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Effect of Point Imperfections on the Electrical Properties of Copper. I. Conductivity*

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Changes in resistivity due to the addition of substitutional impurities and due to the presence of vacancies or interstitials in copper have been evaluated. It was assumed that the free-electron approximation is valid and that Matthiessen's rule holds. Relaxation of the lattice about the imperfections was neglected. The scattering potentials for the various imperfections were derived from the appropriate Hartree fields, and the partial wave method was employed in the evaluation of the scattering cross sections. In each case, the potentials were adjusted until the phase shifts satisfied the Friedel sum rule. The phase-shift calculations were carried out on the ILLIAC (University of Illinois Graduate School High Speed Electronic Digital Computer).

The calculated resistivities due to small concentrations of gallium, germanium, and arsenic in copper, though consistently too large, are in fair agreement with measurements of Linde. The calculated change in resistivity due to interstitials in copper, 1.4 μohm-cm per atomic percent, is essentially the same as that due to an equal concentration of vacancies. This result is at variance with earlier predictions based on annealing experiments on irradiated copper. A recent interpretation of the annealing spectrum of irradiated copper by Cooper, Koehler, and Marx appears to be consistent with the present results and offers agreement with a variety of theoretical and experimental work, although some difficulties remain unresolved.

On the basis of the calculations reported here and comparison with Linde's results for dilute substitutional alloys of copper, it is concluded that the resistivity increase due to a concentration of one atomic percent of Frenkel defects in copper is probably between 1.5 and 2.0 μohm-cm, with vacancies and interstitials contributing about equally to the scattering of conduction electrons.

I. INTRODUCTION

During the past few years interest in the effects of nuclear radiation on solid materials has grown considerably. In particular, radiation damage of metals has been the subject of many experiments and much discussion and speculation.[1,2] These investigations are, in a general sense, directed toward an understanding of the properties of imperfections introduced into the metallic lattice as a result of bombardment by fast, massive particles, and also toward a knowledge of the effects which these imperfections have on the physical properties of the substance under examination.

By far the most numerous imperfections which appear as a result of irradiation are vacancies and interstitials, these being created by collisions of the bombarding particle with atoms of the lattice. If the energy of the incident particle is sufficient, the particle will not only be capable of creating single interstitial-vacancy pairs with each collision, but the primaries so formed may in turn eject secondaries from the normal lattice sites. The problem of the total number of interstitial-vacancy pairs to be expected as a result of bombardment by massive charged and uncharged particles of known energy has been treated by Seitz,[3] and more recently by Harrison and Seitz[4] and by Snyder and Neufeld.[5] These more recent investigations indicate that the original results obtained by Seitz probably underestimated slightly the number of Frenkel defects produced by irradiation.

At sufficiently elevated temperatures the vacancies and interstitials created by radiation become mobile, and annealing of radiation damage takes place. The annealing spectrum is of fundamental interest and has been the object of considerable experimental study. The results of such investigations, yielding values for the mobility energy of the imperfection which is believed to be responsible for the observed annealing peak, are of much concern also in studies of self-diffusion[6] and nuclear resonance.[7]

Vancancies and interstitials as well as other point imperfections, such as substitutional impurities, produce measurable changes of many of the physical properties of the metal in which they are present. For example, conductivity,[8] thermoelectric power,[9] elastic constants,[10,11] and rate of self-diffusion,[12–14] are among the numerous properties which exhibit significant changes for relatively small impurity concentrations.

Because electrical measurements can be performed with high precision and relative ease, by far the most numerous data available pertain to changes of the electrical properties, particularly of the conductivity. Point imperfections in otherwise pure metals cause an increase in the resistivity proportional, at low concentrations, to the concentration of the imperfection. If the resistivity change resulting from the presence of one atomic percent of a given imperfection is known, resistivity measurements lead most directly to a

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knowledge of the concentration of that imperfection in a specimen. Thus, residual resistance is often used as a measure of the purity of a metal sample.[15]

In the case of radiation damage the analysis of resistivity measurements is complicated for two reasons. First, bombardment creates two types of imperfections, vacancies and interstitials. Second—even more serious an obstacle to an interpretation of experimental data—, the magnitude of the effect of these imperfections, particularly of interstitials, on the resistivity is somewhat uncertain. Estimates of the resistivity due to one atomic percent of interstitials in copper range from 0.6 to 10 μohm-cm.[16,17]

In order to arrive at a more reliable value for the resistivity increase due to interstitials in copper, a detailed calculation of the cross section for scattering of conduction electrons by an interstitial copper ion was undertaken. The present work is similar to an investigation of Jongenburger[18] concerning the effect on the resistivity of vacancies in copper.

