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Effect of hydrostatic pressure, temperature, and doping on self-diffusion in germanium

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The tracer-diffusion coefficient for ^{71}Ge has been measured in Ge single crystals as a function of pressure, temperature, and doping. Ion-beam sputtering was used for microsectioning. The activation volume in intrinsic Ge increases slightly with temperature from 0.24Ω at 876 K to 0.41Ω at 1086 K (Ω is the atomic volume). The fairly small values of the activation volume show that the defect or defects which act as diffusion vehicles must be either strongly relaxed and/or spread out. Measurements of the doping dependence performed at 973 K show that the diffusivity increases with *n* doping and decreases with *p* doping. This supports the view that self-diffusion in Ge proceeds by a vacancy mechanism and that the vacancy acts as an acceptor. As a consequence the contribution of negatively charged vacancies, which is about 77% for intrinsic material, increases (decreases) with *n* doping (*p* doping). The measurements of the pressure dependence of the diffusivity in doped materials, also performed at 973 K, show that the activation volume is larger for *p*- than for *n*-doped material. We deduce 0.56Ω for the activation volume for the neutral vacancy and 0.28Ω for the negatively charged vacancy.

I. INTRODUCTION

A measurement of the effects of hydrostatic pressure on diffusion is a powerful, though specialized, tool for determining valuable information about those atomic defects which act as diffusion vehicles under thermal equilibrium conditions. In the case of metals such experiments have contributed considerably to the clarification of the mechanism of self-diffusion.[1-3] To our knowledge no such experiments have been reported for semiconductors. One reason for this lack may be the smallness of the self-diffusion coefficient in semiconductors as compared to that in metals. In the present paper we overcome this difficulty by the application of ion-beam sputtering (IBS), which over the last decade has developed into a reliable serial sectioning technique for tracer-diffusion studies.

From measurements of the *self-diffusion coefficient* (D^T) *as a function of hydrostatic pressure* (p), the activation volume of self-diffusion (V^{SD}) may be deduced according to (see, e.g., Ref. 4)

$$V^{\mathrm{SD}}=k_B T\left[-\frac{\partial \ln D^T}{\partial p}+\frac{\partial \ln \nu^0}{\partial p}\right]. \tag{1}$$

In Eq. (1), k_B denotes Boltzmann's constant and T the absolute temperature. ν^0 is the so-called attempt frequency. The first term in Eq. (1) is obtained by measurement of the variation of D^T with p at constant temperature, whereas the second term represents a small correction not exceeding a few percent of V^{SD}.

For a diffusion mechanism, which requires thermally generated defects, the activation volume contains one term related to the formation (superscript F) and another term related to the migration (superscript M) of the defect, according to

$$V^{\mathrm{SD}}=V^F+V^M . \tag{2}$$

In the case of a vacancy mechanism the magnitude of the formation volume will depend on the degree to which the atoms surrounding the vacancy relax into it. If there is no such relaxation, V^F would be equal to one atomic volume Ω. There will, however, be some relaxation and V^F will be less than Ω. The migration volume V^M is due to the fact that at the saddle point the diffusing atom is expanding a constriction. Experiments on gold[5] show that V^M is positive, but small. Obviously, V^{SD} is an important property of the defect(s) responsible for diffusion.

We also study the *effects of doping* on tracer self-diffusion in Ge. A doping dependence of the diffusion coefficient is expected whenever the diffusion vehicles occur in more than one electrical charge state. According to James and Lark-Horovitz[6] as well as Seeger and Chik,[7] a vacancy in Ge possesses an acceptor level in the lower half of the band gap. If self-diffusion proceeds by a vacancy mechanism, *n* doping is expected to raise the equilibrium concentration of negatively charged vacancies and hence to enhance the diffusivity, whereas *p* doping should have the opposite effect. It is one aim of the present paper to check this model in a quantitative manner.

The measurement of the *diffusivity as a function of tem-*

perature is a common tool in tracer-diffusion studies in solids and has been applied to Ge in the past by several groups.[8–12] Because of the already-mentioned smallness of the self-diffusion coefficient in Ge, most of the previous investigations have been limited to fairly narrow temperature ranges near the melting temperature. The temperature range covered in the present experiments for intrinsic Ge is much wider than in the earlier studies and is similar to the range covered in a recent work from this group.[12]

