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Acceptors Produced in Germanium by Quenching from High Temperatures

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Acceptors were produced in germanium single crystals by heating at high temperatures and then quenching very rapidly. Fuller *et al.* have measured the diffusion coefficient for these thermally produced acceptors and on the basis of their measurements the assumption is made here that the acceptor levels are due to Schottky defects. An expression is derived for the equilibrium density of ionized Schottky defects and on the basis of this theoretical expression and the experiments performed it is found that (1.49±0.12) ev must be supplied to the crystal to form a Schottky defect. An estimate of (2.0±0.1) ev is made for the "activation energy" of self-diffusion in germanium if diffusion occurs by a vacancy mechanism.

I. INTRODUCTION

IT has been found[1,2] that if germanium is cooled rapidly from temperatures greater than 500°C perceptible numbers of acceptors are added. These acceptors can be removed by annealing at temperatures of 500°C or less. Lark-Horovitz and his co-workers[3] have found a similar effect in nucleon bombarded samples of germanium. As with rapidly cooled samples, the acceptors added by nucleon bombardment can be removed by low temperature annealing. DeSorbo and Dunlap's low temperature resistivity measurements[4] indicate that the added acceptor levels are 0.03 ev above the valence band.

Lark-Horovitz[3] has proposed that the thermally produced p-type carriers may be the result of acceptor levels introduced by lattice defects produced by physical displacement of the germanium atoms from their normal lattice sites. This theory has been generally accepted as correct.

II. LATTICE DEFECTS

Frenkel defects occur when an atom leaves its normal lattice position and moves to an interstitial position. Schottky defects occur when atoms move from their normal lattice sites and go to the surface of the crystal. Actually Schottky defects are created by a diffusion of vacant lattice sites from the surface to the interior of the crystal.

There is a deficiency of electrons around a vacant lattice site and, hence, there should be localized acceptor levels at these positions. Thus Schottky defects should introduce p-type carriers. Lark-Horovitz[3] has postulated that interstitial atoms produce localized donor levels, but if these levels lie far below the conduction band they will not introduce many n-type carriers and the net effect of a Frenkel defect will be acceptor levels around the vacant lattice sites.

In Sec. III we discuss the work of Fuller, Theuerer, and van Roosbroeck and conclude from their work that the acceptors created by rapid cooling from high temperatures are due to ionized Schottky defects. For this reason we will concentrate on Schottky defects in this section.

The equilibrium density of Schottky defects, n_s, in a polar crystal is[5]

$$n_s = N_L \exp(\Delta s/k) \exp(-\Delta h/kT), \qquad (1)$$

where N_L is the density of lattice sites, Δs is the change in entropy of the atoms about a vacant lattice site due to the increase of the amplitude of vibration, and Δh is the energy necessary to create a Schottky defect. However, Eq. (1) does not hold for Schottky defects in germanium. In germanium we must take into consideration the fact that these defects are ionized and, hence, when a defect is created we change the density of electrons in the conduction band and holes in the valence band and the electron energy changes accompanying these changes of density must be considered.

The Gibbs free energy should be invariant to small arbitrary changes in n_s, p_v, and n_c, where n_s is the number of Schottky defects and is equal to the number of electrons trapped in these defects if we assume that each defect produces one acceptor level and all these acceptor levels are ionized (see Sec. VI). p_v is the number of holes in the valence band and n_c is the number of electrons in the conduction band. The only restriction on the small arbitrary change is

$$\delta n_c + \delta n_s = \delta p_v. \qquad (2)$$

For thermal equilibrium the total change of the Gibbs free energy is

$$\delta G = \delta G_v + \delta G_c + \delta G_s = 0, \qquad (3)$$

where G_v, G_c, and G_s are the free energies of the p_v holes in the valence band, n_c electrons in the conduction band, and the n_s Schottky defects respectively.

$$G_s = n_s \Delta h - kT \ln \frac{N_L!}{n_s!(N_L - n_s)!} - T n_s \Delta s, \qquad (4)$$

where Δh, Δs, and N_L are the same as in Eq. (1).

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[1] H. C. Torrey and C. A. Whitmer, *Crystal Rectifiers* (McGraw-Hill Book Company, Inc., New York, 1948), p. 365.

