Scattering of Electrons from Clustered Vacancies in Copper*

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The excess resistivity, ρ, and resistivity per unit stored energy, q, associated with dislocations, vacancies, and interstitials are briefly reviewed, and the same quantities are calculated for clustered vacancies. For clusters of more than one hundred vacancies, which seem to exist at room temperature in cold-worked or bombarded copper, q is larger by factors of about 3, 8, and several hundred than the corresponding ratios for vacancies, interstitials, and dislocations.

INTRODUCTION

NUMEROUS experimental and theoretical papers have appeared in the last few years dealing with the stored energy and excess resistivity introduced into a metal upon cold-working or bombarding the sample. For example, Molenaar and Aarts[1] observed that at liquid air temperatures strains of the order of 10% in copper produced a resistivity change of 2.4×10^{-28} ohm cm for each electron volt/cm^3 expended during cold working. We shall be concerned here with the quantity q defined as the ratio of the resistivity change to the energy *stored* per cm^3. Thus, since not all the energy expended is stored, q is somewhat larger than 2.4×10^{-28} ohm cm/(ev/cm^3) under these conditions. As will be seen below, it is difficult to reconcile the calculated scattering cross sections of dislocations and interstitials with a q ratio as large as this, and in fact it is necessary to assume that a large fraction, of the order $\frac{1}{2}$, of the energy expended must be stored in the form of vacancies or small vacancy clusters. The evidence regarding dislocations, interstitials and vacancies will be briefly reviewed, and in the last section another scattering mechanism will be discussed, namely, the scattering by clusters of vacancies.

SCATTERING BY DISLOCATIONS

The extra resistivity of a metal associated with the presence of dislocations has been computed by a number of workers. The most accurate calculation, in which the effects of the shear components of strain are included, was performed by Hunter and Nabarro.[2] For copper, assuming equal amounts of screw and edge component, one may express the excess resistivity, averaged over all orientations of the dislocations, as

$$\langle\Delta\rho\rangle_{Av}=8\times10^{-21}N_D \text{ ohm cm}, \quad (1)$$

where N_D is the dislocation concentration per cm^2. In the limit of free electrons these results agree with those computed in two completely different ways;[3] the numerical coefficient in Eq. (1) has been adjusted (increased) from the calculated value, as described on page 774 of reference 3, so as to make a partly empirical correction for the effects of the potential within the cores of the Cu atoms. Expressing Eq. (1) in a way more suitable for comparing dislocations with other scattering objects, we consider each intersection of a dislocation with an atomic plane as an atomic entity, and find

$$\rho_D=0.15\ \mu\text{ohm cm}, \quad (2)$$

for the average resistivity per atomic percent dislocations. Consideration of the splitting into partial dislocations and stacking faults actually results in a reduction of this figure,[4] which already is appreciably less than the corresponding value for vacancies, interstitials, or impurity atoms.

Koehler[5] has computed the internal energy stored in a straight edge-type dislocation in copper, and concludes that about 1.6×10^8 ev are stored per line cm. Recent work[6] indicates that an appreciably greater energy is stored in a cold-worked crystal in the interactions among dislocations and in jogs, perhaps a factor of ten more. Thus the resistivity per unit stored energy for dislocations is given by

$$q_D\lesssim10^{-29} \text{ ohm cm/(ev/cm}^3), \quad (3)$$

and, comparing with the experimental lower limit,[1] 2.4×10^{-28}, we are led to the conclusion that dislocations are not primarily responsible for the resistivity changes observed by Molenaar and Aarts and others.

SCATTERING BY ISOLATED VACANCIES AND INTERSTITIALS

It is to be expected that vacancies are present in cold-worked metals, being produced by the motion of dislocations through the crystal.[7] This topic has been

* Research supported in part by the U. S. Air Force through the Office of Scientific Research of the Air Research and Development Command.