II. EXPERIMENTAL PROCEDURE

A. Materials and specimen preparation

The diffusivity of the tracer ^{71}Ge was measured as a function of pressure and temperature in intrinsic and doped Ge single crystals. In order to obtain significant doping effects, the doping concentration must be comparable to the intrinsic carrier concentration at the diffusion temperature. n-doped material with 3×10^{24} (Sb atoms)/m^3 and p-doped materials with either 3×10^{24} or 2×10^{25} (Ga atoms)/m^3 were available. Single crystals were grown by the Czochralski technique, cut with a diamond saw, and ground into cylinders about 5 mm in diameter and 5 mm high. Finally, one surface of the samples was lapped and polished with Syton. The radioisotope ^{71}Ge was produced by neutron irradiation of about 30 μg of high-purity Ge. The principal reaction involves the conversion of the stable isotope ^{70}Ge into ^{71}Ge by (n,γ) processes. After ten days of irradiation with a thermal flux of 8×10^{17} neutrons/m^2 s^{-1}, the specific activity was about 6.6 Ci/g. This radioactive material was deposited by evaporation on the surface of the polished Ge samples, providing a thin-film diffusion source.

B. Diffusion anneal under high pressure

Usually, two specimens with the radioactive sides facing each other were placed in the center of the furnace within a ceramic tube with their cylinder axis parallel to the horizontal axis of symmetry of the furnace. The furnace itself was situated within a high-pressure cell. A cross-sectional view of the assembled high-pressure cell with its internal furnace has been already published by Rein and Mehrer[2] and will not be repeated here. An improvement concerned the conduction of the power lead through the pressure plug. Instead of brazing the power lead in sheets into the pressure plug, we used a copper wire, 0.6 mm in diameter, which was brazed in a 16° silver-steel cone isolated with a Kynar sheet against the pressure plug.

The high-pressure cell was loaded using a gas-pressure system from Harwood Engineering Company. The pressure medium was high-purity argon (99.999%) and pressure was measured using a Manganin gauge. Pressures up to 6 kbar (0.6 GPa) could be reached and kept constant for several days.

After the vessel was pressurized, the specimen was heated to the desired temperature. Both temperature and pressure were continuously recorded on a two-channel recorder. The temperature was controlled within ±0.5 K. For temperature measurement and control a Chromel-Alumel thermocouple was used, chosen because it shows only a small pressure effect on the thermoelectric force, as has been reported by Cheng, Allen, and Lazarus.[13] To determine the true temperature inside the pressure system, the temperature corrections were subtracted from the indicated temperature.

C. Sectioning and counting

After the diffusion anneals, the samples were sectioned using an ion-beam sputter-sectioning (IBS) technique. A plasma ion source produces a fairly intense beam of Ar ions with energies of several hundred eV. The beam hits the sample surface at an oblique angle. The samples were rotated at 3 rev/min. A constant fraction of the sputtered material was collected on a heat-resistant polyester ribbon which could be advanced stepwise from outside the sputtering device, so that 20–30 subsequent sections could be taken. The sputtering rate was kept constant by using a constant acceleration voltage (usually 500 V), controlling the pressure in the ion source, and recording the beam current. The sputtering rate was determined for each specimen from an interferometric measurement of the total sputtered thickness and the total sputtering time. The sputtering rate was typically of the order of 15 nm/min.

After sectioning, the polyester foil was cut into sections and put into counting vials together with a liquid scintillation mixture (Aquasol, New England Nuclear Com-

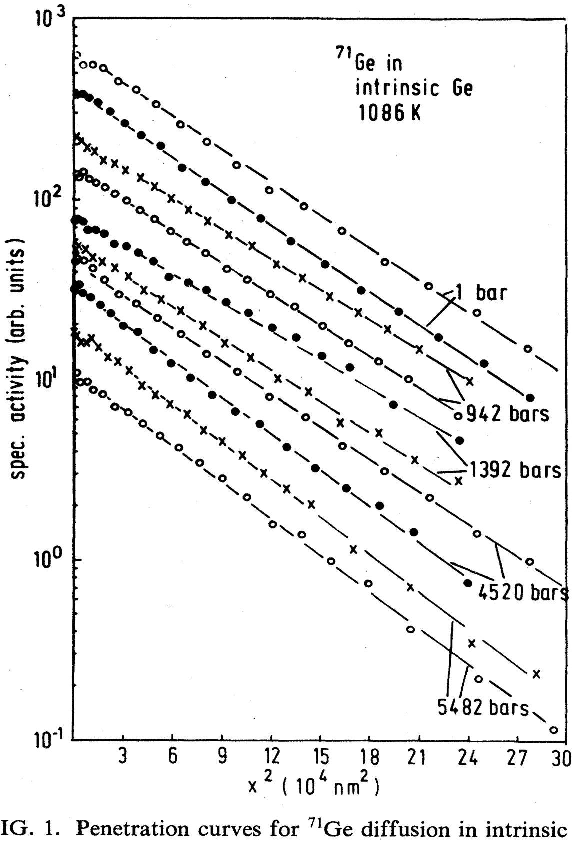

FIG. 1. Penetration curves for ^{71}Ge diffusion in intrinsic Ge at 1086 K and for various pressures.

