Structure of Deuteron-Irradiated Germanium*†

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(Received August 20, 1958)

The structure of deuteron-irradiated germanium is discussed in the light of the following recent experiments: (1) simultaneous measurements of the change in length and resistivity upon low temperature bombardment and annealing, (2) measurement of lattice parameter changes after annealing near room temperature, and (3) low-angle x-ray scattering measurements at liquid nitrogen temperature and above. A model of the damage at liquid nitrogen temperature consisting of separated clusters of vacancies and interstitials, is proposed. The model yields a comparatively small length increase and fairly strong low-angle x-ray scattering in agreement with experiment. The model also appears capable of explaining the experimental observation that resistivity annealing occurs in an earlier stage of the recovery process than appreciable length-change annealing. The clusters must be formed, at or below liquid nitrogen temperature, either by diffusive motion of the defects or by displacement processes directly upon bombardment. If the latter mechanism holds, present theory greatly underestimates displacement distances in germanium. Additional critical experiments are proposed.

I. INTRODUCTION

THE damage induced in crystals by fast-particle irradiation is not completely understood at present, and its detailed nature will be elucidated only by extensive investigation of the different physical properties of the damaged state. Electrical measurements have been the prime tools used to investigate radiation-damaged germanium because of the sensitivity of these measurements to the induced defects. However, the electrical effects are difficult to interpret and do not lead to an unambiguous interpretation of the physical structure of the defect state. Recently several investigations of other properties of deuteron-damaged germanium have been made. Vook and Balluffi[1] have made simultaneous measurements of the length and electrical resistivity after low-temperature irradiation and annealing. Simmons[2] has carried out accurate measurements of lattice parameter changes of deuteron-irradiated germanium during annealing in the vicinity of room temperature. Fujita and Gonser[3] have measured fairly strong low-angle x-ray scattering from deuteron-irradiated germanium near liquid nitrogen temperature.

These measurements, which were made on specimens irradiated under similar conditions on the University of Illinois cyclotron, extend the range of physical measurements which are currently available for deuteron-irradiated germanium. The purpose of the present paper is to discuss the significance of these results and to construct a model for the damage which is consistent with the presently available experimental results.

* A portion of this paper was submitted by Frederick L. Vook to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy in May, 1958.

† This work was supported by the U. S. Atomic Energy Commission.

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[1] See F. L. Vook and R. W. Balluffi, this issue [Phys. Rev. 113, 62 (1959)].

[2] See R.O. Simmons, preceding paper [Phys. Rev. 113, 70 (1959)].

[3] F. E. Fujita and U. Gonser (to be published).

II. EXPERIMENTAL OBSERVATIONS

A brief review of the experimental results available for deuteron-irradiated germanium is given below.

1. Electrical Measurements

Many measurements of the electrical properties of germanium irradiated by fast particles have been made. We shall restrict our attention here mainly to the experiments using deuteron bombardment at liquid nitrogen temperature or below. In several other places reference will be made to pertinent results involving electrons or neutrons. Fan and Lark-Horovitz[4] found that n-type germanium was converted to p type upon 9.6-Mev deuteron bombardment at liquid nitrogen temperature and became even more p type upon subsequent annealing to room temperature. Heavily doped p-type germanium, however, became less p type upon low-temperature deuteron bombardment. These results indicate that both donors and acceptors are introduced by the bombardment. Vook and Balluffi[1] irradiated relatively pure germanium (5×10^{13} donors/cm^3) with 11.4-Mev incident deuterons in two successive irradiations at 25°K and 85°K. Their results agree generally with the work of the Purdue Group.[4] The work is of special interest, however, since simultaneous measurements of the specimen length were also made, and since irradiation was carried out at lower temperatures (25°K). Rapid increases in resistivity occurred upon both bombardments. After the first bombardment at 25°K an irreversible resistivity decrease by a factor of 10^7 was observed on annealing between 60°K and 300°K. By far the largest part of the decrease (10^6) seemed to occur between 150 and 225°K. After the subsequent bombardment at 85°K an irreversible resistivity increase occurred on annealing between 85 and 140°K. The resistivity then decreased by a factor

[4] H. Y. Fan and K. Lark-Horovitz, *Report of the Bristol Conference on Defects in Crystalline Solids, July, 1954* (The Physical Society, London, 1955), p. 232.

