the order of 1, and taking the thickness of the interface as equal to 10^{-6} cm, gives for a 1-cm cell a total voltage of about 50 v, as corresponding to an electromotive force E_0 equal to $\frac{1}{10}$ of a millivolt. A comparison with the measurements of Workman and Reynolds is unfortunately not possible because in their case the assumption of zero conduction for the solid does not hold. However, it is gratifying to see that a mechanism of the type considered here can cause the appearance of the potential differences, and generally of the effects of the kind found by the observers.

In the present case (open circuit) the total amount of surface charge in the liquid adhering to the interface is equal to the total amount of space charge, the entire system remaining neutral. The space charge distribution in the solid is exponential (see Fig. 3). According to (23), the field is given by

$$E(s)=E_0(1-e^{-s/s_0})/(1+k),\quad s\leq x \tag{34}$$

and

$$\rho(s)=\epsilon E_0 e^{-s/s_0}/s_0(1+k),\quad s\leq x. \tag{35}$$

The voltage is at any time proportional to vE_0. Since we found $E_0=c_1+c_2v$, one has

$$U(t)=(c_1v+c_2v^2)f(t). \tag{36}$$

Thus voltage curves obtained with different speeds of phase change differ only by a factor lying roughly between v and v^2.

VI. CONCLUSIONS

The foregoing exposition shows that a relatively simple theory based on existing evidence about interface potentials and behavior of ions in dielectrics can account for charge separation, and the production of voltages and currents during phase changes. The theory leads to expressions for the space-charge distribution in the solid and the voltage-time curves in open circuit that eventually may be compared with experimental data. The differential equation for the short-circuit current can be obtained in a straightforward manner; it is omitted here because it is not easily integrated. In the present form the theory is still incomplete. Among the factors it does not take into account are (a) the conductivity of the solid that affects the reversibility of the effect and the form of the voltage-time curves in aqueous solutions, and (b) the diffusion of ions in the liquid that may also play a rôle when a solid dielectric is dissolved in a solvent. However, we believe that the theory describes correctly the principal mechanism of interface conduction and presents already the basis for a more precise and complete treatment.

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Stored Energy Measurements in Irradiated Copper

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Thin copper foils, cooled to liquid nitrogen temperature, were subjected to bombardment by 12-Mev deuterons. The stored energy released due to annealing of the radiation damage was measured as the foils warmed to room temperature. Below −40°C the stored energy released per °C was approximately uniform and is presumed to result from annihilation of closely spaced interstitial-vacancy pairs produced by the bombardment. A prominent maximum in the annealing spectrum occured at −15°C and is interpreted as binary recombination of interstitial atoms and vacancies by means of interstitial diffusion. Changes in residual electrical resistivity were also measured. The stored energy to resistivity ratio was found to be 1.7 ± 0.2 cal/gram per micro-ohm-cm, both for the low-temperature processes and the −15°C annealing peak. If the energy of formation of an interstitial-vacancy pair is 5 ev, a value of 11 micro-ohm-cm for the resistivity of one atomic percent of pairs is obtained. The atomic concentration of interstitial atoms and vacancies produced by an irradiation of 10^{17} deuterons/cm^2 at liquid nitrogen temperature is, accordingly, 5×10^{-5}.

I. INTRODUCTION

CHANGES in the physical properties of a metal resulting from irradiation with fast particles are difficult to interpret because the types and numbers of imperfections produced by the bombardment are unknown. Interstitial atoms and vacant lattice sites are expected[1] to be the predominant types produced, and this view is supported by the observed annealing properties[2] of the damage. The resulting decrease in electrical resistivity upon anneal has received the greatest amount of experimental study, but the inherent difficulties of corresponding theoretical calculations have prevented a determination of the number of interstitial-vacancy pairs that occur.

The measurement of a fundamental quantity, such as energy, should provide a more reliable method of

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[1] F. Seitz, Discussions Faraday Soc. **5**, 271 (1949).