pany). ^{71}Ge decays by electron capture into ^{71}Ga. The soft x rays emanating from ^{71}Ga were counted in a liquid scintillation counter (Nuclear Enterprises), producing at least 10^4 counts above the background.

For the boundary conditions of the present experiments, the distribution of specific activity c of the radioactive tracer after diffusion for a time t is expressed in the usual exponential form

$$c = c_0 \exp(-x^2/4D^T t) , \tag{3}$$

where x is the distance from the original surface, D^T the diffusion coefficient, and c_0 a constant independent of x.

III. EXPERIMENTAL RESULTS

Altogether, 92 successful diffusion runs were performed. Figure 1 shows as an example typical penetration curves for ^{71}Ge diffusion in Ge for different pressures at 1086 K. Since the penetration curves, plotted as $\log_{10}c$ vs x^2, are linear, the distributions of radioactive tracer follow Eq. (3) and the calculated diffusion coefficients represent bulk diffusion. No evaporation of the radioisotope from the thin surface layer was apparent.

The values of the diffusion coefficient D^T determined from least-squares fits of Eq. (3) to the individual penetration curves are listed in Table I for intrinsic Ge and in Table II for doped Ge. The errors in D^T from the least-squares fit of the data to Eq. (3) are about 2—3 %. The total errors in D^T are about 10% and arise mainly from the accuracy of the interferometric depth measurements.

Figure 2 shows an Arrhenius plot of the D^T values for intrinsic Ge at ambient pressure, together with the data from all previous studies. The present values confirm the data published by Vogel, Hettich, and Mehrer,[12] which also cover a similar wide temperature range. Possible reasons for the small discrepancy with the earlier studies have been already reported by Vogel *et al.* and will not be

TABLE I. Diffusion data for ^{71}Ge diffusion in intrinsic Ge single crystals at various temperatures and pressures.

Temperature (K)	Pressure (10^5 Pa)	Time (s)	D^T (m^2/s)	$2(D^T t)^{1/2}$ (nm)
1177	1	1 020	8.78×10^{-17}	598.5
	1	1 020	8.65×10^{-17}	594.1
	1	1 140	8.55×10^{-17}	624.4
1169	1	1 140	7.20×10^{-17}	573.0
1131	1	1 788	2.59×10^{-17}	430.4
	1	1 788	2.52×10^{-17}	424.5
1086	1	2 520	7.35×10^{-18}	272.2
	1	2 520	7.11×10^{-18}	267.7
	942	2 672	7.34×10^{-18}	280.1
	942	2 672	7.19×10^{-18}	277.2
	1392	2 880	7.45×10^{-18}	292.9
	1392	2 880	6.40×10^{-18}	271.5
	4520	3 000	6.37×10^{-18}	276.5
	4520	3 000	5.45×10^{-18}	255.7
	5482	3 280	5.05×10^{-18}	257.4
	5482	3 280	5.03×10^{-18}	256.9
1025	1	16 380	9.65×10^{-19}	251.5
	1276	13 440	9.55×10^{-19}	226.6
	1276	13 440	9.18×10^{-19}	222.2
	2789	11 900	8.65×10^{-19}	202.9
	2789	11 900	8.24×10^{-19}	198.1
	3183	10 900	8.28×10^{-19}	190.0
	3183	10 900	8.02×10^{-19}	187.0
	4960	15 300	8.08×10^{-19}	222.4
	4960	15 300	6.94×10^{-19}	206.1
973	1	18 200	1.54×10^{-19}	105.9
	1	12 000	1.52×10^{-19}	85.4
	1	12 000	1.51×10^{-19}	85.1
	1	18 200	1.46×10^{-19}	103.1
	1	12 000	1.42×10^{-19}	82.6
	915	12 000	1.39×10^{-19}	81.7
	1100	5 290	1.40×10^{-19}	54.4
	1296	7 800	1.38×10^{-19}	65.5
	2150	12 000	1.35×10^{-19}	80.5
	2316	12 000	1.24×10^{-19}	77.2
	2515	10 900	1.34×10^{-19}	76.4
	2515	10 900	1.23×10^{-19}	73.2
	2982	12 000	1.30×10^{-19}	79.0
	3041	12 000	1.29×10^{-19}	78.7
	3501	11 325	1.26×10^{-19}	75.6
	3972	12 000	1.26×10^{-19}	77.8
	4098	9 900	1.18×10^{-19}	68.4
	4098	9 900	1.17×10^{-19}	68.1
	4278	12 000	1.21×10^{-19}	76.2
	4278	12 000	1.19×10^{-19}	75.6
	4571	12 000	1.18×10^{-19}	75.3
	4638	9 900	1.16×10^{-19}	67.8
	6019	10 780	1.06×10^{-19}	67.6
	6019	10 780	0.96×10^{-19}	64.3
916	1	54 000	1.44×10^{-20}	55.8
	1	54 000	1.39×10^{-20}	54.8
	1317	61 200	1.39×10^{-20}	58.3
	1317	61 200	1.28×10^{-20}	56.0
	2752	62 940	1.35×10^{-20}	58.3
	2752	62 940	1.30×10^{-20}	57.2
	3224	65 360	1.29×10^{-20}	58.1
	3224	65 360	1.27×10^{-20}	57.6
	5869	70 800	1.07×10^{-20}	55.1
	5869	70 800	1.06×10^{-20}	54.8
876	1	508 800	2.27×10^{-21}	68.0
	1	508 800	2.25×10^{-21}	67.7
	1232	360 000	2.25×10^{-21}	56.9
	1232	360 000	2.14×10^{-21}	55.5
	1914	457 600	2.21×10^{-21}	63.6
	1914	457 600	2.11×10^{-21}	62.2
	5480	473 600	1.84×10^{-21}	59.0
	5480	473 600	1.81×10^{-21}	58.6
808	1	1 897 200	$9.7\ \times10^{-23}$	27.1
	1	1 897 200	$9.0\ \times10^{-23}$	26.1