of 10^3 between 150°K and 200°K. Complete thermal recovery of the resistance of deuteron-irradiated germanium has required annealing to 450–500°C.[4]

Electrical measurements, consisting mainly of electrical resistivity, Hall effect, and mobility measurements, have generally led to the accumulation of much valuable data which focus attention on the energy band diagram and the position and type of levels introduced into the forbidden band by the defect state.[4] However, the structure of the damaged material is of major interest, and the difficulty of deducing this structure on the basis of electrical measurements alone has already been noted. The electrical effects are particularly complicated since the defects not only reduce the mobility of the carriers but can also produce changes in carrier concentration of many orders of magnitude and even changes in the type of carrier conduction. The resistivity may be affected by thermally unstable trapping processes, changes in defect distribution, changes in the number and type of defects, and also by the normal equilibrium thermal ionization of donors and acceptors. The low temperatures required to freeze-in the damage during bombardment cause difficulties in electrical measurements since the approach to carrier equilibrium may become very slow. Fan and Lark-Horovitz observed changes in the carrier concentration in *n*-type germanium which was electron-irradiated and subsequently illuminated at liquid nitrogen temperature.[4] The changes which occurred after the illumination was removed were far from complete 21 hours later. This means that electronic processes in bombarded germanium cannot be assumed to be in thermal equilibrium at all times.

2. Length Measurements

A comparatively small expansion has been found to occur upon irradiation at 25°K and 85°K.[1] The expansion was linear with flux and was the same at both temperatures $[\Delta L/L=(1.5\pm0.3)\times10^{-21}$ per deuteron/cm$^2]$. This expansion is at least an order of magnitude less than that found in the III–V compounds[5,6] and is about one-half that found in copper.[7] The radiation-induced expansion exhibited little or no annealing upon warming below 200°K (within the experimental accuracy of 20%). Recovery of the expansion was ~50% complete at 300°K and ~85% complete at 360°K. Simultaneous measurement of electrical resistivity[1] indicated that large irreversible changes in electrical resistivity occurred in the annealing temperature range below 200°K where little or no length-expansion annealing occurred. Electrical resistivity annealing, therefore, appeared to occur in an earlier stage of the recovery than the length-change annealing.

3. Lattice Parameter Measurements

Lattice parameter measurements have been made[2] in germanium which was first given the following treatment: (1) deuteron bombarded at ~25°K and then warmed to 308°K; (2) bombarded at ~85°K and warmed to 320°K. A small residual lattice expansion $[\Delta d/d=(+3.0\pm0.7)\times10^{-5}]$ was found at 320°K after this treatment. This expansion annealed out completely upon further warming to ~350°K and an apparent slight contraction was observed in the annealing temperature range 350°K–420°K which never exceeded $\Delta d/d=-2\times10^{-5}$. The original lattice parameter was restored by warming to ~430°K. No appreciable line broadening of the (422) x-ray reflection was observed.

4. Low-Angle X-Ray Scattering Measurements

Fujita and Gonser[3] have measured the low-angle scattering of x-rays from deuteron-irradiated germanium. The specimens were irradiated at ~90°K with incident 8-Mev deuterons (6.5 Mev average) to a flux of about 1×10^{17} deuterons/cm^2. The x-ray scattering was then measured at ~90°K using a line-focused monochromator technique employing Cu $K\alpha$ x-rays. The scattered intensity was measured on photographic films and was measured over scattering angles ranging between about 7×10^{-3} and 30×10^{-3} radian. The curve of scattered intensity *versus* the square of the scattering angle was approximately Gaussian over the angular range investigated, indicating that regions having a different electronic density from the matrix were present with a radius of gyration of about 23 A (see Appendix B). The scattered intensity was fairly strong, and the intensity extrapolated to zero angle was about 3×10^{25} I_e,[8] where I_e is the intensity which would be scattered at zero angle by one electron (see Appendix B). Further measurements were made after annealing to room temperature, and it was found that the scattered intensity decreased by about a factor of 5.

III. MODELS

The chief possible models for deuteron-irradiated germanium that might be discussed are the following: (I) isolated vacancies and interstitials distributed homogeneously throughout the entire volume, (II) clustered vacancies and interstitials,[9] (III) displacement spikes consisting of small regions where the atoms are in a different structure than the matrix,[9] and (IV) combinations of the above.