[1] J. Molenaar and W. H. Aarts, Nature **166**, 690 (1950).
[2] S. C. Hunter and F. R. N. Nabarro, Proc. Roy. Soc. (London) **A220**, 542 (1953).
[3] D. L. Dexter, Phys. Rev. **85**, 936 (1952); **86**, 770 (1952). References to other work are given in these papers.
[4] Blatt, Ham, and Koehler, Bull. Am. Phys. Soc. Ser. II, **1**, 114 (1956).
[5] J. S. Koehler, Phys. Rev. **60**, 398 (1941).
[6] A. Seeger and G. Schoeck, Acta Metallurgica **1**, 519 (1953); G. Schoeck and A. Seeger, *Proceedings of the Conference on Defects in Crystalline Solids*, Bristol, 1954 (Physical Society, London, 1955), p. 340; A. N. Stroh, Proc. Roy. Soc. (London) **A218**, 391 (1953).
[7] F. Seitz, Phil. Mag. Suppl. **1**, 43 (1952).

thoroughly reviewed by Seitz in a recent article, and the reader is referred to reference 7 for the pertinent arguments.

Several sources of information now exist for the resistivity associated with vacancies and interstitials, but general agreement does not seem to have been achieved. From resistivity measurements on copper irradiated with deuterons at liquid helium temperatures[8] and making use of calculations on the number of displacements to be expected,[9] one may conclude that one atomic percent of vacancy-interstitial pairs gives rise to an additional resistivity of 0.5−0.8 μohm cm. It is difficult to see how this result could be very much in error.

Another experiment, performed by Overhauser,[10] involved simultaneous calorimetric and resistivity measurements in the annealing of radiation-damaged copper. On the assumption that the annealing process was the recombination of vacancies with interstitials, and using the value 5.3 ev as the energy released in the annealing of a Frenkel defect, one may compute about 11 μohm cm as the resistivity per atomic percent of Frenkel defects. Blatt has argued,[11] on the basis of Huntington's calculations,[12] that interstitials would not have been present in the irradiated crystals at these temperatures, and has suggested another interpretation for the experiment. In the writer's opinion, however, a detailed understanding of the experiment has not yet been arrived at.

The third source of information on the scattering by vacancies and interstitials is the direct calculation of the scattering cross section, a calculation now having been performed by a number of workers. The first of these, based on a rather crude approximation and largely on analogy with dilute alloys, resulted in 1.0 μohm cm per atomic percent of vacancy-interstitial pairs,[13] about half arising from each imperfection. More recent calculations have been phase-shift analyses with various potentials, of which the most thorough treatment is that by Blatt,[11] who has reviewed the other work. Blatt obtained 1.5 μohm cm and 1.4 μohm cm for 1% of vacancies and interstitials, respectively. He also computed by the same method the excess resistivity for Ga, Ge, As impurities in copper, a computation which can be unambiguously compared with experiment. In all cases his calculated values were substantially higher than the experimental values, and he has concluded that his values for vacancies and interstitials are likewise too large, 0.75 to 1.0 μohm cm per atomic percent being a better range. The writer, with no demonstrable justification, prefers the range 0.5 to 0.75 μohm cm, and in the following will arbitrarily use the value 0.7 μohm cm for both interstitials and vacancies.

An accurate treatment of the effects on resistivity of the lattice distortion around the defects does not seem to have appeared as yet. In the initial treatment[13] a smearing-out, integral approximation was used, from which it appeared that the effects would be small. For the vacancy this may well be the case. However, for the interstitial use was made of the older calculations on the magnitude of the displacements of the neighbors, calculations which have recently been supplanted by a more accurate one.[12] Since the older displacements used were too small by more than a factor of two, a new treatment is certainly required for the interstitials. A recent treatment by Jongenburger[14] has been shown by Blatt[11] to be too unrealistic to allow faith in the results.

Using 1.3 ev as the energy stored in a vacancy and 4.0 ev for the interstitial, we obtain

$$q_v \sim 6.3\times10^{-28} \text{ ohm cm}/(\text{ev}/\text{cm}^3), \quad (4)$$

and

$$q_i \sim 2.1\times10^{-28} \text{ ohm cm}/(\text{ev}/\text{cm}^3), \quad (5)$$

for the resistivity per unit stored energy ratios for vacancies and interstitials. The value for interstitials is quite uncertain, because of possible effects of distortion, and presumably could only be measured by annealing from helium or hydrogen temperatures.