In Sec. II, the method of calculation is briefly described. Section III is devoted to the application of this method to a calculation of the resistivities of dilute solid solutions of gallium, germanium, and arsenic in copper. The results which are obtained and the measured resistivity changes due to these impurities are compared, and it is found that the calculated resistivity changes are consistently too large although they are of the correct magnitude. The method is next applied, in Sec. IV, to the calculation of the resistivity changes due to interstitials in copper. In Sec. V the results of these calculations are discussed and compared with results of recent annealing experiments on irradiated copper. The experiments are examined in the light of the present and previous theoretical as well as experimental work, and a tentative interpretation of the annealing spectrum is advanced which is consistent with many related results, although certain difficulties still remain unresolved. A conclusion summarizes the significant results and speculations.

II. METHOD OF CALCULATION

A. The Scattering Cross Section

The following assumptions, commonly made in calculations of the resistivity due to point imperfections, are used:

(1) The free-electron approximation for conduction electrons is valid.

(2) The scattering potential associated with the imperfection is spherically symmetric.

(3) Matthiessen's rule is valid.

(4) The effect on the resistivity of relaxation of the lattice about the imperfections is negligible.

The first three assumptions need no further discussion; the effect of relaxation of the lattice about imperfections had not been considered in detail until Dexter showed that the last of the above assumptions is justified.[16]

The resistivity increment due to a concentration of one atomic percent of a point imperfection is given by[19]

$$\Delta\rho=\frac{\hbar k}{100ne^2}\int[1-\cos\theta]\sigma(\theta)d\omega, \tag{1}$$

where k is the magnitude of the wave vector of the electrons at the Fermi surface, n is the number of free electrons per atom, θ is the angle through which the electron is scattered by the imperfection, $\sigma(\theta)$ is the differential scattering cross section, and $d\omega$ is the element of solid angle.

The differential scattering cross section is calculated by the partial wave method.[20] The application of this method, in which the scattering cross section is given in terms of the phase shifts δ_l, requires the solution of the radial wave equation

$$\frac{d^2u_l}{dr^2}+\left[k^2-U(r)-\frac{l(l+1)}{r^2}\right]u_l=0, \tag{2}$$

where $U(r)=2mV(r)/\hbar^2$, and $V(r)$ is the potential associated with the scattering center.

Since analytic solutions of Eq. (2) can be obtained only for the very simplest potentials, the differential equation usually must be integrated by numerical methods. Generally, the partial wave method is suitable when the only nonvanishing phase shifts are those for small values of l. For the potentials which appear appropriate to scattering by either substitutional impurities or vacancies and interstitials, $\delta_l\simeq0$ for $l\geqslant4$ and for energies corresponding to those of conduction electrons in copper. Although it is, therefore, necessary to perform at most four numerical integrations for each potential, a great deal of time is still required if this is to be done with the aid of a desk calculator only. The task would have been all the more tedious because the criterion which, in part, determines the potential that is to be used, involves the phase shifts themselves [see Eq. (5) below]. Fortunately, Dr. R. Rubenstein made available to the writer a program he had written for the solution of the radial wave equation by the ILLIAC,[21] and the calculation could be performed in very short order. The coding was done most expertly by Mrs. M. C. Huse.

Once the phase shifts are known, the differential

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scattering cross section is obtained from the expression

$$\sigma(\theta)=\frac{1}{k^2}\left|\sum_{l=0}^{\infty}(2l+1)\exp(i\delta_l)\sin\delta_l\,P_l(\cos\theta)\right|^2. \quad (3)$$

The resistivity can be evaluated directly in terms of the phase shifts. When Eq. (3) is substituted into the integrand of Eq. (1) the following results[22]:

$$\Delta\rho=\frac{4\pi\hbar}{100ne^2k}\left[\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l - 2l\sin\delta_{l-1}\sin\delta_l\cos(\delta_{l-1}-\delta_l)\right]. \quad (4)$$

As a partial check on the self-consistency of the potential, one may employ the Friedel sum rule.[23] Friedel has shown that if N is the number of electrons which must be attracted locally to the imperfection to give effective screening, then

$$N=\frac{2}{\pi}\sum_{l=0}^{\infty}(2l+1)\delta_l. \quad (5)$$

In the case of a vacancy in a monovalent metal $N=-1$, for an interstitial $N=+1$.

B. Choice of Potential

Changes in resistivity of the ideal metals due to addition of small concentrations of substitutional impurities were measured by Linde,[8] and his results were explained by Mott,[24] who calculated the cross section for scattering of conduction electrons by a substitutional impurity in the free-electron approximation. Mott assumed that the impurity could be represented by the screened Coulomb potential of a point charge Ze, where Z is the valence difference between solvent and solute atom, and he made use of the Born approximation in the evaluation of the scattering cross sections. He found that agreement between calculated and experimental results could be obtained only if the screening radius, which appears as a parameter in the expression for the resistivity increase, was chosen to be about half that predicted by the Fermi-Thomas model. However, an important empirical conclusion of Linde, namely that the change of resistivity is proportional to the square of the valence difference, is a direct consequence of Mott's calculation.