We first discuss evidence which indicates that homogeneously distributed interstitials and vacancies (model I) are probably not the sole defect configuration produced by irradiation. James and Lark-Horovitz[10]

[5] D. Kleitman and H. J. Yearian, Phys. Rev. **108**, 901 (1957).
[6] U. Gonser and B. Okkerse, Phys. Rev. **109**, 663 (1958); Bull. Am. Phys. Soc. Ser. II, **2**, 157 (1957).
[7] R. W. Vook and C. Wert, Phys. Rev. **109**, 1529 (1958).
[8] F. E. Fujita and U. Gonser (private communication).
[9] J. A. Brinkman, Am. J. Phys. **24**, 246 (1956).
[10] H. M. James and K. Lark-Horovitz, Z. physik. Chem. **198**, 107 (1951).

have given arguments that interstitials and vacancies introduce localized energy levels in the forbidden gap of a semiconductor. The James-Lark-Horovitz model proposes specifically that isolated interstitials may act as donors and that isolated vacancies may act as acceptors, not just for one electron but for several. Interpretations of radiation damage in germanium and specifically resistivity and Hall measurements have generally been made in terms of this model. Electrical evidence is available which indicates that model I probably does not apply. Measurements of the Hall mobility at liquid nitrogen temperature after room-temperature neutron bombardment[11] show carrier scattering effects which Brooks[12] attributes to the existence of defects in clusters. Erratic and strongly temperature-dependent carrier mobility effects in room-temperature neutron-irradiated specimens have been observed[11–13] and are attributed by Cleland and Crawford[11] to the clustering of defects. Carrier mobility effects are not as striking in deuteron- and electron-bombarded material. However, an appreciable reduction in mobility introduced by deuteron irradiation at liquid nitrogen temperature remains after annealing to room temperature.[4] Electron irradiation with comparable fluxes, on the other hand, shows almost complete recovery of the reduction in mobility after annealing to room temperature.[4] This type of behavior is consistent with clustering since the production of defects in clusters would be expected to be very large in neutron-bombarded specimens, to occur to a lesser degree in deuteron-bombarded specimens, and to be negligible in electron-bombarded specimens.

The low-angle x-ray scattering experiments of Fujita and Gonser[3] also constitute strong evidence for the existence of defects in clusters. These results indicate that regions of approximately 20–30 A in radius, having a different electronic density from the matrix, are present.

The above considerations tend to eliminate model I as the sole effect and center interest in models II, III, and IV. In the following discussion we analyze in some detail various models of types II and III. It turns out that the possibilities which are consistent with all the experimental results are fairly restricted. Several types of damage may be distinguished. For model II vacancies and interstitials may be present in clusters in which they are finely intermixed, or they may be concentrated in separated vacancy and interstitial clouds. In model III the atoms may be stirred up in the displacement process and homogeneously rearranged on a fine scale in a different crystal structure with a different coordination number from the matrix. Either a relatively uniform density may be retained, or density gradients may be developed by directed mass displacements associated with the primary knock-on.

We would like first a model of reasonable structure at liquid nitrogen temperature that is capable of explaining both the small length changes upon irradiation[1] and the fairly strong low-angle x-ray scattering intensity from the damaged material found by Fujita and Gonser.[3] The density changes and over-all volume changes associated with the various postulated models may be calculated approximately using Eshelby's results[14] if the defect regions are considered as centers of dilatation embedded in an elastic matrix. In defect regions where mass is not conserved, the region may be divided into subregions each of which has gained or lost atoms rather uniformly over its volume. A defect region may be constructed in the following way: (1) cut out each subregion to be damaged; (2) produce the defects by atomic rearrangement and the addition or subtraction of mass, thereby causing a relatively uniform strain, ϵ; (3) force the material back into the original cavity. Calculations giving the approximate density changes and over-all volume changes which are associated with such subregions possessing spherical symmetry are given in Appendix A. These defect regions will cause low-angle x-ray scattering since their electronic density differs from the matrix. The scattering from a general configuration consisting of a pair of associated subregions separated by a distance **a** is calculated in Appendix B. These results will be used to discuss several configurations. We will use the simplifying assumption that the defect regions in each case are of a uniform size. It will be shown later that the presence of a range of sizes will not greatly change the conclusions reached.