[2] A. W. Overhauser, Phys. Rev. **90**, 393 (1953).

counting interstitial-vacancy pairs. Such a method depends upon knowledge of the energy of formation of a pair. This energy is stored in the lattice after formation and is released in the form of lattice phonons and degraded into heat upon annihilation of the pair. If, then, one can identify the annealing stages of an irradiated material that are due to annihilation of interstitial atoms and vacancies and can measure the quantity of heat that is released during the process, one can determine the number of defects that were destroyed. If changes in electrical resistivity are measured for the same annealing stages, one can determine also the resistivity increase per atomic percent of interstitial-vacancy pairs.

The present interpretation of the annealing behavior of copper, irradiated at low temperature, is based on measurements of electrical resistivity changes. It is observed[2] that the residual resistivity increase recovers about an equal amount at all temperatures above that of bombardment, as the sample is allowed to warm to room temperature, with the exception of a prominent annealing peak at about $-35°C$. This peak was found to obey second-order reaction kinetics and to have a unique activation energy of 0.68 ev. This process is attributed, therefore, to binary annihilation of interstitial atoms and vacancies, made possible by the diffusion of either of the defects. Recent experiments[3] on the energy of formation of vacancies in copper yield a value of 0.9 ev. Since the activation energy for self-diffusion[4] is about 2.1 ev and is assumed to be due to a vacancy mechanism, the energy for vacancy motion is 1.2 ev. By elimination, it follows that the 0.68-ev activation energy is to be associated with interstitial motion.

The low-temperature annealing processes do not have a unique activation energy and are interpreted as the recombination of very close interstitial-vacancy pairs, of which there are several types. Such pairs are expected to constitute a large fraction of the damage, and to recombine at low temperatures by slip-back of the vacancy towards the interstitial. This action is made possible by large elastic strains about the nearby interstitial atom, which open up the lattice in such a way that the activation energy for motion of the vacancy towards the interstitial is greatly reduced. (Elastic strains due to a vacancy are such as to impede slightly the approach of an interstitial.) Quantitative estimates of such strain effects indicate that they are sufficiently large to account for the observed activation energies.

The foregoing description, though difficult to establish conclusively, is supported by the results of the present study. The major contribution is the observation that the stored energy to resistivity ratio is the same for the low temperature processes and the second-order reaction peak. This result would be fortuitous if the basic processes (e.g., annihilation of pairs) were not the same for both parts of the spectrum.

In order to determine the number of interstitial-vacancy pairs present in the damaged material, it is necessary to know the energy of formation of such a pair. Recent calculations of Huntington[5] indicate that the energy of formation of an interstitial atom in copper is about 4 ev. If this result is combined with the measured value associated with vacancy formation, one obtains about 5 ev for the energy of a pair. We shall adopt this tentative value when interpreting the results of the present experiment. An experimental determination of this quantity is very desirable. Unfortunately, threshold measurements for production of pairs by electron bombardment do not yield this quantity, since an interstitial atom must travel more than a lattice constant in order to form a stable pair, and consequently needs extra energy to expend in collisions.

The principle difficulty in measuring the stored energy that is released during the anneal of a damaged sample is one of sensitivity. Irradiation with 12-Mev deuterons, having a range of 0.008 inch in copper, was used. It is necessary, then, to use thin foils in order to achieve a fairly uniform distribution of damage. Consequently, the mass of a specimen is small (0.2 g for 2 cm^2 of a 0.005-inch foil) and the total stored energy available is, as the results indicate, of the order of 0.01 calorie for a deuteron irradiation of $10^{17}/cm^2$. Furthermore, this small quantity of heat does not appear in a narrow temperature interval as the sample is heated, but is liberated over the entire temperature spectrum between liquid nitrogen and room temperature. It follows that an absolute sensitivity of better than 10^{-5} cal/°C is required if an accuracy of 10 percent is to be achieved. A differential technique was employed and is described in Sec. III.

II. DESIGN OF CALORIMETER

A schematic diagram of the calorimeter, which was machined from a solid block of copper, is shown in Fig. 1. The purpose of the double wall construction was to provide as far as possible an isothermal enclosure for the foils. The outer cylindrical shell provided a heat path to the inner one and served also as a thermal shield. The inner shell was supported by the outer one through an annular ring halfway between the top and the bottom. The calorimeter came apart at this midpoint so as to provide access to the interior.