[2] H. C. Theuerer and J. H. Scaff, Trans. Am. Inst. Mining Met. Engrs. **189**, 59 (1951).

[3] K. Lark-Horovitz in *Semi-Conducting Materials*, H. K. Henisch, Editor (Butterworths Scientific Publications, London, 1951).

[4] W. DeSorbo and W. C. Dunlap, Jr., Phys. Rev. **83**, 869, 879 (1951).

[5] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1948), Chap. 2.

We let $(\delta n_s, \delta n_c, \delta p_v)=(1, -\frac{1}{2}, \frac{1}{2})$ which is the same as saying we ionize a vacancy by taking one-half an electron from the valence band and one-half an electron from the conduction band.[6] With this variation, we have

$$\delta G_v=\tfrac{1}{2}(E_s-E_v)+\text{entropy term}, \tag{5}$$

$$\delta G_c=\tfrac{1}{2}(E_s-E_c)+\text{entropy term}, \tag{6}$$

where E_s is the energy of an electron trapped at a defect, and E_c and E_v are the energies of electrons at the bottom of the conduction band and at the top of the valence band respectively. With the variation used here it can be shown that the entropy terms in (5) and (6) are equal in magnitude but of opposite sign.

From (4) we find

$$\delta G_s=\Delta h-T\Delta s-kT\ln[(N_L-n_s)/n_s], \tag{7}$$

and substituting (5), (6), and (7) into (3) we obtain the relation

$$E_s-E_F+\Delta h-T\Delta s-kT\ln[(N_L-n_s)/n_s]=0, \tag{8}$$

where $E_F=\frac{1}{2}(E_c+E_v)$ is the Fermi level in an intrinsic semiconductor. (Germanium is in the intrinsic range at all temperatures used to produce thermal acceptors.)

Rewriting (8) and using the approximation $n_s \ll N_L$ we get

$$n_s=N_L\exp(\Delta s/k)\exp(-\Delta H/kT), \tag{9}$$

where $\Delta H=\Delta h-(E_F-E_s)$. DeSorbo and Dunlap's[4] low temperature resistivity measurements show that E_s is 0.03 ev above the top of the valence band. Then if we assume that the energy gap in germanium is 0.72 ev, E_F is 0.36 ev above the top of the valence band and $\Delta H=\Delta h-0.33$ ev. Hence in creating a vacancy at high temperatures an energy Δh is needed, 0.33 ev of which comes from the electrons in the crystal and ΔH comes from the heat reservoir surrounding the crystal.

The assumptions used in the derivation of Eq. (9) limit its use to temperatures where germanium is an intrinsic semiconductor. This is true, however, at all temperatures where a perceptible number of defects are formed.[7]

Mott and Gurney[5] show that $\Delta s/k=\ln(\nu/\nu')^x$, where x is the number of nearest neighbors, ν is the normal frequency of vibration and ν' is the frequency of vibration along a line between an atom and an adjacent vacant site. For germanium $x=4$, and if we assume that $(\nu/\nu')=\sqrt{2}$ then $\exp(\Delta s/k)=4$. It should be emphasized that this prediction for $\exp(\Delta s/k)$ is only a rough approximation to give the order of magnitude and depends on the magnitude of (ν/ν').

III. PREVIOUS STUDIES OF THERMALLY PRODUCED ACCEPTORS

In studies of thermally produced acceptors it has always been assumed that the equilibrium number of defects is reached in a reasonable time at high temperatures and that these defects are "frozen in" when the crystal is rapidly cooled to lower temperatures. At room temperature the approach to equilibrium is extremely slow and the number of defects present is dependent upon the temperature from which the sample was rapidly cooled.

Fuller, Theuerer, and van Roosbroeck[8] have observed the diffusion of these acceptors from the surface to the interior of the crystal and they measured the diffusion coefficients at several temperatures. The values they obtained for diffusion coefficients fit the relation

$$D=D_0\exp(-E/kT), \tag{10}$$

where $D_0=0.02$ cm^2/sec and $E=0.5$ ev. The diffusion coefficients they measured ranged from 3.2×10^{-5} cm^2/sec at 670°C to 9.5×10^{-5} cm^2/sec at 850°C. The observed value of E is small compared to most energies found in diffusion measurements and should be equal to the height of the potential barrier that an atom must go through or pass over when moving to an adjacent lattice site that is vacant (if we assume we are observing the diffusion of Schottky defects).