Recently, Friedel has redetermined the scattering cross section from a screened Coulomb potential using a partial wave analysis.[25] He obtained reasonably good agreement with Linde's results by requiring that the phase shifts give the correct Friedel sum when substituted into the right-hand side of Eq. (5), N being set equal to the valence difference Z. He also found that under these conditions the appropriate screening radii did not differ greatly from those obtained by the Fermi-Thomas model.

In his calculation of the resistivity due to vacancies in copper, Jongenburger[18] also made use of the free-electron approximation, but he assumed that the removal from the lattice of an ion with its associated potential is equivalent to adding, at that position in the lattice, a potential of opposite sign. He, therefore, chose for his scattering potential the negative of the Hartree potential of a free copper ion,[26] and this potential he then modified to account for the screening by the conduction electrons. Since the vacancy must be neutral, screening is accomplished by effectively displacing one conduction electron from the vicinity of the vacancy. Jongenburger assumed that this screening can be approximated by creating in the electron gas a spherical hole of unit charge and of radius r_s, where r_s is defined by $4\pi r_s^3/3=\Omega$, Ω being the atomic volume. On calculating the phase shifts he found that they nearly satisfied the Friedel sum; substitution of these phase shifts into Eq. (4) gave for the resistivity due to one atomic percent of vacancies in copper

$$\Delta\rho_v=1.25\ \mu\text{ohm-cm}.$$

The scattering potentials for the calculations which will be reported in the following sections were obtained by taking the difference between the Hartree potentials for the case with and without the presence of the imperfection, and then adjusting the screening charge distribution until the phase shifts satisfied Eq. (5). It was found that if, in Jongenburger's calculation of the resistivity due to vacancies, r_s is used as an adjustable parameter and so chosen that Eq. (5) holds exactly,

$$\Delta\rho_v=1.33\ \mu\text{ohm-cm}.$$

It has been pointed out by Friedel[25] that the calculated resistivities do not depend critically on the choice of potential as long as Eq. (5) is satisfied. Thus, for example, the use of a square barrier of extension equal to the radius of one atomic volume may be used to represent a vacancy. If the height of the barrier is adjusted so that the Friedel sum is -1, the resistivity which is obtained is[27]

$$\Delta\rho_v=1.28\ \mu\text{ohm-cm},$$

in agreement with the values quoted above. For calculations of the thermoelectric power, however, the choice of potential appears to be more critical, and, in the case of substitutional arsenic in copper, the potential derived from the Hartree self-consistent fields by the method which has just been outlined gives better agreement with experiment than an equivalent square potential well.[28]

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III. SUBSTITUTIONAL IMPURITIES IN COPPER

The Hartree potentials for gallium, germanium, and arsenic for various states of ionization are known,[29] and the resistivity increments due to small concentrations of these impurities in copper have been measured by Linde.[8] These substitutional dilute alloys of copper are, therefore, ideally suited to test the validity of this method of determining the resistivity increases due to point imperfections and of the assumptions which have been made.

Since the valences of these impurities exceed that of copper, the scattering potentials will be attractive, and the screening electrons may go into bound states in such potentials. This is likely to be the case for the two 4*s*-electrons of the impurities considered here, and may also occur for all but one of the remaining valence electrons. Indeed, it was found that the phase shifts added to nearly the correct Friedel sum if a scattering potential was used which is the difference in the Hartree potentials of Cu^+ and, for example, As^+. However, use of the Hartree potentials of As^{++} or As^{+++} screened by one, respectively two, negative charges distributed uniformly in one atomic volume, did not give rise to phase shifts which met with the condition imposed by Eq. (5). This is indicated in Table I which also lists the calculated and measured resistivity increases per atomic percent due to these impurities when in solid solution in copper. The calculated resistivities were obtained by making slight adjustments in the scattering potentials so that the Friedel sums were exactly equal to Z. The required changes were made by extending the range of the scattering potential for the case of Ga^+, and reducing the ranges for the cases of Ge^+ and As^+; these adjustments were accomplished by slightly altering the screening charge distributions, leaving the core potentials unchanged.

From the tabulation of the calculated and experimental resistivities it appears that the calculated resistivities, although of the correct magnitude, are consistently larger than the measured. Figure 1 shows the results of the present calculation and the resistivity changes as measured by Linde, as well as those obtained by Friedel using a screened Coulomb potential to represent the impurity. It is seen that the best agreement occurs for large valence differences; this is not particularly surprising in view of the fact that nearly all effects except those attributable to valence difference were neglected. Part of the discrepancy may well be due to neglect of relaxation of the lattice, since, as Dexter has shown,[16] relaxation tends to reduce the resistivity changes. On the whole, agreement between calculated and experimental values is reasonably good. Further justification for the use of scattering potentials derived from the Hartree fields may be the good agreement between calculated and measured thermoelectric power changes due to small concentrations of arsenic in copper.[28] It is also significant that the most satisfactory potentials are those obtained by taking the difference between singly ionized copper and the impurity in the same state of ionization. Apparently, the screening of the impurity is accomplished by electrons whose charge distribution closely resembles that of electrons occupying bound states in the Hartree potential of the free impurity ion.