The formidable problem of transfering an irradiated foil from a cyclotron target to a calorimeter, all at liquid nitrogen temperature, was eliminated by allowing the foil to be irradiated within the calorimeter. The

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[3] C. J. Meechan and R. R. Eggleston, Phys. Rev. **93**, 953 (1954). See also: Brinkman, Dixon, and Meechan, Acta Metallurgica **2**, 38 (1954).

[4] M. S. Maier and H. R. Nelson, Trans. Am. Inst. Mining Met. Engrs. **147**, 39 (1942).

[5] H. B. Huntington, Phys. Rev. **91**, 1092 (1953).

deuteron beam passed through a rectangular hole in the calorimeter wall and this hole was covered with a 0.0005-inch copper foil in order to restore the integrity of the outer shell as a thermal shield. The foil to be irradiated was held in place over the hole in the inner shell by means of a spring and plunger shown in Fig. 1. A length of fuse wire provided tension to the device and was blown out after the bombardment so as to allow the damaged foil to drop into place alongside the dummy foil.

The calorimeter was mounted on the base of a liquid nitrogen flask, as shown in Fig. 1, and was cooled by conduction to about −190°C. The foil in the deuteron beam was considerably hotter since a pressure contact at one point between the foil and jacket is not a very good thermal path. With a deuteron beam of 5×10^{-8} amp/cm^2 the foil temperature increased to about −150°C. The flask and calorimeter were enclosed in an evacuated chamber. After bombardment dry nitrogen was admitted to the chamber at atmospheric pressure and the system was allowed to warm up freely. If the system were allowed to warm up in a vacuum, the warmup rate was found to be extremely erratic due to the liberation of gases that had condensed on the system during the week-long irradiation.

Two copper foils were suspended inside the calorimeter with 0.002-inch copper wire. Prior to bombardment the foils (of at least 99.95 percent purity) were annealed in vacuum at 450°C for four hours. A 10-cm length of 0.002-inch constantan wire joined the two foils so as to form a copper-constantan differential thermocouple that measured the temperature difference between the irradiated and dummy foils. Another length of 0.002-inch constantan wire joined the copper wall of the jacket and the midpoint of the constantan wire connecting the two specimens, so that a differential thermocouple between either of the foils and the wall of the calorimeter was provided. A third thermocouple was attached to the outside wall for measuring the temperature of the calorimeter. All leads were brought through the vacuum jacket by means of wax seals.

The three measurements made during the warmup of the system were, (a) the temperature difference between the irradiated and dummy foils, (b) the temperature difference between the calorimeter wall and the dummy foil, and (c) the temperature of the calorimeter. Since the temperature difference between the foils was of the order of 0.01°C, a thermal potential of about 3×10^{-7} volt was produced. This potential was amplified by a Leeds and Northrup stabilized dc amplifier operating at a gain of 1000 and the output voltage was measured with a potentiometer. The amplifier was found to reproduce readings to 10^{-8} volt over a 24-hour period for the small potential range that was required. The temperature difference between the calorimeter wall and the dummy foil was about 1°C and the resulting thermal potential was measured with a Leeds and Northrup type K2 potentiometer.

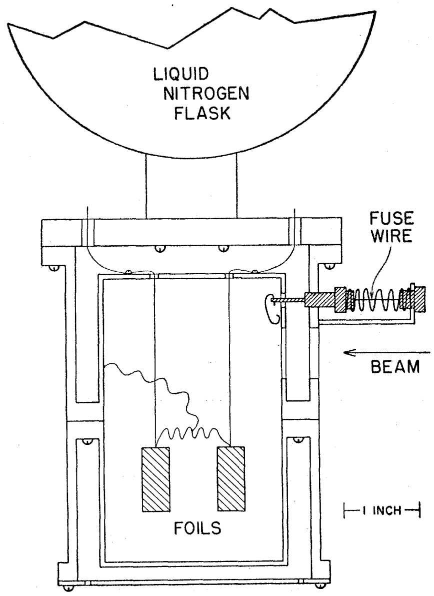

FIG. 1. Schematic diagram of calorimeter. The unit has cylindrical symmetry about a vertical axis.