Case A: single uniformly damaged spheres containing either finely mixed interstitials and vacancies (model II), or a homogeneous phase transformed structure (model III). From Eqs. (A.3), (A.7), and (B.3), an expression may be found relating the strain, ϵ, to the scattered x-ray intensity which is proportional to $N_0(\Delta n)^2$, the length change, $\Delta L/L$, and the volume of the defect region, v. If ρ_0 is the normal electronic density, Δn the excess or deficit number of electrons in v over the normal number in an equal undamaged volume, and N_0 the number of single spheres per cc, then

$$\epsilon = A/(1-2A); \quad A = N_0(\Delta n)^2/[4(\Delta L/L)v\rho_0^2].$$

Since the defect regions are taken to be spheres, the observed[3] radius of gyration of 23×10^{-8} cm implies that $v = 1.1\times10^{-19}$ cm^3. The bombardment consisted of 1×10^{17} deuterons/cm^2 of average energy about 6.5 Mev.[3] This treatment should have produced an expansion of 2.35×10^{-4} using the length change results[1] and the E^{-1} correction for the dependence of damage on

[11] J. W. Cleland and J. H. Crawford, Jr., Phys. Rev. **98**, 1742 (1955).
[12] H. Brooks, *Annual Review of Nuclear Science* (Annual Reviews, Inc., Stanford, 1956), Vol. 6, p. 215.
[13] Cleland, Crawford, and Pigg, Phys. Rev. **99**, 1170 (1955).
[14] J. D. Eshelby, J. Appl. Phys. **25**, 255 (1954); *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 3, p. 79.

energy.[15,16] From these values and $N_0(\Delta n)^2=3\times10^{25}$,[8] and using $\rho_0=1.4\times10^{24}$ electrons/cm^3, we find that $\epsilon=0.19$. This large value of ϵ tends to reject single uniformly damaged regions as a possible model since it is difficult to imagine structural changes which would produce the $\sim57\%$ volume expansion implied by this strain in the loosely packed diamond cubic lattice. For example, the rearrangement of germanium atoms on melting produces a volume contraction of 5%.

Case B: a configuration consisting of randomly distributed vacancy clusters and interstitial clusters. In this case we shall find it possible to satisfy the requirement of small length change and strong low-angle scattering without the necessity of postulating unreasonably large strains. This comes about since the clouds of vacancies and interstitials represent negative and positive centers of dilatation, respectively, and their contributions to the length change tend to cancel out. However, both types of clusters tend to contribute additively to the low-angle scattering intensity. At nitrogen temperature no length-change annealing was observed, and it seems reasonable to make calculations for the case where equal numbers of vacancies and interstitials are present. For order-of-magnitude purposes we assume the particularly simple case where equal numbers of vacancy and interstitial clusters are present and where each cluster is of the same size and possesses N point defects. Letting Ω_i be the volume increase of the crystal when a germanium atom not originally belonging to the crystal is added as an interstitial, and letting Ω_v be the corresponding change in volume when an atom is completely removed from the crystal leaving a vacancy, we find that

$$\Delta v/v_{i0}=3\epsilon_i=N\Omega_i/v_{i0},$$

$$\Delta v/v_{v0}=3\epsilon_v=N\Omega_v/v_{v0},$$

and from (A.7),

$$\Delta L/L=N_0N(\Omega_i+\Omega_v)/3.$$

Here N_0 is the number of vacancy clusters per unit volume. A consideration of (B.5) shows that the mutual interference term will disappear for a random dispersion of clusters and that the Fujita and Gonser value of 3×10^{25} may be set equal to $N_0[(\Delta n_i)^2+(\Delta n_v)^2]$. From (B.3),

$$\Delta n_i=Nz-2\rho_0v_{i0}\epsilon_i=N(z-\tfrac{2}{3}\Omega_i\rho_0),$$

$$\Delta n_v=-Nz-2\rho_0v_{v0}\epsilon_v=N(-z-\tfrac{2}{3}\Omega_v\rho_0).$$

Then

$$N_0[(\Delta n_i)^2+(\Delta n_v)^2]=6N\frac{\Delta L}{L}\frac{[z^2-\frac{2}{3}z\rho_0(\Omega_i-\Omega_v)+\frac{2}{9}\rho_0^2(\Omega_i^2+\Omega_v^2)]}{(\Omega_i+\Omega_v)},$$