TABLE I. Resistivities due to one atomic percent of gallium, germanium, and arsenic in copper. The state of ionization of the impurity refers to the Hartree potential which was employed in arriving at the scattering potential for use in Eq. (2).

Impurity and state of ionization	$(2/\pi)\Sigma_l(2l+1)\delta_l$	$N=Z$	$\Delta\rho$ (calc)	$\Delta\rho$ (meas)
Ga^{+++}	1.0	2.0		
Ga^+	1.86	2.0	2.7	1.4
Ge^{++}	1.87	3.0		
Ge^+	3.2	3.0	5.0	3.75
As^{+++}	2.0	4.0		
As^{++}	2.75	4.0		
As^+	4.25	4.0	8.2	6.8

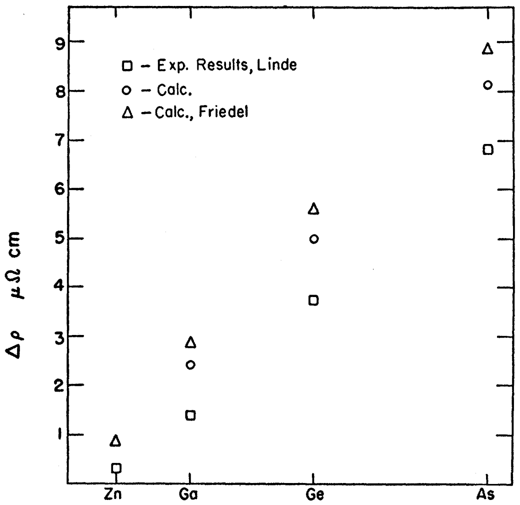

FIG. 1. Resistivity increase due to small concentrations of impurities in copper. Circles show the results of the present calculation; squares show the measured resistivities obtained by Linde; triangles are the calculated values obtained by Friedel.

IV. RESISTIVITY DUE TO INTERSTITIALS IN COPPER

An interstitial copper atom presumably enters the copper lattice in the state Cu^+. Hence, for the scattering of electrons by an interstitial in copper, the scattering potential which is to be used in our approximation is the Hartree potential of Cu^+, suitably screened.

The self-consistent potential of Cu^+ is, of course, sufficiently strong to bind all of the core electrons. In particular, the bound states lying closest to zero energy are the 3*s*, 3*p*, and 3*d* states. In calculating the phase shifts for an electron of energy slightly greater than

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zero, the $l=0$ phase shift, for example, will be in excess of $5\pi/2$, that phase shift which corresponds to the $n=3$, $l=0$ bound state. However, this state is already occupied by two electrons of the core, and these are not taken from the conduction electron distribution. It is only the $l=0$ phase shift in excess of $5\pi/2$ which gives the zero angular momentum contribution to the screening charge associated with a local disturbance of the electron gas. Thus, before evaluating the Friedel sum the values $5\pi/2$, $3\pi/2$, and $\pi/2$ must be subtracted from the $l=0$, $l=1$, and $l=2$ phase shifts, respectively.

As in the case of the substitutional alloys, it was assumed that the core potentials of the free ion and of the ion in the lattice are the same, and only the screening charge distribution was adjusted to meet the Friedel sum condition. Since, in the case of the substitutional alloys of valences higher than copper the most satisfactory screening charge distributions were those corresponding to bound states, a screening charge distribution resembling that of a 4*s*-electron was used for the interstitial calculation. This is, of course, a somewhat arbitrary choice, but, as anticipated,[25] the results are not very sensitive to these particular details as long as the phase shifts conform to Eq. (5).

Figure 2 shows twice the effective nuclear charges for singly ionized copper,[26] for the assumed screening charge distribution, and for the resulting interstitial potential as functions of radius. For this potential the calculated phase shifts are

$$\delta_0=3\pi+0.258;\ \delta_1=2\pi+0.516;\ \delta_2=0.252;\ \delta_3=0.011.$$

When the phase shifts corresponding to the highest bound states of the core are subtracted from the above values one finds that the Friedel sum is unity. Substitution of the phase shifts into Eq. (4) gives for the resistivity increase due to one atomic percent of interstitials in copper:

$$\Delta\rho_i=1.40\ \mu\text{ohm-cm}.$$

Twice the effective nuclear charges for two different screening distributions are shown in Fig. 3. The solid curve is the same as the corresponding one of Fig. 2; the other two distributions were also adjusted until the phase shifts calculated from the resulting scattering potentials satisfied the Friedel condition. The sharp cut-off distribution (dot-dash curve) leads to the following phase shifts:

$$\delta_0=3\pi+0.32;\ \delta_1=2\pi+0.52;\ \delta_2=0.24;\ \delta_3=0.01;$$

the corresponding resistivity increase per atomic percent is

$$\Delta\rho_i=1.29\ \mu\text{ohm-cm}.$$

The scattering potential obtained by using the long-tailed distribution (dotted curve) gives rise to phase shifts:

$$\delta_0=3\pi+0.22;\ \delta_1=2\pi+0.50;\ \delta_2=0.27;\ \delta_3=0.01.$$

Substitution of these phase shifts into Eq. (4) leads to a resistivity change:

$$\Delta\rho_i=1.41\ \mu\text{ohm-cm per atomic percent}.$$

It is seen that although the assumed screening charge distributions for these three cases differ considerably (the effective nuclear charges are drawn to logarithmic scale in Fig. 3) the change in the calculated resistivity increase is not very significant.

Thus, the calculated increase in resistivity due to the presence of interstitials in copper is about 1.4 μohm-cm per atomic percent, and this is practically the same as the resistivity due to an equal concentration of vacancies.

To the extent to which it is valid to extrapolate the results of the previous section to the effect of Frenkel defects on the resistivity of copper, it is reasonable to presume that the calculated values reported here and also by Jongenburger overestimate the true resistivity increase. A reasonable estimate for the change in resistivity due to vacancy-interstitial pairs in copper is probably 1.5–2.0 μohm-cm per atomic percent, with each type of lattice defect contributing about equally to the total. These conclusions are in good agreement with earlier estimates of Dexter.[16]

V. DISCUSSION OF RESULTS

In recent years, a number of experiments on the annealing of radiation damage in copper have been performed, and two of these will be considered in some

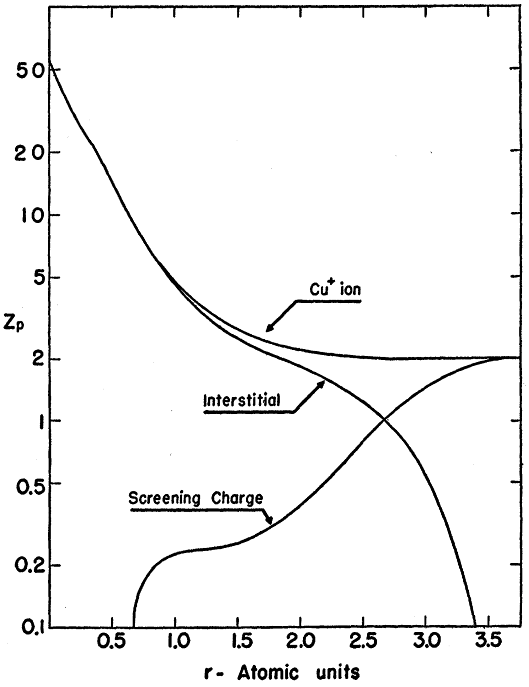

FIG. 2. Twice the effective nuclear charges as functions of radius for singly ionized copper, for the assumed screening charge distribution, and for the resulting interstitial potential.

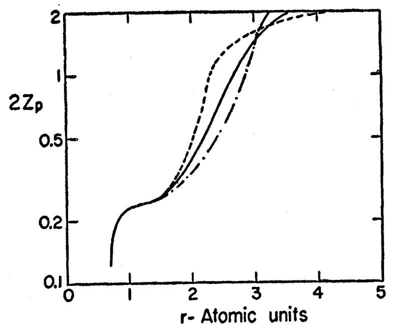

FIG. 3. Twice the effective nuclear charges for three screening charge distributions as functions of radius. Solid curve is the same as the corresponding curve of Fig. 2.

detail here. In addition to this work, the results of investigations on self-diffusion in the noble metals and on the quenching-in of vacancies in gold also yield valuable information on the properties of lattice defects in copper.

Simultaneous resistivity and calorimetric measurements on irradiated copper were carried out by Overhauser,[17,30] who studied in this manner the annealing spectrum in the temperature range extending from about −180°C to room temperature for samples irradiated at liquid nitrogen temperature. Some annealing was observed over the entire temperature range from −180°C to −40°C, but no unique activation energy could be assigned in that range. An initial bending of the resistivity *versus* bombardment curve was apparent, and this was attributed, in part, to thermal annealing at the bombardment temperature. This anneal was ascribed to a recombination of close pairs, and an activation energy of approximately 0.2 ev was assigned to that process.