If there is an equilibrium density of defects at the surface, then there will be an appreciable fraction of the equilibrium density at a distance x from the surface after a time $t=x^2/4D$. At 560°C Eq. (10) gives $D=1.8\times10^{-5}$ cm^2/sec, and we would expect equilibrium in a sample 1 mm thick in less than one minute. This is in contradiction to the experimental evidence. Theuerer and Scaff[2] indicate that it is a matter of hours before equilibrium is reached at this temperature, so Eq. (10) does not give the proper values for D at low temperatures.

Although there may be some doubt about the accuracy of Eq. (10), the diffusion experiments do have one important conclusion which can be reached from the qualitative results. These experiments show that the thermally produced acceptors are produced at the surface and diffuse into the bulk of the crystal from the surface. From the discussion in Sec. II we can see that if these acceptors are due to lattice defects, these defects must be Schottky and not Frenkel defects because there would be no diffusion from the surface in the case of Frenkel defects. (The diffusion experiment does not give us any information about the type of defect produced by nucleon bombardment and it seems quite likely that bombardment may produce Frenkel defects.) If we assume that each Schottky defect produces one acceptor and that all these acceptors are ionized at room temperature (these assumptions are discussed in Sec. VI) Δn, the increase in the number

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[6] Although the Gibbs free energy should be invariant for any arbitrary variation $(\delta n_s, \delta n_c, \delta p_v)$ it is shown in the appendix to this paper that when $\delta n_s=1$, then $\delta p_v=-\delta n_c=\frac{1}{2}$.

[7] The equilibrium density of ionized Frenkel defects can also be derived by the method used in this paper. The result is

$$n_f=N_L\exp(\Delta s/2k)\exp(-\Delta H/2kT),$$

where ΔH is the same as in Eq. (9) and $\Delta s=\Delta s_i+\Delta s_v$, with Δs_i and Δs_v being the entropy changes of the atoms surrounding an interstitial atom and a vacancy, respectively.

[8] Fuller, Theuerer, and van Roosbroeck, Phys. Rev. **85**, 678 (1952).

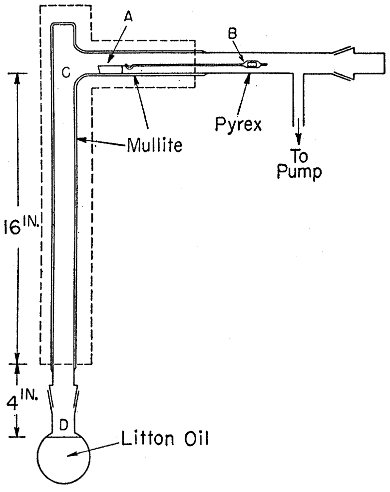

FIG. 1. Rapid quenching apparatus.

of carriers at room temperature created by quenching from temperature T, should be [see Eq. (9)]

$$\Delta n = N_L \exp(\Delta s/k) \exp(-\Delta H/kT), \qquad (11)$$

with $\exp(\Delta s/k) \simeq 4$.

Fuller, Theuerer, and van Roosbroeck also measured the equilibrium density of acceptors added as a function of the temperature at which the samples were heat treated before quenching. Their data fit Eq. (11) with $\exp(\Delta s/k) = 0.053$ and $\Delta H = 1.2$ ev. They used resistivity measurements to determine the number of acceptors introduced, using the relation $1/\rho = ne\mu$, where ρ is the resistivity, n the density of carriers, e is the electronic charge, and μ the mobility.

Taylor[9] has studied the number of acceptors introduced by quenching from different temperatures. (He assumed that the acceptor levels were due to Frenkel defects.) He treated his samples in a vacuum of 10^{-2} mm. After approximately one hour of heating, air was admitted to the system, the sample was quickly removed and quenched in ethyl alcohol that was at room temperature. (Renzema[10] feels that the air admitted when the system is opened so that the sample may be removed may be the mechanism of the rapid cooling. However, from simple calorimetric considerations this does not seem very probable. The air would not cool the sample more than a few degrees.)