Measurements of electrical resistivity changes were made during the experiment also. A copper specimen cut from the same foil as used for the thermal measurements was mounted on a bracket adjoining the rectangular hole in the calorimeter wall and received the same irradiation as the foil inside. Resistance measurements were made by standard potentiometric techniques.

III. THEORY OF MEASUREMENT

We must consider the variation with time of the foil temperature during the warmup of the system. Let T_1 and T_2 be the temperatures of the dummy and bombarded foils, respectively, and T_w the temperature of the inner wall of the calorimeter, which at any instant is assumed to be an isothermal enclosure. We shall discuss later the effects of temperature gradients in the calorimeter. Since the temperature differences between the foils and the jacket are small (~1°C), Newton's law of cooling applies and, consequently, the variation in temperature of the dummy foil with time t is

$$dT_1/dt=\alpha(T_w-T_1), \tag{1}$$

where the coefficient α is a function of temperature. We have neglected any thermal contact between the dummy and bombarded foils and shall justify this omission later. Let us assume, temporarily, that the dummy and bombarded foils are perfectly balanced and have the same thermal contact with the caloirmeter wall. The variation in temperature of the bombarded foil is then,

$$dT_2/dt=\alpha(T_w-T_2)+(MC)^{-1}dU/dt. \tag{2}$$

The second term on the right-hand side of Eq. (2) is due to the release of stored energy as the imperfections produced by the irradiation anneal. M is the mass of the foil, $C(T)$ its specific heat, and U is the energy of formation of the imperfections. Equations (1) and (2) can be combined so as to eliminate αdt, giving

$$\frac{1}{MC}\frac{dU}{dT_1}=\frac{(T_2-T_1)}{(T_w-T_1)}+\frac{d(T_2-T_1)}{dT_1}. \qquad (3)$$

The stored energy released per degree is seen to be directly related to the three measurements of temperature made during the warmup. If one neglects the second term on the right-hand side of Eq. (3), which is very small compared to the first, the resulting relation seems quite obvious. The ratio of stored energy released per degree to heat capacity equals the ratio of the temperature difference to the temperature lag.

We have assumed above that the foils were perfectly balanced, a condition manifestly impossible to achieve, and must modify our equations accordingly. It is sufficient to introduce an extra parameter into Eq. (2) as follows:

$$dT_2/dt=\alpha(T_w-T_2)/(1-\beta)+(MC)^{-1}dU/dt. \qquad (4)$$

Here, $\beta(T)$ is a parameter that measures the unbalance of the foils due to differences in mass and thermal contact with the surroundings, and must be determined experimentally. If one eliminates αdt from Eqs. (1) and (4), one obtains

$$\frac{1-\beta}{MC}\frac{dU}{dT_1}+\beta=\frac{(T_2-T_1)}{(T_w-T_1)}+(1-\beta)\frac{d(T_2-T_1)}{dT_1}. \qquad (5)$$

It is clear that measurements taken during one warmup are no longer sufficient to determine dU/dT_1. After the first warmup is completed, the system must be cooled to liquid nitrogen temperature and allowed to warm up again. Since the imperfections have already annealed, the stored energy term in Eq. (4) will be absent, and we can assume (and shall show later) that $\beta(T)$ has not changed appreciably as a result of the first anneal. Equation (1) will remain unchanged and Eq. (5) will appear the same except for the absence of the stored energy term. The second warmup provides, therefore, a measurement of $\beta(T)$. Observed values of the unbalance between the foils were of the order of a few percent. Figure 2 shows a plot of $(T_2-T_1)/(T_w-T_1)$ for three successive warmups of one specimen. The agreement of the data for the second and third warmups suggests that the experimental method gave results that were adequately reproduceable. Such a check was made for each bombardment.

We shall consider next a number of systematic errors associated with the measurement. In writing Eqs. (1) and (2) we assumed that the thermal enclosure was at a unique temperature T_w for any instant in time. Since measurements are made while the system is warming up, temperature gradients due to thermal conduction will exist along the inner wall of the calorimeter, and T_w must be considered as some appropriate average temperature seen by the foils. For a rate of warmup of 1°C per minute, one can calculate an average temperature gradient along the vertical wall of the inner jacket of about 0.05°C/cm. For such a warmup rate T_w-T_1 was about 1°C. The foils were suspended in the lower half of the calorimeter and the thermal junction that was soldered to the inner wall was at a distance above the plane of symmetry equal to the distance that the foil midpoints were below the plane. Measurements indicated that there was never an appreciable temperature difference across the joint between the halves of the calorimeter, so that one can assume a symmetric temperature distribution about the bisecting plane of the inner jacket. A liberal estimate of the error in measurement of T_w-T_1 due to such gradients is 5 percent.