At about −30°C Overhauser found a sharp annealing peak with an activation energy of 0.68 ev. An analysis of the kinetics of the anneal indicated that it was governed by a process of bimolecular recombination, and from this it was inferred that the anneal corresponded to a recombination of vacancies and interstitials. The simultaneous measurements of resistivity and of stored energy released during anneal lead to the value of 1.7 (cal/gram) per μohm-cm for the stored energy to resistivity ratio in this material at −30°C as well as in the lower temperature range. If one now uses a specific value for the energy of formation of a Frenkel defect in copper, the resistivity due to one atomic percent of vacancy-interstitial pairs may be obtained. Overhauser used energies of formation of 4 ev for interstitials and 1 ev for vacancies; the latter value is probably somewhat low, 1.3 to 1.5 ev being perhaps more nearly correct.[31] Taking 5.3 ev as the energy of formation of a Frenkel defect, the stored energy from one atomic percent concentration of pairs is 19 cal/gram. Hence, the resistivity per atomic percent of Frenkel pairs is $19/1.7=11.2$ μohm-cm. When the calculated resistivity due to one atomic percent of vacancies is subtracted from the above, one arrives at the estimate of Overhauser, namely a resistivity increase of approximately 10 μohm-cm per atomic percent of interstitials in copper. This value is evidently in substantial disagreement with the results of the previous section.

Before discussing the second experiment, some difficulties in the interpretation which was outlined above will be indicated. If the anneal at −30°C is due to recombination of vacancies and interstitials, then the activation energy of the process must be that associated with motion of the more mobile of the two imperfections. The most recent measurement of the activation energy for self-diffusion in copper yielded the value 2.04 ev.[32] Since it is fairly certain that self-diffusion in copper proceeds by a vacancy mechanism, 2.04 ev is the sum of the energies of formation and of motion of vacancies in copper. Subtracting the calculated energy of formation of vacancies, one arrives at an energy of about 0.7 ev for motion of vacancies in copper. Further evidence that the energy of motion of vacancies is approximately 0.7 ev is provided by the measurements of Kauffman and Koehler,[33] who found that in gold the activation energies of formation and motion of vacancies are 1.28 ev and 0.68 ev, respectively. Although similar measurements on copper have not been reported, the fact that the two metals have the same crystal structure, have almost identical activation energies for self-diffusion, and are otherwise similar in many respects, gives support to the belief that the activation energy for motion of vacancies in copper is about 0.7 ev. If, then, the energy of 0.68 ev of the −30°C anneal is associated with motion of vacancies, recombination of Frenkel pairs at that temperature can occur only if interstitials are less mobile than vacancies. However, Huntington[34] recently calculated the energy of motion of interstitials in copper and found that it is rather small, in the neighborhood of 0.1 or 0.2 ev. It then follows that interstitial-vacancy recombination should occur at a temperature considerably below −30°C, and it is the low-temperature anneal reported by Overhauser, to which he assigned a tentative activation energy of 0.2 ev, that might well be due to recombination.

A more recent experiment[35] throws considerable light on these questions. Copper, silver, and gold were bombarded with 12-Mev deuterons at liquid helium temperature, and the resistivity increases were determined as functions of the integrated beam intensity. Following the irradiation the samples were permitted

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to warm to room temperature, and the resistivity annealing spectrum was obtained.

A small amount of curvature of the resistivity *versus* bombardment curve was observed even at these low temperatures, the effect being attributed to so-called radiation annealing. The annealing spectrum of copper observed by Cooper, Koehler, and Marx exhibited a very marked annealing peak at about 40°K, at which temperature about half of the initial resistivity increase annealed out. Additional resistivity decrease was observed in the range 45°K to 220°K, which was followed by another peak corresponding to the one found by Overhauser.

The estimated activation energy for the 40°K anneal is about 0.1 ev, and this is approximately the same as the activation energy for motion of interstitials as calculated by Huntington. It is, therefore, reasonable to associate this low-temperature anneal with motion of interstitials. Since the activation energy for motion of vacancies in copper is very nearly identical to the energy of 0.68 ev assigned to the -30°C anneal observed in both experiments, it is concluded that this anneal arises from the motion of vacancies.

According to this interpretation, however, there should be essentially no interstitials in the lattice at the higher temperature, and the bimolecular nature of the process requires an explanation other than vacancy-interstitial recombination. It has been suggested[35] that as vacancies become mobile they will combine to form divacancies, and that this process accounts for the second-order kinetics. Calculations of Bartlett and Dienes[36] indicate that such combined pairs should be stable and also considerably more mobile than single vacancies. Because of their high mobility, the effect of divacancies on the resistivity will not be subject to measurement, for these double vacancies will anneal out practically as soon as they are formed, moving to traps such as dislocations or grain boundaries, or giving rise to small holes by clustering.

Further confirmation of a divacancy process comes from the work of Kauffman and Koehler on the annealing of vacancies in gold. The annealing here also proceeds by a bimolecular reaction,[37] and since vacancies only are present, formation of divacancies is the only consistent interpretation of these findings.