where z is the atomic number of germanium, 32. All of the parameters of the model may be calculated from the above relations if we assume reasonable values of Ω_i and Ω_v. Unfortunately, no calculations of those quantities have been made for germanium as they have for copper.[17] However, if $\Omega_i=+0.5\Omega$ where Ω is the atomic volume of germanium and $\Omega_v=0.0$, then $N=318$, $N_0=3.3\times10^{17}$ cm^{-3}, $\epsilon_i=+3.1\times10^{-2}$, $\epsilon_v=0$ using $\Delta L/L=2.35\times10^{-4}$. If $\Omega_i=+0.5\Omega$ and $\Omega_v=-0.2\Omega$ then $N=231$, $N_0=7.6\times10^{17}$ cm^{-3}, $\epsilon_i=+2.3\times10^{-2}$, $\epsilon_v=-8.0\times10^{-3}$, and $\Delta L/L=2.35\times10^{-4}$ as above. We see that the model of clustered interstitials and vacancies can more satisfactorily explain both the small-angle scattering and the observed volume changes with reasonable values of Ω_i, Ω_v, N, and N_0. It is worth noting that the assumed magnitudes of Ω_i and Ω_v are generally consistent with the predictions of the simple displacement theory.[15] Simple displacement theory predicts $N_p=1.44\times10^{20}$ Frenkel pairs/cm^3 for 10^{17} deuterons/cm^2 of average energy 10.2 Mev, using[18] $E_d=30$ ev and an average of 6 progeny per primary. Using the observed length change in

$$\frac{3\Delta L}{L}=N_p\Omega\left[\frac{\Omega_i+\Omega_v}{\Omega}\right],$$

we find that $\Omega_i+\Omega_v=+0.14\Omega$.

Case C: a case similar to B except that the vacancy and interstitial clouds are paired in dipole or concentric shell configurations.[9] The length change will be the same as in Case B. At moderately large scattering angles the intensity will not be greatly different from Case B. However, the scattering intensity will be reduced at low angles because of interference effects between the highly correlated positive and negative regions in each pair (we may assume that the pairs themselves are randomly distributed). Inspection of (B.5) shows that mutual interference in the dipole case causes the scattering *versus* φ curve to go through a maximum as $\sin(2\pi a\varphi/\lambda)/(2\pi a\varphi/\lambda)\sim0$. This condition is met for $2\pi a\varphi/\lambda\sim5\pi/6$. As an example, for copper $K\alpha$ x-rays, this occurs for $a=60\times10^{-8}/C$ and $\varphi=1.1\times10^{-2}C$ where $C\sim1$ is a constant and can be determined if either a or the angle of the maximum intensity φ is known. For the spherical shell case the scattering intensity goes through a maximum at an angle given by

$$\varphi_{\max}{}^2=\frac{3\lambda^2\ln(R_1/R_2)}{\pi^2(R_1{}^2-R_2{}^2)}.$$

Fujita and Gonser found no maximum in the scattering curve. However, the region of low angles is not easily accessible experimentally. It is conceivable that if dipoles were present the separations were such that

[15] F. Seitz and J. S. Koehler in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 305.

[16] R. O. Simmons and R. W. Balluffi, Phys. Rev. **109**, 1142 (1958).

[17] Ludwig Tewordt, Phys. Rev. **109**, 61 (1958).

[18] E. E. Klontz, Atomic Energy Commission Report AECU-2267, 1952 (unpublished).

an intensity maximum occurred at an angle smaller than their limit of observation. However, in the concentric sphere model of reasonable size, typical calculations indicate that φ_{max} should have been observed. Some doubt is therefore cast on the latter model.

IV. DISCUSSION

The sample calculations which we have carried out for these idealized models indicate generally that a model consisting of displaced positive and negative clouds of imperfections is consistent with the small length change and rather strong low-angle scattering. Other models of somewhat different cluster geometry based upon the same general picture may be visualized. Further discussion of detailed structure on the basis of presently available results does not seem warranted.