In writing the basic equations we neglected any thermal contact between the two foils. Since the rate of release of stored energy is proportional to the difference of $(T_2-T_1)/(T_w-T_1)$ for successive warmups, the measurements will be in error to the extent that the stored energy released by the irradiated foil is

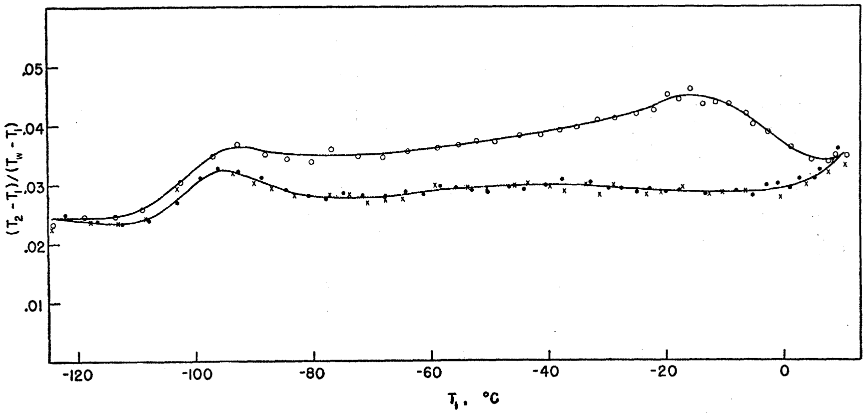

FIG. 2. Plots of $(T_2-T_1)/(T_w-T_1)$ for three successive warmups of one specimen. ○—first warmup; ×—second warmup; ●—third warmup.

transferred to the other foil instead of to the wall of the calorimeter. We must estimate the stored energy lost to the dummy foil per second and compare it with the total rate of release of stored energy, which was about 5×10^{-6} cal/sec. An estimate of the heat transfer through the constantan wire joining the foils yields 5×10^{-10} cal/sec, and is therefore negligible. However, an estimate of the thermal transfer through the nitrogen atmosphere yields about 10^{-7} cal/sec, so that an error of about 3 percent is possible due to neglect of such effects.

Since temperatures were measured thermoelectrically, errors will be introduced by the presence of stray thermal emf's. Let us consider first the effect of a stray potential in the circuit measuring T_2-T_1. A consideration of the analysis by which U is determined shows that stray thermals here will not affect the numerical results provided that they are not too large and are equal for each warmup, and provided that T_1 *versus* time is approximately the same for successive warmups. This result follows from the fact that dU/dT is obtained, essentially, by subtracting $(T_2-T_1)/(T_w-T_1)$ for two warmups. Stray thermals were not observed, the warmup rates were almost identical, and large stray emf's, introduced artificially by running leads through solder seals instead of wax seals, were found to be reproduceable. On the other hand, stray emf's in the circuit measuring T_w-T_1 will cause a proportional error. The potentiometer used for this measurement was checked for internal emf's before and after each warmup, and no appreciable potentials were observed when the calorimeter and foils were in thermal equilibrium at -190°C or room temperature.

We have heretofore neglected any changes in the specific heat of the sample due to the presence of imperfections. In order to demonstrate that such effects are not important in the present experiment, we shall derive the appropriate equations for the case of a dummy and bombarded foil that are otherwise perfectly matched. For the purpose of discussion we shall assume that the damaged foil contains only interstitial atoms and vacancies and that they anneal out completely during the first warmup. Let f be the atomic fraction of interstitial-vacancy pairs. For $f\ll1$ (and constant) the specific heat per gram will be given with sufficient approximation by,