Taylor determined the number of acceptors introduced by making resistivity measurements before and after quenching. He had previously[11] prepared a graph giving the number of carriers as a function of resistivity. This graph was prepared from a study of the correlation between Hall constant and resistivity. A straight line was drawn through a log log plot of resistivity and Hall constant. Inspection of this plot leaves considerable doubt as to the accuracy of carrier concentration that could be obtained from resistivity measurements using the straight line approximation.

Taylor's quenching experiments show that Δn fits Eq. (11) with $\Delta H = 1.8$ ev and $\exp(\Delta s/k) = 330$.

IV. EXPERIMENTAL APPARATUS

The apparatus used for rapid quenching is shown in Fig. 1. A vacuum of better than 10^{-5} mm was attainable. The "T" shaped Mullite tube was made to our specifications by the McDanel Refractory Porcelain Company, Beaver Falls, Pennsylvania. The parts of the system within the dashed line are inside a furnace. The germanium sample was placed in a porcelain boat and the boat was moved to the position A. A slug of iron was enclosed at B in the frame connected by a hook to the boat containing the germanium. To cool the sample rapidly a magnet was used to move the iron slug at B to the left, the germanium dropping into the Litton oil quenching bath when the boat got to position C. Due to the fact that the germanium was heated during the early part of its fall, it was moving rapidly when it left the furnace. Simple calculations show that the sample took only 0.034 second to fall the last 4 inches. The total time of fall is only 0.323 second. If the entire furnace is at the same temperature then the sample goes from the temperature at which is was heat treated to the quenching bath in 0.034 second. In actual practice the temperature at the lower part of the furnace was less than at the top. If the top of the furnace was at 900°C, the lower part of the furnace was at about 670°C. We have not made quantitative calculations concerning the effect this would have on the temperature of the sample as it left the furnace, but we feel it is safe to say that the sample reached the quenching bath in a time considerably less than 0.3

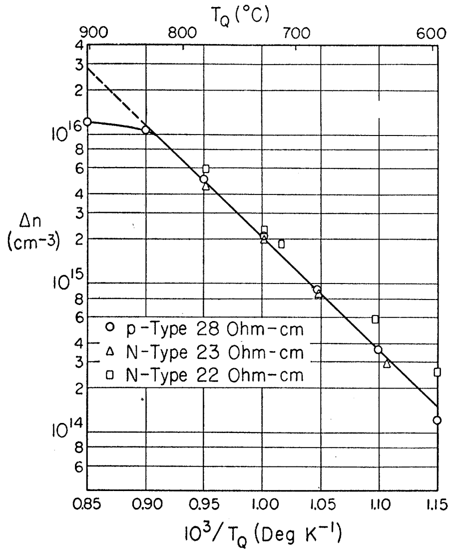

FIG. 2. Change in carrier density produced by quenching from temperature T_Q.

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[9] W. E. Taylor, Purdue Sixth Quarterly Report (1950) p. 1; Phys. Rev. 86, 642 (1952).

[10] T. S. Renzema, Purdue Twelfth Quarterly Report (1951) p. 16 (unpublished).

[11] W. E. Taylor, Purdue Sixth Quarterly Report (1950) p. 3 (unpublished).

second, which is a marked improvement over other systems described in the literature.

V. RESULTS AND ANALYSIS OF THE MEASUREMENTS

Single crystals of germanium of both *n*- and *p*-type were used. Sample thickness was between 0.3 and 0.8 mm. After low temperature annealing to insure that there were very few lattice defects present, Hall measurements were made. The density of carriers present was determined from the well-known approximation

$$n = 7.37\times10^{18}/R\ \text{cm}^{-3},$$

where R is the Hall constant. Hall measurements were again made after quenching and n was determined by the above relation. The increase in carriers was then determined by algebraic subtraction of the two values:

Δn = Carriers after quenching minus carriers in annealed sample.