From a comparison of the experimental ratio of Molenaar and Aarts[1] with the values for dislocations and vacancies, it is clear that internal consistency can only be found if a very large fraction of the energy expended in cold work at liquid air temperatures is stored in the form of vacancies, or perhaps clusters of vacancies. It would be extremely valuable to make calorimetric measurements on copper cold-worked at nitrogen temperatures. In metal cold-worked at room temperatures only a small fraction of the energy expended is stored, perhaps three percent.[15] It is clear that if our present views are correct, of the order of 50% of the energy expended at nitrogen temperatures must be stored in the metal, most of it in the form of vacancies or perhaps small clusters.

SCATTERING BY CLUSTERED VACANCIES

As the material anneals upon warming, the vacancies apparently cluster and remain within the sample. This is evidenced by the circumstances that a sizeable fraction of the excess resistivity in copper cold-worked or bombarded at nitrogen temperatures remains at room temperature, and that most of the volume change accompanying radiation damage at low temperatures remains at room temperature.[16] There is additional evidence for large vacancy clusters from the small-angle

[8] Cooper, Koehler, and Marx, Phys. Rev. **97**, 599 (1955).
[9] F. Seitz, Disc. Faraday Soc. **5**, 271 (1949); W. S. Snyder and J. Neufeld, Phys. Rev. **97**, 1637 (1955); **99**, 1326 (1955); W. A. Harrison and F. Seitz, Phys. Rev. **98**, 1530 (1955).
[10] A. Overhauser, Phys. Rev. **90**, 393 (1953).
[11] F. J. Blatt, Phys. Rev. **99**, 1708 (1955).
[12] H. B. Huntington, Phys. Rev. **91**, 1092 (1953).
[13] D. L. Dexter, Phys. Rev. **87**, 768 (1952).
[14] P. Jongenburger, Nature **175**, 545 (1955).
[15] B. Welber, Phys. Rev. **87**, 211 (1952); J. Appl. Phys. **23**, 876 (1952).
[16] H. A. Kierstadt, Phys. Rev. **98**, 245 (1955).

x-ray scattering experiments of Blin and Guinier,[17] though some doubt has been cast on their interpretation by the work of Beeman and co-workers.[18] Thus it was felt worthwhile to compute the excess resistivity to be expected from clusters of vacancies, in the event that their presence may ultimately be demonstrated conclusively.

We shall take as our zero of energy the energy of the bottom of the conduction band of copper. Thus the kinetic energy of the electrons of interest is the Fermi energy, $E_F=7.04$ ev, and the energy of an electron at rest outside the crystal is equal to the inner potential, 11.1 ev, the sum of the Fermi energy and the work function, 4.1 ev.[19] The concentration of conduction electrons is 8.5×10^{22} per cm^3, so that the propagation vector of an electron at the Fermi surface is $k=1.37\times10^8$ cm^{-1} and that of an electron with kinetic energy equal to the inner potential is $k_0=1.70\times10^8$ cm^{-1}.

Our physical model is based on the following: we shall treat the conduction electrons as free electrons, the important ones having 7.04-ev kinetic energy. We shall envisage the cluster of vacancies as a spherical cavity of volume equal to the atomic volume times n, the number of vacancies in the cluster. Within the cavity the potential energy is 11.1 ev, according to our foregoing specification of the zero of energy. Thus we have the problem of the scattering of free electrons from a spherical potential barrier, a problem which can be solved exactly.[20] This model is clearly inadequate for small clusters, inasmuch as it completely neglects the "spilling-over" of the conduction electrons into the cavity, and thus neglects shielding effects. It also clearly neglects the shape of the cavity, which must deviate appreciably from a sphere for small clusters. However, we are particularly interested in large clusters, for which the shielding and shape effects are relatively reduced, although even in this case our neglect of shielding tends to overestimate the scattering cross section.