$$C(f,T)=C_0(T)[1+fs(T)],$$

where

$$s(T)=\frac{1}{C_0(T)}\left[\frac{\partial C(f,T)}{\partial f}\right]_{f=0}.$$

Here, $C_0(T)$ is the specific heat of the undamaged material. Let E_0 be the energy of formation of an interstitial-vacancy pair at 0°K and $U(T)$ be the internal energy per gram. Then, if N is the number of atoms per gram,

$$U(f,T)=U_0(T)+f\left[NE_0+\int_0^T C_0(T')s(T')dT'\right], \quad (6)$$

where $U_0(T)$ is the corresponding function for $f=0$. The rate of warmup of the bombarded foil is, instead of Eq. (2),

$$\frac{dT_2}{dt}=\frac{\alpha(T_w-T_2)}{1+fs(T_2)}+\frac{NE_0+\int_0^{T_2} C_0(T')s(T')dT'}{C_0(T_2)[1+fs(T_2)]}\left(-\frac{df}{dt}\right). \quad (7)$$

The first term on the right side of Eq. (7) accounts for thermal transfer from the surroundings, whereas the second term results from the *adiabatic* annealing of the damage and is obtained by equating the total derivative of Eq. (6) to zero. As before, αdt can be eliminated by the use of Eq. (1) and we obtain after manipulation,

$$NE_0\left(-\frac{df}{dT_1}\right)=C_0\left[\frac{T_2-T_1}{T_w-T_1}+(1+fs)\frac{d(T_2-T_1)}{dT_1}+fs\right]+\frac{df}{dT_1}\int_0^{T_2} C_0(T')s(T')dT'. \quad (8)$$

This expression is to be compared with Eq. (3). It is seen that there are two extra terms on the right side of Eq. (8), both of magnitude fsC_0, which must be compared with the leading term, $C_0(T_2-T_1)/(T_w-T_1)$. It is sufficient to estimate the magnitude of f and s. From the results of the following section it follows that $f\sim2\times10^{-5}$ for the measured portion of the stored energy spectrum. A rough estimate of s can be made as follows. Consider the specific heat as given by the Einstein model. If one assumes that the vibrational frequencies of the six nearest neighbors of and interstitial atom are altered 100 percent, then s might be of order of magnitude 6. This is, undoubtedly, an overestimate in spite of our neglect of other neighbors and neighbors of vacancies, since the temperature region of interest is not much lower than the Debye temperature of the lattice, where the specific heat is nearly 6 cal/mole and, consequently, not strongly frequency dependent. Furthermore, partial cancellation will occur since the frequency of some modes will increase, whereas others will decrease. The magnitude of fs is therefore not greater than 10^{-4}, which is smaller by a factor of 100 than the term $(T_2-T_1)/(T_w-T_1)$. The two extra terms in Eq. (8) always tend to cancel, so that the stored energy spectrum is probably in error by less than one percent as a result of their omission. If the stored energy spectrum were integrated from 0°K to a temperature at which annealing is complete, one can show that all of the terms in Eq. (8) involving s cancel identically.

We have shown that the neglect of any variations in the specific heat due to annealing of the radiation damage is justified to a good degree of approximation. It follows from Eq. (8) that in the same approximation the energy U in Eqs. (2) through (5) can be interpreted as the energy of formation of the imperfections at 0°K.

Radioactive heating of the damaged sample as a result of bombardment induced activities could produce a spurious source of stored energy. The foil temperatures were measured, therefore, for several hours after irradiation, when they were still in a vacuum, and no heating effects were observed. Changes in the properties of thermal junctions were avoided by shielding all junctions from the deuteron beam.

The foregoing considerations, if complete, indicate that the over-all experimental uncertainty of the stored energy measurements is about 10 percent.

IV. RESULTS AND DISCUSSION

The stored energy spectrum obtained for two samples is shown in Fig. 3. Both samples weighed 0.219 g and they received an irradiation of 0.9 and 1.5×10^{17} deuterons/cm^2, respectively. The fact that the spectrum does not extend below -140°C for the first specimen is due to the sample being heated to about -150°C by the deuteron beam, so that annealing processes occurring at lower temperatures were already complete. The second specimen received a larger irradiation in an equal length of time so that the beam current and heating effects were correspondingly greater and also more erratic. The two curves can be compared above -80°C and are seen to be almost identical except for a constant ratio equal to the ratio of the integrated fluxes. This result is to be expected since, for copper, bombardment saturation effects are not apparent for irradiations of 10^{17}/cm^2. The annealing peak at -15°C, most likely due to annihilation of interstitial atoms and vancancies as a result of interstitial diffusion, is quite prominent.