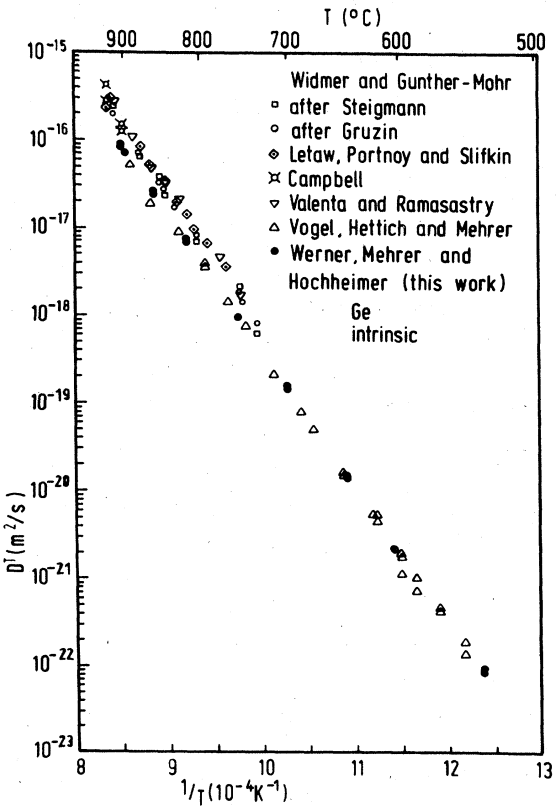

FIG. 2. Arrhenius plot of self-diffusion in intrinsic Ge at ambient pressure.

TABLE II. Diffusion data for diffusion of ^{71}Ge in doped single crystals at 973 K for various pressures.

Doping	Pressure (10^5 Pa)	Time (s)	D^T ($m^2 s^{-1}$)	$2(D^T t)^{1/2}$ (nm)
n doped	1	12 000	1.79×10^{-19}	92.7
3×10^{24} m^{-3}	1		1.77×10^{-19}	92.2
	915		1.75×10^{-19}	91.7
Sb atoms	2150		1.54×10^{-19}	86.0
	3041		1.58×10^{-19}	87.1
	3972		1.46×10^{-19}	83.7
	4278		1.40×10^{-19}	82.0
p doped	1	12 000	1.31×10^{-19}	79.3
3×10^{24} m^{-3}	1		1.22×10^{-19}	76.5
	1480		1.21×10^{-19}	76.2
Ga atoms	1480		1.20×10^{-19}	75.9
	2982		1.00×10^{-19}	69.3
	4571		1.06×10^{-19}	71.3
	5950		0.85×10^{-19}	63.9
p doped	1	12 000	6.1×10^{-20}	54.1
2×10^{25} m^{-3}	1		5.8×10^{-20}	52.8
	915		5.8×10^{-20}	52.8
Ga atoms	2316		5.3×10^{-20}	50.4
	3041		5.2×10^{-20}	50.0
	3972		4.5×10^{-20}	46.5
	4571		4.5×10^{-20}	46.5
	5950		4.1×10^{-20}	44.4
	5950		3.8×10^{-20}	42.7

