and it is easy to show that the electron density at a distance z from the surface is

$$\Delta \rho(z)/\rho = 1 + 3 \cos 2k_F z / (2k_F z)^2$$

$$- 3 \sin 2k_F z / (2k_F z)^3, \quad (39)$$

an equation given previously by Stratton.¹⁹ The inter-

action energy between a vacancy and this electron density is

$$E_{vb} = \lim_{z \rightarrow \infty} [E_F/\pi(k_F z)^2][\eta_0(k_F) - 3\eta_1(k_F)] \cos 2k_F z. \quad (40)$$

Having now the asymptotic forms (32), (38), and (40) for the interaction energy in the case of the various vacancy defect interactions, it is interesting to compare their characteristics. Firstly, it may be noted that the energy oscillates with period k_F/π in each case, and exhibits a proportionality to the Fermi energy of electrons in the undisturbed lattice. The significant difference between the various interactions lies in the change of long-range character with the symmetry of the defect considered. Thus, on changing the symmetry from spherical to cylindrical and then plane, the range of the interaction increases from an r^{-3} through r^{-2} to a z^2 dependence on the vacancy-defect separation.

While it is clear that the oscillatory nature of the electronic energy precludes this interaction from giving rise to a net driving force for migration of vacancies to the various defects one may note with Lomer³⁵ that dislocations in the close-packed metals almost certainly lead to a local increase in crystal volume. Electrons must therefore be repelled from the neighborhood of the dislocation, as occurs also in the case of crystal boundaries and vacancies. Thus all three types of vacancy-defect interaction considered here will show tendencies towards attraction at sufficiently short range, because of the sharing of surface energy of the electron gas at the common boundary of the two defects. This effect has already been noted in the case of the divacancy, and appears to follow in an equally natural manner from the physical processes occurring in the neighborhood of the extended defects.

IX. CONCLUSIONS

The interaction of vacancies, as represented by the simplified model given in part I of this paper, with various other defects in the noble metals, has been

studied using a partial wave treatment of electron scattering by the defects.

In the case of the interaction of vacancies with substitutional impurities in silver and copper, the energy of association of the defect pairs has been calculated for the nearest neighbor configuration of the two defects. The resulting binding energies cannot be compared with direct experimental data, but appear reasonable in view of the activation energies for self-diffusion of the impurity ions in the appropriate noble metal lattice. This may be taken as a further vindication both of the description afforded by the partial wave treatment of processes occurring in the neighborhood of an anomaly in a metal lattice, and of the model of a vacancy used here, although it may be commented once more that models and techniques having less physical justification have also been used to supply sensible data.

The long-range characteristics of the interaction between vacancies and both point and extended defects have also been investigated, and particular attention has been drawn to the oscillatory nature of the interaction as a function of separation of the defects, together with the increase in range of the interaction evident on passing from point to more extended defects. These effects could not, of course, be predicted from consideration of the statistical model of an electron gas. It has also been noted that a short-range attractive interaction between vacancies and other defects which repel the electron gas will result from the decrease in conduction electron surface energy produced by the proximity of the defects.

The present paper is part of a more extensive treatment of interactions between defects in the monovalent metals in general. Computations of impurity-impurity interaction energies in various solvents are in progress and will be reported in due course.

ACKNOWLEDGMENTS

It is a pleasure to thank Professors D. Lazarus and J. S. Koehler for many helpful discussions and for their encouragement throughout the course of this work.

³⁵ W. M. Lomer, *Phil. Mag.* 2, 1053 (1957).