The formation of such clusters near liquid nitrogen temperatures could come about in two different ways. One mechanism would be the direct production of the clusters upon bombardment. In this mechanism the interstitials would be displaced over appreciable distances in the knock-on process leaving the vacancies behind. The values of N_0 in Cases B and C should then be small compared with the number of primaries calculated from the simple displacement theory (3.4×10^{19}/cm^3 for 6.5-Mev average energy deuterons). The fitting of the length and scattering data gave N_0 values consistent with this requirement. The clusters could also form by the grouping together of defects by diffusive motion after bombardment.

There are difficulties associated with the production of separated clusters on the basis of either of the mechanisms suggested above. The direct production of clusters separated by distances on the order of 60–90 A during bombardment is difficult to understand on the basis of previous displacement theory.[15] It might be postulated that focusing effects[19] analyzed by Silsbee[20] could play a role. One would not expect as much focusing in germanium as in copper since copper has close-packed rows of atoms whereas germanium does not. A range of cluster sizes should be expected in the direct-production model. We may assume approximately that $v\propto N\propto E$, where E is the primary knock-on energy.[9] The number of clusters with volumes between v and $v+dv$ then varies as v^{-2}. The presence of such a distribution of cluster sizes will not greatly change the general conclusions previously reached on the basis of an assumed uniform cluster size. Detailed calculations taking into account the size distribution indicate that the larger clusters make a relatively larger contribution to the total observed low angle x-ray scattering intensity than they do to the total observed length change. The x-ray measurements also tend to measure the radius of gyration of the larger clusters.[21] The calculations indicate that the strains calculated from the data on the assumption of a uniform cluster size are, if anything, somewhat smaller than the true strains. The conclusions rejecting Case A are, therefore, still valid. The fact that the x-rays measure mainly the large clusters may be taken as further evidence that focusing is not primarily responsible for the large apparent cluster spacing since the large clusters should be formed by the high-energy knock-ons where focusing is expected to be weak. Some difficulty is also encountered with the clustering mechanism based on diffusive motion. It is highly probable that appreciable annihilation of the irradiation-induced defects is accompanied by a considerable volume change. Since appreciable recovery of the length change is not observed below 200°K, we may conclude that only a relatively small fraction of the defects can be annealed out below this temperature. The diffusive clustering mechanism, which requires considerable movement of the defects at or below 90°K, must occur without the large-scale annihilation of the defects. It may be possible that interstitials and vacancies repel each other in certain configurations and, therefore, avoid mutual annihilation at low temperature. This is yet to be demonstrated, however.

The vacancy-interstitial displaced cloud model at liquid nitrogen temperature, however produced, must be capable of explaining the resistivity annealing data above nitrogen temperatures where large irreversible resistivity changes were observed before appreciable length changes occurred.[1] Two main mechanisms could account for this behavior: (1) rearrangement of the vacancies and interstitials in various configurations by diffusive motion without appreciable annihilation, and (2) establishment of electronic equilibrium without structural rearrangement. Interstitials are generally believed to contribute donor states and vacancies to contribute acceptor states. The resistivity annealing below 140°K gives an increase in resistivity of the specimens as a result of either thermal defect annealing or the emptying of minority-carrier (electron) traps. We might identify defect annealing with a change in the cluster configuration of the interstitials. The emptying of electron traps would correspond to the establishment of electronic equilibrium. The first explanation agrees with the suggestion of Cleland and Crawford[11,13] for neutron irradiation. The large decrease of resistivity observed between 140°K and 200°K, due to the annealing or emptying of majority-carrier (hole) traps, could also be identified with the rearrangement of the cluster configuration of the vacancies or the re-establishment of thermal electronic equilibrium. Annealing processes continue up to 364°K as shown by the length-change annealing curves.[1]

In discussing these mechanisms it should be mentioned that carrier trapping processes may tend to stabilize the defect and that once the carrier is released the mobility of the defect could be changed. Also, the high dielectric constant of germanium causes the simple

[19] R. C. Bradley, Bull. Am. Phys. Soc. Ser. II, 3, 193 (1958).
[20] R. H. Silsbee, J. Appl. Phys. 28, 1246 (1957).
[21] A. Guinier and G. Fournet, *Small Angle Scattering of X-Rays* (John Wiley and Sons, Inc., New York, 1955).