repeated here. The conclusion was that it is well conceivable that the earlier data may be slightly too high. If a single Arrhenius equation

$$D^T = D_0^{\mathrm{eff}} \exp(-Q^{\mathrm{eff}}/k_B T) \quad (4)$$

with an effective preexponential factor D_0^{eff} and an effective activation enthalpy Q^{eff} is fitted to the present data, we get $D_0^{\mathrm{eff}} = 13.6\times10^{-4}$ $m^2 s^{-1}$ and $Q^{\mathrm{eff}} = 3.09$ eV. Vogel *et al.* report quite similar values: $D_0^{\mathrm{eff}} = 24.8 \times 10^{-4}$ $m^2 s^{-1}$ and $Q^{\mathrm{eff}} = 3.14$ eV.

The diffusivities are shown in semilogarithmic plots as functions of pressure in Fig. 3 for intrinsic Ge at various temperatures and in Fig. 4 for various doping concentrations at 973 K. The slope of a certain pressure isotherm is related to the activation volume according to Eq. (1). Estimates for the correction term in Eq. (1) may be obtained in one of the following two ways:

(i) Assuming that the attempt frequency of the diffusing atom has the same pressure dependence as the Debye

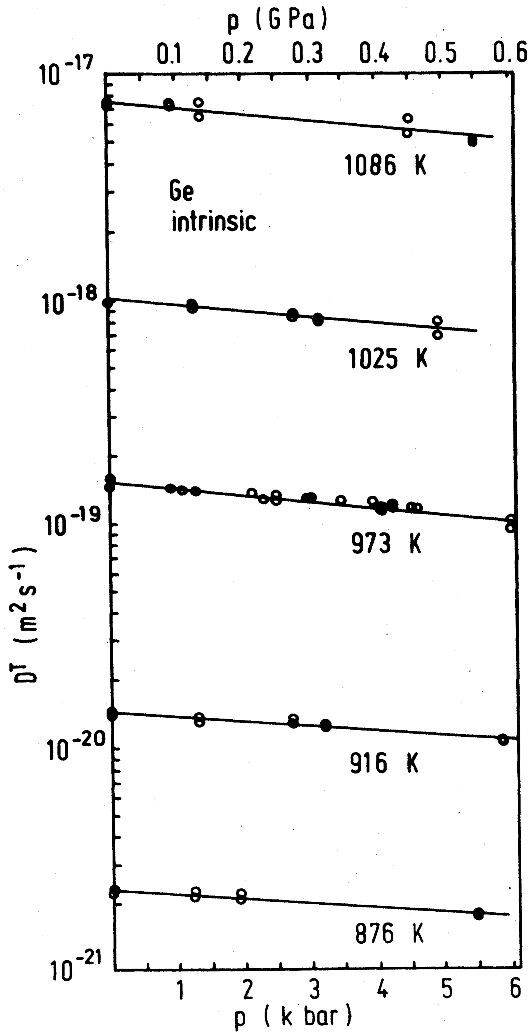

FIG. 3. Diffusion coefficients of ^{71}Ge in intrinsic Ge as functions of pressure for various temperatures.

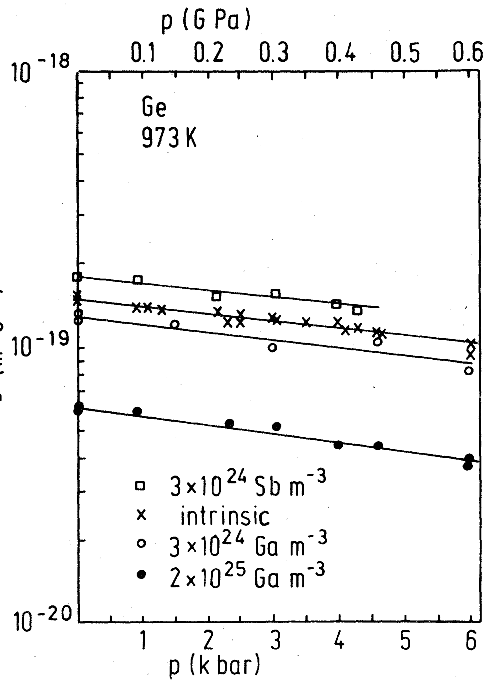

FIG. 4. Diffusion coefficients of ^{71}Ge at 973 K as functions of pressure for various doping concentrations. The notation Sb m^{-3} means number of Sb atoms per m^3.