With the apparatus used in our early experiments, it took at least 6 seconds for the sample to move from the furnace to the quenching bath. These experiments indicated that the density of carriers added by quenching from 904°C was not much greater than the density added by quenching from 727°C. We felt that this might be due to the fact that in six seconds that elapsed from the time the sample was removed from the furnace to the time that it was dropped into the quenching bath the sample may have cooled appreciably by radiation. If equilibrium is reached very quickly at these high temperatures, the number of defects frozen in would correspond to a lower temperature than that of the furnace.

As mentioned in Sec. IV, the system shown in Fig. 1 was constructed so that the sample would be transported from the furnace to the quenching bath in minimum time. The results obtained with this furnace are shown in Fig. 2 and fit Eq. (11) with $\Delta H = (1.49\pm0.12)$ ev, $\exp(\Delta s/k) = 1.5$. This value for $\exp(\Delta s/k)$ compares favorably with our estimated value of 4 when we consider the possible error involved in the extrapolation to $1/T = 0$ when there is an uncertainty in ΔH. From the discussion following Eq. (9) we see that a value of $\Delta H = (1.49\pm0.12)$ ev means that the energy necessary to form a Schottky defect is (1.82 ± 0.12) ev, 0.33 ev being supplied by electrons and (1.49 ± 0.12) ev being supplied by the surroundings of the crystal.

The values of Δn were reproducible for different samples as long as the sample was not quenched from temperatures greater than 850°C. If the samples were quenched from temperatures greater than 850°C and later quenched from lower temperatures, the value of Δn at these lower temperatures would be about 20 percent higher than values obtained before the high temperature quenching. One sample was heated to 900°C and then cooled to 727°C before quenching. This treatment did not cause the effect described above so the effect must be due to the quenching from high temperatures and not to the high temperature heat treatment. We have not been able to explain this phenomenon.

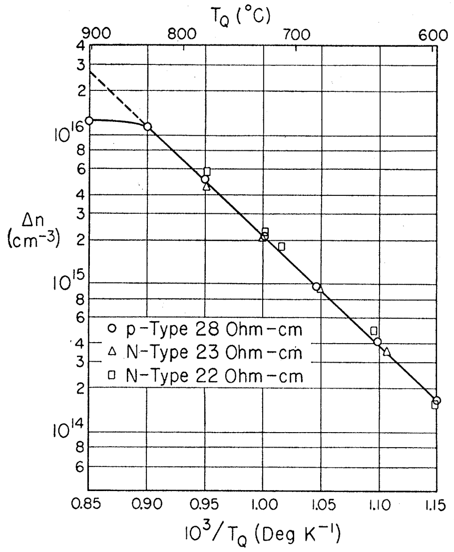

FIG. 3. Corrected data from Fig. 2 (see text).

Our data are scattered more at the lower temperatures than at the higher temperatures. This is to be expected since an error in measuring the Hall constant before quenching would have a greater effect on the low temperature results than on the high temperature results. We have found that if we make a small correction to the number of carriers in each sample before quenching, the data will almost all fall on a straight line (Fig. 3) and at temperatures below 840°C this straight line will fit Eq. (11) with $\exp(\Delta s/k) = 0.96$ and $\Delta H = (1.45\pm0.05)$ ev.

The leveling off at the higher temperatures is probably due to the fact that at high temperatures equilibrium is reached in a time which is short compared to the time that the sample takes to cool to low temperatures in the quenching bath. This seems reasonable because other workers whose systems did not quench as rapidly as ours found the leveling off at lower temperatures.

Our values of Δn are roughly equal to those of Fuller, Theuerer, and van Roosbroeck[8] (see Sec. III). However, our data gives a better value for $\exp(\Delta s/k)$ and a higher value for ΔH.

VI. MISCELLANY

As pointed out in Sec. II, there is a deficiency of electrons around a vacant lattice site and the vacant site can act as an acceptor of electrons. We have assumed that each vacancy accepts but one electron, whereas a vacant site may be able to accept a maximum of four electrons and, if this were the case, each vacancy should act as four acceptors. However, we would expect that it would take much more energy to doubly ionize a vacancy than it would for single ionization. This is the same as assuming that of the four acceptor levels the lowest one is close to the valence band and the others lie above any donor levels that happen to be present.