Let us now see if the above interpretation of the annealing spectrum of irradiated copper leads to agreement with the calculated resistivities due to vacancies and interstitials. Bartlett and Dienes obtained for the energy of dissociation of a divacancy 0.6 ev, and this is then the energy released when two vacancies combine to form such a pair. Additional energy will, however, be released as the divacancies anneal out at -30°C either by going to trapping sites or by the formation of small pores. That most of the divacancies do not disappear at the surface is indicated by measurements on the recovery of volume change due to radiation damage.[38] It is found that on warming to room temperature only a very small fraction of the original volume increase disappears. The existence of small holes in cold-worked copper has also been postulated by Blin and Guinier[39] from measurements of small-angle x-ray scattering. If it is assumed that divacancies form pores encompassing about 200-lattice sites, the energy released per vacancy in the annealing process may be estimated. To obtain the energy of a small hole we assume that all of the energy is due to the surface,[40] and taking as the surface tension that of the molten metal, the surface energy of such a hole is then about 10^{-11} erg. The energy released per vacancy as they combine to form divacancies which, in turn, cluster into these holes, is then about 0.9 ev, assuming that the energy of formation of a vacancy is 1.3 ev. The measured stored energy to resistivity ratio of 1.7 (cal/gram) per μohm-cm now leads to a resistivity increase due to one atomic percent of vacancies of about 1.6 μohm-cm, in fair agreement with the calculated values.

A rough estimate of the resistivity due to interstitials may also be obtained. Let us assume that, immediately following bombardment at helium temperature, interstitials and vacancies exist in equal concentrations. It follows that annealing of interstitials with a simultaneous decrease of residual resistivity by half implies that the resistivity due to these imperfections is probably of the same order of magnitude and definitely less than that due to vacancies, since interstitials will combine at least in part with vacancies. This conclusion is also in qualitative agreement with the present results.

Although so far the foregoing interpretation of the annealing spectrum appears to be internally consistent and in agreement with a variety of theoretical and experimental results, there remain several difficulties which are unresolved. Overhauser reported that the ratio of energy released to resistivity change was the same in the region -100°C to -40°C as at -30°C, an observation which would indicate that the same process is responsible for the annealing over the entire temperature range studied by him. This conclusion may be difficult to reconcile with a process other than vacancy-interstitial recombination.

Another discrepancy arises when one calculates the expected resistivity increase due to bombardment with that which is actually observed. Multiplication of the estimated resistivity due to Frenkel defects by the number of defects as calculated by Harrison and Seitz[4] yields values about three times as large as those measured by Cooper, Koehler, and Marx.

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VI. CONCLUSIONS

The results of calculations on the resistivity increase due to substitutional impurities and due to vacancies and interstitials in copper were presented. The partial wave method was used to obtain the differential scattering cross section for scattering of conduction electrons by these point imperfections. The calculations were carried out in the free-electron approximation, and relaxation of the lattice about the imperfections was neglected.

The scattering potential was approximated by taking the difference of the Hartree potentials with and without the imperfection present, and suitably screening this potential by an appropriate charge distribution. The screening charge distribution was adjusted until the calculated phase shifts satisfied the Friedel sum criterion, Eq. (5). Approximate agreement with resistivity changes measured by Linde was obtained under these assumptions, although the calculated resistivities are consistently too high. The most satisfactory screening charge distributions about impurities with valences greater than copper are very similar to the charge distributions corresponding to bound states in the free ion. As anticipated by Friedel, the details of the scattering potential do not influence the results very much as long as the phase shifts satisfy the Friedel sum condition.

The resistivity due to interstitials in copper was determined in the same manner. The calculated resistivity, 1.4 μohm-cm per atomic percent of interstitials, is practically the same as the calculated resistivity due to an equal concentration of vacancies. In view of the results in the case of substitutional alloys, it is believed, however, that the true resistivity increase due to Frenkel defects is overestimated by these calculations, and that a reasonable value lies between 1.5 and 2.0 μohm-cm per atomic percent of vacancy-interstitial pairs.

This result is in substantial disagreement with an earlier estimate of Overhauser. An attempt is made to reinterpret Overhauser's results in the light of more recent work of Cooper, Koehler, and Marx. It is suggested that at 40°K interstitials become mobile, and that the annealing peak observed by Overhauser and also by Cooper, Koehler, and Marx at about $-30°$C is due to motion of vacancies. These presumably combine to form divacancies, thereby accounting for the bimolecular nature of the anneal, and the divacancies, in turn, rapidly combine to form larger clusters. With this interpretation the resistivity due to vacancies as deduced from Overhauser's measurements is in fair agreement with the present estimates. This interpretation of the annealing spectrum is also consistent with the estimated resistivity due to interstitials.

Furthermore, the approximate mobility energy of interstitials as obtained from the 40°K anneal is in agreement with theoretical estimates of Huntington. The energy of motion of 0.68 ev associated with the $-30°$C anneal is in very close agreement with mobility energies of vacancies as deduced from self-diffusion measurements and quenching experiments on gold. There remain, however, several difficulties which have not been resolved.