frequency, and using the Grüneisen model for the perfect crystal, one gets[14,4]

$$k_B T \frac{\partial \ln \nu^0}{\partial p} \approx k_B T \gamma_G \varkappa \ , \tag{5}$$

where $\varkappa$ denotes the isothermal compressibility and γ_G the Grüneisen constant.

(ii) Another estimate[4] relates the correction term to the migration volume V^M and the migration enthalpy H^M of the defect or defects which act as diffusion vehicles according to

$$k_B T \frac{\partial \ln \nu^0}{\partial p} \approx k_B T \left[\frac{\varkappa}{3} + \frac{V^M}{2H^M} \right] . \tag{6}$$

Since no experimental values for V^M are available for Ge, we applied Eq. (5) to calculate the correction term using $\varkappa = 1.44\times10^{-11}$ m^{3}N^{-1}m^{-1} and $\gamma_G = 0.72$. The activation volumes are listed in units of the atomic volume Ω in Table III for intrinsic Ge at various temperatures and in Table IV for various doping concentrations at 973 K using $\Omega = 2.26\times10^{-29}$ m^3/atom (Smithells[15]). In Tables III and IV the values for the slopes of the pressure isotherms and the correction terms are also included.

IV. DISCUSSION

A. Doping dependence of self-diffusion

An enhancement of self-diffusion in *n*-doped material and a retardation in *p*-doped material similar to the effects described in Sec. III had already been observed by Valenta and Ramasastry[9] and by Vogel, Hettich, and Mehrer.[12] Since the direction and magnitude of the doping effects had been already established in the previous studies, the aim of the present experiments was a more quantitative investigation and understanding of these effects.

As already mentioned in the Introduction, a doping dependence of self-diffusion via a Fermi-level change is expected whenever the defect or defects which act as diffusion vehicles occur in more than one electrical charge state. Theoretical expressions for the self-diffusion coefficient due to multiply ionized defect states have been developed by Seeger and Chik[7] and by Shaw.[16] (For a recent review, see Ref. 17). Let us consider the simple case in which self-diffusion proceeds by the migration of one type of defect which occurs in a neutral and in a singly ionized acceptor state. The resulting self-diffusion coefficient may be written as

$$D^T = D_x^T + D_-^T \ , \tag{7}$$

where D_x^T and D_-^T are the contributions to self-diffusion due to the neutral (subscript x) and negatively charged (subscript $-$) defect states. These contributions are given by

$$D_x^T = fga^2 c_x \nu_x \tag{8}$$

$$D_-^T = fga^2 c_- \nu_- \ , \tag{9}$$

where f denotes the correlation factor, g a geometry factor ($f = 0.5$ and $g = \frac{1}{8}$ for a vacancy mechanism in the diamond lattice), and a the cubic lattice parameter. ν_x and ν_- denote the jump frequencies and c_x and c_- the concentrations of neutral and charged defects.

For nondegenerate extrinsic material (superscript dop) it is readily shown[7,16] that

TABLE III. Activation volumes for intrinsic Ge.

Temperature (K)	Number of D^T values	Slope of the pressure isotherm $-k_B T \frac{\partial \ln D^T}{\partial p}$ (units of Ω)	Correction term $k_B T \gamma_G \varkappa$ (Ω)	Activation volume V^{SD} (units of Ω)
1086	10	0.40	0.007	0.41
1025	9	0.35	0.006	0.36
973	24	0.34	0.006	0.35
916	10	0.27	0.006	0.28
876	8	0.23	0.005	0.24

TABLE IV. Activation volumes for Ge with various doping concentrations.