The phase shifts required for the calculation of the cross section depend on the parameters k and $k'\equiv(k_0^2-k^2)^{\frac{1}{2}}$ as well as the cavity radius $a\equiv n^{\frac{1}{3}}r_0$. (Here $r_0=1.41$ A is the radius of the sphere whose volume is the atomic volume.) The phase shifts, η_l, are given in terms of the unmodified and the modified Bessel functions of the first kind, J and I,

$$\tan\eta_l=(-1)^l\times\frac{kI_{l+\frac{1}{2}}(k'a)J_{l-\frac{1}{2}}(ka)-k'J_{l+\frac{1}{2}}(ka)I_{l-\frac{1}{2}}(k'a)}{kI_{l+\frac{1}{2}}(k'a)J_{-l+\frac{1}{2}}(ka)+k'J_{-l-\frac{1}{2}}(ka)I_{l-\frac{1}{2}}(k'a)}, \quad (6)$$

[17] J. Blin and A. Guinier, Compt. rend. **233**, 1288 (1951); J. Blin, *Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 420; D. L. Dexter, Phys. Rev. **90**, 1007 (1953).

[18] Neynaber, Brammer, and Beeman, Phys. Rev. **99**, 615 (1955).

[19] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 146.

[20] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford Univesity Press, London, 1949), second edition, p. 36.

TABLE I. Calculated resistivities per atomic percent, ρ, and resistivities per unit stored energy, q, for various imperfections.

Scattering entity		ρ μohm cm	$q\times10^{23}$ ohm cm/(ev/cm^3)
Dislocations		0.15	$\lesssim$0.1
Vacancies		0.7	6.3
Interstitials		0.7	2.1
Clusters $n=$	1	(2.22)	(12.2)
	3.5	(1.76)	(14.6)
	10	(1.35)	(16.0)
	35	(0.94)	(16.9)
	100	0.686	17.4
	350	0.501	19.3
	1000	0.343	18.8
	3500	0.237	19.6
	10 000	0.168	19.8

and the scattering cross section, $|f(\theta)|^2$, is found from the relation

$$f(\theta)=\frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta)(e^{2i\eta l}-1). \quad (7)$$

The excess resistivity associated with the presence of N cavities per cm^3 is easily found to be

$$\rho_c=(3\pi^2\hbar N/e^2k^2)Q, \quad (8)$$

where Q is the effective integrated cross section,

$$Q=2\pi\int_0^{\pi}(1-\cos\theta)\sin\theta|f(\theta)|^2d\theta. \quad (9)$$

The presence of the factor $(1-\cos\theta)$ arises in resistivity calculations, as contrasted with usual atomic scattering, from the increased effectiveness of large angle collisions upon the resistivity. Making use of Eqs. (7), (8), (9) and the orthogonality and recursion relations for Legendre polynomials, we obtain the relation

$$\rho_c=\frac{12\pi^3\hbar N}{e^2k^4}\sum_{l=0}^{\infty}(2l+1)\sin^2\eta_l-2l\sin\eta_l\sin\eta_{l-1}\times(\sin\eta_l\sin\eta_{l-1}+\cos\eta_l\cos\eta_{l-1}). \quad (10)$$

This expression has been evaluated by using Eq. (6) and the values of the parameters given above, for a number of choices of the cluster size. The number of phase shifts required for four-figure accuracy in Q was 4, 9, 25, 47, for n equal to 1, 35, 10^3, 10^4. In Table I is shown the resistivity per atomic percent of vacancies as a function of the cluster parameter, n. As expected, this quantity decreases with increasing n. For comparison, the values for dislocations and isolated vacancies and interstitials are also shown.

For large cavities the stored energy is simply equal to the surface energy, $4\pi a^2S$, where S, the surface tension, is 8.56×10^{14} ev/cm^2.[21] Thus in column three we give the resistivity change per unit stored energy, as a function of cluster size. The values given for small clusters are, of course, not at all trustworthy, because

[21] H. B. Huntington, Phys. Rev. **81**, 1035 (1951).

both the stored energy model and the scattering model are inadequate for small n.