VII. ACKNOWLEDGMENTS

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Note added in proof.—Recently, Jongenburger [Nature **175**, 545 (1955) hereafter referred to as J] reported results of a calculation of the change in resistivity due to interstitials in copper, using a square-well potential as an approximation to the scattering potential of the interstitial. He found that $\Delta\rho_i$, the resistivity increase due to the interstitial, is between 1 and 2 μohm-cm/atomic percent, in substantial agreement with the results reported here. The contribution to $\Delta\rho$ arising from the displaced nearest and next nearest neighbors was also estimated with the result that $\Delta\rho_d$, the resistivity increase due to these displacements, is 3.5 μohm-cm/atomic percent, leading to a total resistivity due to interstitials of about 5 μohm-cm/atomic percent. The writer believes, however, that, for the following reasons, assumption 4 is valid and that the influence of the displaced atoms was considerably overestimated by Jongenburger.

(1) It is assumed in J that an ion which has suffered a *static* mean-square displacement from its equilibrium position contributes just as much to the resistivity as an ion in thermal vibration at a high temperature ($T>\theta$) with the same mean-square displacement. In the latter case, however, primarily phonons of maximum wave vector are excited, so that in each collision an electron suffers a large momentum change. In the case of a static displacement the same is not true and a much smaller average momentum transfer is to be expected.

(2) In J the mean-square displacements of all the nearest and next nearest neighbors to the interstitial are added to give a total mean-square displacement about the imperfection. In this approximation all interference effects between the several displaced atoms are neglected, an approximation which is probably not

very good when the displaced atoms are nearest neighbors to each other. Including interference terms need not, of course, necessarily reduce the scattering, and may, when treated in detail, even lead to an enhancement of $\Delta\rho_D$.

(3) The results of J would indicate that $|m|^2$ and $|M|^2$, in the notation of Dexter,[16] are, in arbitrary units, of order 1.5 and 3.5, respectively. Now it was shown in reference 16 that the matrix elements m and M are, in the case of interstitials, very likely of opposite sign. Since the resistivity is in fact related to $|m+M|^2$, the above values for $|m|^2$ and $|M|^2$ may well lead to a rather small resistivity change due to interstitials, perhaps of order 0.5 μohm-cm/atomic percent. This crude argument is used here only to point out that it is essential to include interference effects when scattering from the imperfection and from the associated lattice distortion appears to be of the same magnitude when considered independently. [See also D. L. Dexter, Phys. Rev. **98**, 543 (1955).]

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de Haas-van Alphen Effect in Arsenic

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The de Haas-van Alphen effect has been studied in single crystals of rhombohedral (metallic) arsenic in the liquid helium temperature range and in magnetic fields up to 25 kilogauss. The effect in arsenic is characterized by long-period (up to $\sim 4\times 10^{-5}$ gauss^{-1}) oscillations upon which are superposed three short period (up to $\sim 6\times 10^{-7}$ gauss^{-1}) terms. Analysis in terms of existing theory attributes the long-period oscillations to electrons occupying a constant energy surface in momentum or wave-number space which to a first approximation is an ellipsoid of revolution with a degeneracy energy $E_{0l}=1.59\times 10^{-14}$ erg. The pertinent electrons in the case of the short-period oscillations can be attributed to three identical ellipsoidal constant-energy surfaces oriented so as to satisfy the trigonal symmetry of the arsenic lattice and having a degeneracy energy $E_{0s}=29.4\times 10^{-14}$ erg. In addition, the electronic effective masses have been evaluated. A method for growing arsenic single crystals is described.

INTRODUCTION AND THEORY

THE de Haas-van Alphen effect is characterized by a periodic dependence of the magnetic susceptibility of metal single crystals upon reciprocal magnetic field at low temperatures. Since its discovery by de Haas and van Alphen[1] in bismuth, the effect has been observed in fourteen other metal single crystals,[2] and correlations have been established between the susceptibility oscillations and similar oscillations in the magnetoresistance,[3–5] Hall effect,[6,7] thermoelectric effect,[8] and thermal conductivity.[9]

The discovery of short-period susceptibility oscillations in arsenic was reported briefly in an earlier communication[10] by the author. In addition, much-longer-period oscillations have subsequently been detected, and the present paper concerns detailed investigations of both the long- and short-period terms.

The theory of the de Haas-van Alphen effect was developed by Peierls,[11] Blackman,[12] and Landau[13] and is based upon a free-electron model. In the presence of a magnetic field the electronic energy levels coalesce into quantized levels of field-dependent spacing and degeneracy. As the field is varied, the electrons are redistributed among these levels in such a way as to give rise to the susceptibility oscillations. The effect of the periodic electric field of the lattice is taken into account by the introduction of anistropic effective electronic masses, and in many cases (including arsenic) the pertinent constant-energy surfaces in momentum or wave-number space may be approximated by one or more ellipsoids. Such approximately ellipsoidal pockets of electrons (or holes) presumably exist where the Fermi surface overlaps (or underlaps) Brillouin zone boundaries. The resulting high curvature and correspondingly low degeneracy energy and low effective electronic masses favor easy detection of the de Haas-van Alphen effect.

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