Doping concentration (m^{-3})	Number of D^T values	Slope of the pressure isotherm $-k_BT\frac{\partial \ln D^T}{\partial p}$ (units of Ω)	Correction term $k_BT\gamma_G\varkappa$ (units of Ω)	Activation volume V^{SD} (units of Ω)
p doped				
2×10^{25}	9	0.42	0.006	0.43
3×10^{24}	7	0.36	0.006	0.37
Intrinsic	24	0.34	0.006	0.35
n doped				
3×10^{24}	7	0.31	0.006	0.32

$$c_-^{\text{dop}}/c_- = n/n_i \;, \tag{10}$$

where n and n_i denote the free-electron concentrations in the extrinsic and intrinsic states. Using Eqs. (7)—(10) the expression for the self-diffusivity in doped material can be written in the following form:

$$D^{T,\text{dop}} = D_x^T + (n/n_i)D_-^T \;, \tag{11a}$$

which leads to

$$D^{T,\text{dop}}/D^T = D_x^T/D^T + (n/n_i)D_-^T/D^T \tag{11b}$$

for the ratio between the extrinsic and intrinsic diffusivities, where now D_-^T/D^T denotes the relative contribution of charged defects to the intrinsic diffusivity. It is obvious that Eqs. (11) predict an enhanced diffusivity in *n*-doped material ($n/n_i > 1$) and a retarded diffusivity in *p*-doped ($n/n_i < 1$) material. Furthermore, Eqs. (11) predict a *linear* dependence of the diffusivity on the ratio of the free-electron concentrations. It is important to note that we arrived at this linear relationship by assuming that the vacancy occurs in a neutral and in a singly ionized acceptor state. The occurrence of additional charge states would lead to additional terms comprising a diffusivity multiplied by $(n/n_i)^r$ for an acceptor or by $(n_i/n)^r$ for a donor state, where r is the multiplicity of the ioniced state. A comparison with Eqs. (11) or its appropriate generalizations should therefore permit an identification of the charge states of the defect(s) involved in self-diffusion.

The ratio n/n_i follows from the electroneutrality condition and from the law of mass action for the free-electron and hole concentration. Denoting the concentrations of chemical donors (acceptors) by N_D (N_A), we get, for *n*-type material,

$$n/n_i = N_D/2n_i + (1 + N_D^2/4n_i^2)^{1/2} \;, \tag{12a}$$

and, for *p*-type material,

$$n/n_i = (1 + N_A^2/4n_i^2)^{1/2} - N_A/2n_i \;. \tag{12b}$$

The values of n/n_i can be determined if n_i and either N_D or N_A are known. In the present experiments the latter are known and n_i can be calculated from the work of Morin and Maita.[18]

Figure 5 shows a comparison between the ambient-pressure diffusivities measured at 973 K and Eqs. (11), which indicates that indeed only a neutral and a negative charge state of a defect contribute to self-diffusion. From the fit of Eqs. (11) to the data also shown in Fig. 5 we deduce $D_x^T/D^T = 23\%$ and $D_-^T/D^T = 77\%$ at 973 K.

For vacancies in Ge and Si the acceptor nature was predicted by James and Lark-Horovitz.[6] Recent ESR experiments for Si by Watkins and co-workers[19,20] have confirmed the acceptor nature of a vacancy in Si, although in this case a single donor level close to the valence band and a double acceptor level close to the conduction band have also been detected. The present experiments show that in the case of Ge an acceptor-type defect is responsible for self-diffusion and that additional levels are not essential for a description of the doping dependence.

B. Pressure dependence of self-diffusion

To our knowledge the present experiments provide for the first time activation volumes of self-diffusion in a semiconductor. The values of Table III for intrinsic material have been plotted in Fig. 6 as a function of tempera-

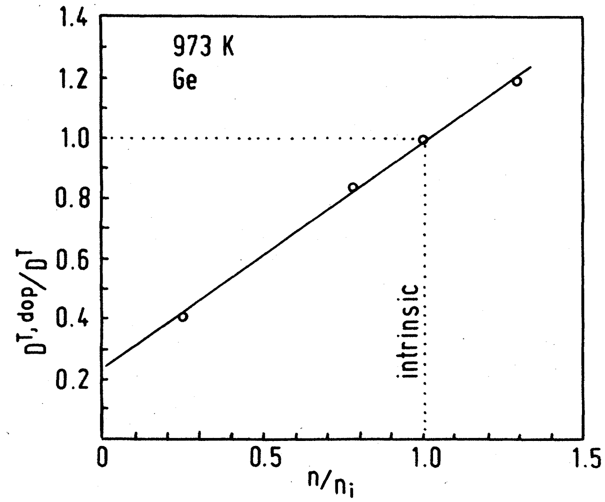

FIG. 5. Doping dependence of the diffusion coefficient of ^{71}Ge in Ge at 973 K.