It is seen that for sizable clusters of 10^2 or more vacancies, the resistivity per unit stored energy is about 3 times greater than for isolated vacancies. Thus if vacancies cluster as the sample is warmed from low temperatures we may expect to remove a larger fraction of the stored energy than of the excess resistivity. At sufficiently high temperatures we expect the vacancies to evaporate from the clusters and diffuse away, the excess over the equilibrium figure characteristic of the temperature leaving the crystal, annealing of the vacancies becoming complete.

Unquestionable evidence that the vacancies formed at low temperatures actually cluster in the form treated here does not seem to exist. If it were not for the arguments at the beginning of this section, it would seem plausible on geometrical grounds that they tend to cluster in platelets, which form collapsed vacancy disks. However, in this event they would scatter much less effectively for a given energy storage. That vacancies are created both by cold-work and by high energy bombardment at low temperatures seems inescapable; that they cluster in some form or another, upon warming the crystal, likewise appears so. A number of experiments of the type proposed by Seitz[7] seem capable of deciding in detail the fates of the vacancies created by radiation damage and by cold-work. Most of the crucial experiments have either not been performed or have been carried out on alloy systems which introduce additional complexity into the interpretations. An imperfection similar to the type discussed here would seem to be required if, for a given stored energy, there is a relatively large excess resistivity, a relatively large volume increase in the sample, and a large amount of small angle x-ray or neutron scattering.

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Ground-State Solution of the Nonrelativistic Equation for Helium*

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By the inclusion of half-integral powers in the Hylleraas functions for the ground state of the helium atom, it is possible to obtain more rapid convergence in the Ritz variational method applied to the nonrelativistic Schrödinger equation (for infinite nuclear mass), as shown by results of calculations involving from four to thirteen parameters. The energy obtained with 13 parameters, -2.903719 a.u., is the lowest so far published. The coefficients for the normalized wave functions are given.

THE recent remeasurement[1] of the ionization potential of the helium atom with an accuracy of perhaps a few parts per million,[2] is making it possible to undertake a meaningful check on the relativistic theory for this state.[3] To that end, one requires the solution of the nonrelativistic helium wave equation to a corresponding accuracy. The recent calculations by Chandrasekhar and Herzberg[4] using the Ritz-Hylleraas method may perhaps have yielded such results. Uncertainty arises from present ignorance as to the rapidity of convergence of the Ritz-Hylleraas method.[5] The determination of an upper bound on the error for the energy by using the best method available for finding a lower bound to the energy,[6] is handicapped by the rather poor approximation of this lower bound to the true energy.[6,7] Under these circumstances it seemed worth while to explore modifications in the Hylleraas type solutions that may lead to improvement in convergence. A simple modification consisting in the introduction of half-integral powers in the Hylleraas poly-

* This work is supported in part by the U. S. Atomic Energy Commission.

[1] By G. Herzberg and R. Zbinden (as reported by S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955), reference 12).

[2] The experimental result, I.P.(He) = 198 310.$_5$ ± 1 cm^{-1}, quoted in reference 4, is termed "provisional."

[3] Ta-You Wu and G. E. Tauber, Phys. Rev. **100**, 1767 (1955), and references therein to earlier work on the relativistic solution. For preliminary calculations on lowest order radiative corrections see M. Günther, Physica **15**, 675 (1949); H. E. Håkansson, Arkiv Fysik **1**, 555 (1950); P. K. Kabir and E. E. Salpeter, Bull. Am. Phys. Soc. Ser. II **1**, 46 (1956).

[4] S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955).

[5] Some uncertainty still exists even with regard to convergence. The proof given by A. S. Coolidge and H. M. James [Phys. Rev. **51**, 855 (1937)] can be shown to be valid in what concerns the completeness of the Hylleraas set, but the part dealing with convergence involves an unproven assumption.

[6] L. Wilets and I. J. Cherry, Phys. Rev. **103**, 112 (1956).

[7] A. F. Stevenson and M. F. Crawford, Phys. Rev. **54**, 375 (1938).