Bohr orbit model for carriers to predict electronic interaction at relatively great distances between defects. This means that electronic effects produced by rearrangement can take place at distances where elastic forces tending to promote annihilation are small. Above 200°K the resistivity annealing may be attributed to the above mechanisms and also to defect annihilation. It is known that the conductivity does not anneal to its original value until the specimen is heated to 450–500°C. Therefore, the annealing spectrum is spread over a very broad temperature range.

The detailed mechanisms of the defect annihilation cannot be deduced from the presently available results. In copper, it is observed that the irradiation-induced length increase, the electrical resistivity, and the lattice parameter increase anneal out in closely parallel fashion.[7,16] This behavior may be taken as evidence that most of the vacancies and interstitials anneal out by mutual annihilation.[7,16] In the case of germanium the residual length change and lattice parameter change after annealing to 320°K are both small and of roughly the same magnitude.[1,2] This result is, therefore, consistent with mostly parallel (and possibly mutual) annihilation of the vacancies and interstitials. The fact that the reported residual lattice-parameter expansion is somewhat smaller than the residual length-change effect may be a result of the experimental procedure and is further discussed in the preceding paper.[2] The observation that the residual lattice-parameter effect becomes slightly negative in the annealing range 350°K–420°K[2] indicates that all of the defects may not be destroyed by mutual annihilation. Apparently some extra vacancies remain causing a slight lattice parameter contraction. The observed lack of line broadening in the x-ray work[2] is consistent with the presence of point defects.

The previous models, which must be regarded as tentative, appear capable of explaining qualitatively the experimental results in irradiated germanium at the present time. The models are not unique, of course, and other more complicated arrangements may be involved. The vacancy-interstitial cluster model has the advantage that it is relatively simple and seems to require the least number of arbitrary assumptions. It would be rather difficult to account for the uniform nature of the length-change annealing on the basis of a number of independent annealing processes which would be inherent in more complicated models. Further work must be done to establish a unique model. Of particular interest would be information about the dilatation due to vacancies and interstitials, information dealing with the electrical interactions of point defects, further measurements of low-angle scattering at very low angles and low temperatures, and further x-ray lattice parameter measurements over a wide temperature range which could be correlated with the available length change results.

ACKNOWLEDGMENTS

The writers would like to thank Professor J. S. Koehler and Dr. R. O. Simmons for reading the manuscript and for making several helpful suggestions. We would also like to thank Dr. U. Gonser and Dr. F. E. Fujita for informing us of their results prior to publication.

APPENDIX A. DENSITY AND VOLUME CHANGES ASSOCIATED WITH DAMAGED REGIONS

We wish to calculate the density and volume changes associated with the center-of-dilatation models described in Sec. IV, 2. Following Eshelby,[14] and using his notation, we consider first a spherical region of original radius r_0 and volume v_0 which has been strained an amount ϵ and placed in a spherical cavity of radius r, in the center of a spherical body of radius R. The radial displacement is

$$u(r_0)=\frac{r_0\epsilon}{\gamma}\left[1+\frac{4\mu}{3K}\left(\frac{r_0}{R}\right)^3\right]. \tag{A.1}$$

The displacement at the surface of the body is

$$u(R)=\frac{\epsilon r_0^3}{\gamma R^2}\left[1+\frac{4\mu}{3K}\right]=\frac{\epsilon r_0^3}{R^2}. \tag{A.2}$$

The volume changes of the defect region and of the entire body are then

$$\Delta v=4\pi r_0^2 u(r_0)\approx 3\epsilon v_0/\gamma\approx 2\epsilon v_0, \tag{A.3}$$

$$\Delta V=4\pi R^2 u(R)=3\epsilon v_0. \tag{A.4}$$

In order to obtain expressions for the density difference between the defect region and the matrix, we first establish that the density changes in the matrix are negligible compared to changes in the defect region. The displacement $\epsilon r_0^3/\gamma R^2$ in (A.2) is divergenceless and does not change the density in the material surrounding the defect region. The displacement $(\epsilon r_0^3/\gamma R^2)(4\mu/3K)$ causes a very small uniform dilatation and the density in the matrix is, therefore

$$d_m=\frac{d_0}{1+[3v_0\epsilon(\gamma-1)/V_0\gamma]}\approx d_0, \tag{A.5}$$

when $V_0\gg v_0$. However, the density in the defect element differs appreciably from d_0. For an element gaining mass M and undergoing the volume change $2\epsilon v_0$

$$d-d_0=(1/v)(M-2d_0v_0\epsilon). \tag{A.6}$$

So far we have considered the special case where the defect region is at the center of a spherical body. We are interested in the general case where a large number of defect regions are distributed more or less randomly throughout a body of arbitrary shape. For this case