The total stored energy released between -80°C and room temperature is found by integrating the curves in Fig. 3, and is 1.03×10^{-2} and 1.68×10^{-2} cal for specimens 1 and 2, respectively. If these results are normalized to an irradiation of 1.0×10^{17} and unit mass, one finds 0.052 cal/gram for the heat released in this temperature range. This result can be compared with the (residual) electrical resistivity increase that anneals out in the same temperature interval in order to obtain the stored energy to resistivity ratio that characterizes the imperfections. From reference 2, we find a resistivity decrease of 3.1×10^{-8} ohm-cm (normalized to 1.0×10^{17} deuterons/cm^2) between -80°C and room temperature. Thus, the U/ρ (stored energy to resistivity) ratio is 1.7 cal/gram per micro-ohm-cm. This value is, perhaps, the most important and unambiguous result of the present study.

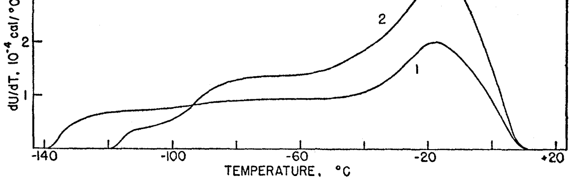

FIG. 3. Stored energy annealing spectrum observed for two irradiated samples, both weighing 0.219 gram.

It is interesting to compare the U/ρ ratio obtained here with that obtained in copper as a result of plastic deformation. Stored energy measurements[6] of heavily cold-worked polycrystaline copper yield about 0.5 cal/gram. On the other hand, the resistivity change[7] is only 3.6×10^{-8} ohm-cm. Hence, the U/ρ ratio for imperfections resulting from cold work is 14 cal/gram per micro-ohm-cm, an order of magnitude larger than the result obtained for radiation damage.

The U/ρ ratio we have determined above was for the integrated U and the total $\Delta\rho$ between -80°C and room temperature. Since this temperature region includes (at least) two distinct annealing processes, the -15°C annealing peak and the low-temperature processes, one must examine the U/ρ ratio for both. This ratio should be the same for both if the low-temperature processes are due to the annihilation of close interstitial-vacancy pairs and the -15°C, second-order reaction is due to annihilation of separated pairs as a result of volume diffusion. This comparison could be made by comparing directly the corresponding annealing spectra for stored energy and resistivity. The spectrum for the latter was obtained[2] by successive isothermal anneals instead of by continuous warmup, as in the present experiment. Some calculation, therefore, is needed to effect the comparison.

For anneal of the resistivity, the second-order reaction process was found[2] to obey the following equation.

$$df/dt = -ae^{-E/\kappa T}f^2e^{bf}, \tag{9}$$

where f is the concentration of imperfections, E is an activation energy = 0.68 ev, and a and b are constants. The factor $\exp(bf)$ appeared[8] (theoretically) as an enhancement in the diffusion process resulting from elastic strains in the lattice due to interstitial atoms, and such a factor was needed to fit the isothermal annealing data. Using Eq. (9) with the values of a and b determined from the resistivity curves, an annealing spectrum was computed for this process

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[6] H. Quinney and G. I. Taylor, Proc. Roy. Soc. (London) **A163**, 157 (1933); H. Kanzaki, J. Phys. Soc. Japan **6**, 90 (1951); **6**, 456 (1951).

[7] K. Takahasi, Science Repts. Tôhoku Univ. **19**, 265 (1930).