The low temperature resistivity measurements of DeSorbo and Dunlap[4] indicate that the acceptor levels introduced by rapid cooling are 0.03 ev above the conduction band. Calculations based on the work of Longini[12] show that for acceptor levels 0.03 ev above the valence band the fraction of un-ionized acceptors at room temperature will be 10^{-3} for $(N_a-N_d)=10^{16}$; 10^{-4} for $(N_a-N_d)=10^{15}$; and 10^{-5} for $(N_a-N_d)=10^{14}$. From these calculations we see that it is safe to assume that all acceptor levels introduced by rapid cooling are ionized at room temperature.

If the diffusion process for chemical impurities in germanium is a vacancy mechanism, we can make an estimate as to the temperature dependence of the diffusion coefficient. The diffusion coefficient can be represented as $D=D_0\exp(-W/kT)$. For a vacancy mechanism of diffusion $W=E'+E''$, where $E'=\Delta H$, the energy that has to be supplied to form a Schottky defect, and E'' is the height of the potential barrier that a diffusing atom must pass through or over in moving from a normal lattice site to an adjacent vacant lattice site. From our data $E'=1.49$ ev and the measurements of Fuller, Theuerer, and van Roosbroeck (see Sec. III) indicate that $E''=0.5$ ev for self-diffusion in germanium. Hence the "activation energy" for self-diffusion in germanium should be about (2.0 ± 0.1) ev. The activation energy for diffusion of impurities in germanium would depend on the value of E'' for these impurities. It is reasonable to assume that for those impurities that fit into the normal lattice sites of germanium (the Group III and V elements) E'' would not be too much different from the value for self diffusion. Dunlap[13] reports a value of $W=2.5$ ev for the diffusion of antimony in germanium compared with our estimated value of (2.0 ± 0.1) ev for self-diffusion. Our, comments in Sec. III indicate that if the experiments of Fuller, Theuerer, and van Roosbroeck are in error, the correct value should be higher than the 0.5 ev they report. If this is true our estimate of the activation energy for self-diffusion will be raised closer to the value that Dunlap reports for the diffusion of antimony in germanium.[14]

The early part of this work was carried out in collaboration with Mr. R. E. Brown and we wish to thank him for the many valuable suggestions he made at that time. Thanks are also due to Drs. R. L. Longini and C. Zener who contributed many useful ideas.

APPENDIX

Effect of Adding an Ionized Vacancy on the Number of Conduction Band Electrons and Valence Band Holes

If there are n_c electrons in the conduction band and p_v holes in the valence band then

$$n_cp_v=A(T), \tag{1}$$

where $A(T)$ depends only on temperature. If we add n_s ionized vacancies to a crystal then

$$n_s+n_c=p_v. \tag{2}$$

Substituting (2) in (1) we find

$$p_v^2-n_sp_v-A(T)=0, \tag{3}$$

and solving this by the quadratic formula

$$p_v=\frac{n_s}{2}+\tfrac{1}{2}[n_s^2+4A(T)]^{\frac{1}{2}},$$

$$\delta p_v=\delta n_s/2, \tag{4}$$

since $n_s^2\ll A(T)$. Using (4), (2) gives us

$$\delta n_c=-\delta n_s/2.$$

Note added in proof:—Recently Fuller and Struthers (Phys. Rev. **87**, 526 (1952)) have published evidence that thermal acceptors in germanium may be due to the presence of copper as an impurity.

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[12] R. L. Longini, Westinghouse Research Report R-94416-3-D (1951) (unpublished).

[13] W. C. Dunlap, Jr., Phys. Rev. **86**, 615 (1952).

[14] C. Fuller has recently [Phys. Rev. **86**, 1936 (1952)] published the results of measurements on the diffusion coefficients of arsenic and antimony in germanium. He finds an "activation energy" of 2.2 ev which is to be compared with our estimated value of (2.0 ± 0.1) ev. If "probable errors" were given for Fuller's measurement of the activation energy for diffusion of impurities in germanium and for Fuller, Theurer, and van Roosbroeck's measurement (reference 8) of the activation energy for diffusion of vacancies in germanium, our estimate of the activation energy for self diffusion in germanium would undoubtedly agree within the probable errors with Fuller's measurement of the activation energy for impurity diffusion in germanium. This is a strong indication that the mechanism of diffusion in germanium is a vacancy mechanism.