Eshelby[14] has shown that

$$\Delta V/V=3\Delta L/L=3\epsilon v_0 N_0, \tag{A.7}$$

where N_0 is the number of defect regions per unit volume. In addition, we conclude that the difference in density between the matrix and the defect regions in various parts of the body is still given by (A.6) to sufficient accuracy for present purposes.

APPENDIX B. SMALL-ANGLE X-RAY SCATTERING FROM DAMAGED REGIONS

We shall calculate the low-angle x-ray scattering from a defect region consisting of two associated subregions, one of which has gained mass from the other. For concreteness, we take a specific case where the two regions have spherical symmetry and are separated by **a**. Let ρ_1 be the electronic density in subregion 1 which has gained mass M, ρ_2 the electronic density in subregion 2, and ρ_0 the electronic density in the matrix. Using the notation of reference 21, the scattered amplitude from a defect region is then

$$\frac{A(\mathbf{h})}{A_e(\mathbf{h})}=(\rho_0-\rho_1)\int_{v_1}\exp(-i\mathbf{h}\cdot\mathbf{r})d\mathbf{r} +(\rho_0-\rho_2)\int_{v_2}\exp(-i\mathbf{h}\cdot\mathbf{r})d\mathbf{r}, \tag{B.1}$$

where $A_e(\mathbf{h})$ is the scattering amplitude produced at zero angle by an electron at the origin.

Carrying out the integration and making the Guinier exponential approximation, we obtain

$$A(\mathbf{h})/A_e(\mathbf{h})=\Delta n_1\exp(-2\pi^2\varphi^2R_1^2/3\lambda^2) +\Delta n_2\exp(-2\pi^2\varphi^2R_2^2/3\lambda^2)\exp(-i\mathbf{h}\cdot\mathbf{a}), \tag{B.2}$$

where R_1 and R_2 are the radii of gyration of the subregions, and φ is the scattering angle (the angle between the incident and scattered beams). For a spherical shell, R is related to the inner and outer radii by

$$R^2=3(r_1^5-r_2^5)/5(r_1^3-r_2^3).$$

Δn_1 and Δn_2 are given (from Appendix A) by

$$\begin{aligned}\Delta n_1&=n-2\rho_0 v_{10}\epsilon_1,\\ \Delta n_2&=-n-2\rho_0 v_{20}\epsilon_2,\end{aligned} \tag{B.3}$$

where n is the number of transferred electrons. The scattered intensity is then

$$I(\mathbf{h})/I_e(\mathbf{h})=(\Delta n_1)^2\exp(-4\pi^2\varphi^2R_1^2/3\lambda^2) +(\Delta n_2)^2\exp(-4\pi^2\varphi^2R_2^2/3\lambda^2)+2\Delta n_1\Delta n_2 \times\{\exp[-2\pi^2\varphi^2(R_1^2+R_2^2)/3\lambda^2]\}\cos(\mathbf{h}\cdot\mathbf{a}). \tag{B.4}$$

The intensity for N_0 damaged regions is then

$$I(\mathbf{h})/I_e(\mathbf{h})=N_0[(\Delta n_1)^2\exp(-4\pi^2\varphi^2R_1^2/3\lambda^2) +(\Delta n_2)^2\exp(-4\pi^2\varphi^2R_2^2/3\lambda^2)+2(\Delta n_1)(\Delta n_2) \times\{\exp(-2\pi^2\varphi^2(R_1^2+R_2^2)/3\lambda^2)\} \times\sin(2\pi a\varphi/\lambda)/(2\pi a\varphi/\lambda)], \tag{B.5}$$

if we assume that **a** is randomly orientated. It is noted that $\sin(2\pi a\varphi/\lambda)/(2\pi a\varphi/\lambda)$ falls to zero when $(2a\varphi/\lambda)\gtrsim 1$ and approaches unity as φ goes to zero.