[8] The detailed theory given in reference 2 applies to vacancy motion. Similar results are obtained for interstitial motion.

if it were subjected to the thermal treatment occuring in the stored energy experiments. This spectrum was converted to energy units by use of the U/ρ ratio obtained for the *entire* spectrum. The result of the calculation is shown as curve 2 in Fig. 4, and should be compared with the experimental energy spectrum, curve 1. Since no arbitrary constants were available, the good agreement in the region of the peak proves that the U/ρ ratio is the same for the low-temperature processes and for the second-order reaction. This result is consistent with the interpretation that interstitial-vacancy annihilation is the mechanism in both parts of the spectrum. The agreement obtained for the position of the peak provides an additional check of the 0.68-ev activation energy measured during the resistivity study since, then, the effective warmup rate was about 20 times slower and the annealing peak occured 20°C lower in temperature.

For comparison, similar curves were computed assuming pure second-order reaction kinetics and first-order kinetics, and are shown in Fig. 4 as curves 3 and 4, respectively. The necessary constants were determined by best fit of the resistivity data and converted to energy units in the foregoing manner. It is apparent that a pure second-order reaction [Eq. (9) without the factor $\exp(bf)$] is not as satisfactory and that a first-order process has an entirely different shape. It should be noted, however, that the high-temperature tail of the experimental curve is cut off like that of the first-order reaction curve. This behavior is due likely to interstitial traps in the copper that compete with vacancies so as to impose first-order kinetics when the concentration of interstitials and vacancies becomes small. It should be emphasized, though, that the transition to first-order kinetics occurs only after the second-order process has proceeded about 90 percent towards completion, so that any residual damage at room temperature due to trapped interstitials and vacancies can be but a small fraction in magnitude of the damage associated with the second-order reaction. Experimentally the residual resistivity at room temperature due to damage is about equal in magnitude to the resistivity change of the second order reaction. The origin and nature of the imperfections that remain at room temperature is, at present, unknown. They anneal out only at relatively high temperatures.[9]

Further results can be obtained if one uses a specific value, say 5 ev, for the energy of formation of an interstitial-vacancy pair. The stored energy per atomic percent of pairs would be 18 cal/gram. Using the measured U/ρ ratio (1.7 cal/gram per micro-ohm-cm) one obtains a value of 11 micro-ohm-cm for the resistivity due to one percent of pairs. Jongenburger[10] has calculated the resistivity associated with one percent of vacancies. His result, 1.3 micro-ohm-cm, together with the above value would imply that the resistivity of an equal number of interstitial atoms is about 10 micro-ohm-cm.

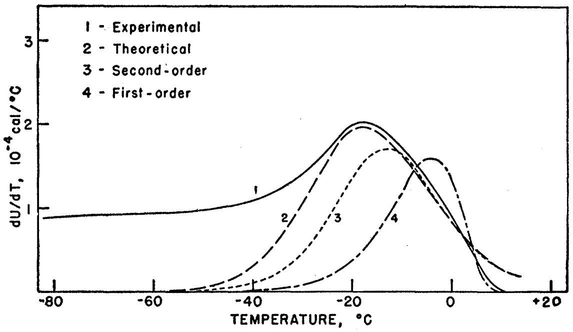

FIG. 4. Experimental annealing spectrum and three computed spectra for the 0.68-ev activation energy annealing process.

The number of interstitial-vacancy pairs produced by bombardment can now be estimated. An irradiation of 10^{17} deuterons/cm^2 (average energy = 9 Mev) at -180°C causes a residual resistivity increase of 7×10^{-8} ohm-cm. Presumably, only 75 percent of this increase is due to interstitial atoms and vacancies, the remaining fraction being associated with imperfections that remain at room temperature. The total concentration of pairs resulting from such a bombardment is, then, 5×10^{-5}. This value is smaller by a factor of 50 then the concentration, 2.5×10^{-3}, obtained from Seitz's theory,[1] using the observed[11] energy threshold (25 ev) for formation of imperfections stable at -170°C. The origin of this discrepancy seems to be the approximation of letting a knocked-on copper atom of energy E have unit probability to form a stable interstitial-vacancy pair if E is greater than the threshold. Rough calculations indicate that this probability increases from 0 only very slowly with increasing E above the threshold. Consequently, the number of stable pairs resulting from secondary atoms that recoil from the primary deuteron is drastically reduced, especially since the energy distribution of secondaries is inversely proportional to E^2. A further consequence is that production of more than one interstitial-vacancy pair as a result of a primary collision and subsequent secondary or tertiary collisions is unlikely.

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