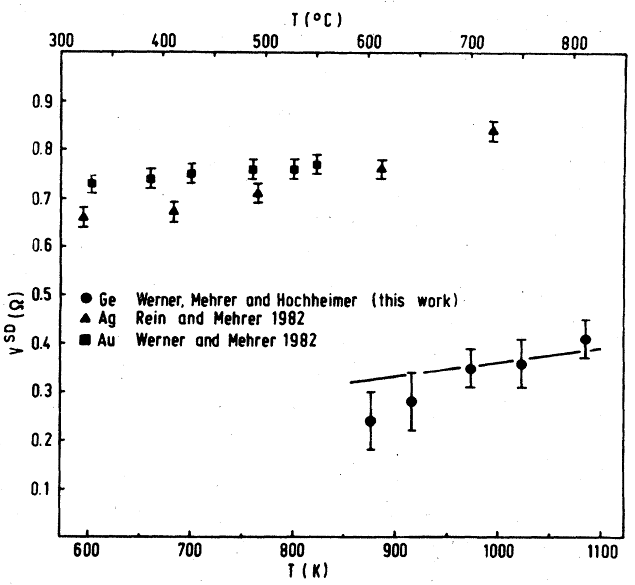

FIG. 6. Activation volumes of self-diffusion in intrinsic Ge and in Ag and Au.

ture. For reasons of comparison the activation volumes from recent work on self-diffusion in Ag (Ref. 2) and Au (Ref. 3) have been also included. The values for Ge are considerably smaller than the activation volumes for noble metals, which are found to range from 0.6Ω to 0.9Ω. Activation volumes in bcc metals are somewhat smaller than in fcc metals, but are still larger than those for Ge. In the case of Na,[21] which is the most thoroughly investigated bcc metal, V^{SD} values range from 0.4Ω to 0.55Ω. The small values in the case of Ge indicate that both charge states of the vacancy must be strongly relaxed and/or spread out. The concept of a spread-out vacancy had been proposed by Seeger and Chik,[7] who interpreted the large preexponential factor (D_0^{eff}) in terms of a large self-diffusion enthropy of the vacancy (about $10k_B$). They argued that this large entropy arises from additional configuration entropy due to a spreading out of the vacancy over several atomic volumes.

For diamond and Si, Larkins and Stoneham[22,23] have attempted to calculate the lattice distortions near vacancies. They deduce a relaxation volume of -0.31Ω for diamond and -0.61Ω for Si. These values are obtained by treating the distortions strictly within the harmonic approximation. However, this treatment neglects terms of anharmonic origin which may be important.[24,25] For Ge no theoretical calculation is available at all. We hope that the present experimental results encourage further calculations.

According to Sec. IV A neutral and negatively charged defects—very likely vacancies—contribute to self-diffusion. Under such conditions measurements of the pressure dependence yield an effective activation volume which corresponds to a weighted average of the individual activation volumes, V_x^{SD} and V_-^{SD}, of the two defect states. It is readily shown that

$$V^{\mathrm{SD}} = V_x^{\mathrm{SD}} D_x^T / D^T + V_-^{\mathrm{SD}} D_-^T / D^T \tag{13a}$$

for intrinsic material, and

$$V^{\mathrm{SD,dop}} = V_x^{\mathrm{SD}} D_x^T / D^{T,\mathrm{dop}} + V_-^{\mathrm{SD}} D_-^T n / (n_i D^{T,\mathrm{dop}}) \tag{13b}$$

for extrinsic material. The weighting factors in Eqs. (13) are the relative contributions of the two defect states to the pertaining total diffusivity.

With the aid of Eqs. (11) the expression for $V^{\mathrm{SD,dop}}$ can be recast in a form which, apart from the activation volumes, only contains the ratio n/n_i and the intrinsic diffusivity ratios D_x^T/D^T and D_-^T/D^T. Using the values from Sec. IV A for the two latter ratios, we have fitted Eq. (13b) to the experimental data of Table IV using V_x^{SD} and V_-^{SD} as adjustable parameters. We obtain $V_x^{\mathrm{SD}} = 0.56\Omega$ and $V_-^{\mathrm{SD}} = 0.28\Omega$. The fit itself is shown in Fig. 7. The numerical values indicate that the negatively charged vacancy is more strongly relaxed than the neutral vacancy.

C. Temperature dependence of self-diffusion and activation volume

As already stated in Sec. III, within the experimental errors the present data of self-diffusion in intrinsic material shown in Fig. 2 can be reasonably represented by an Arrhenius equation with an effective preexponential factor and an effective activation energy. On the other hand, the preceding discussion has shown that in a more detailed analysis we must consider contributions from the two charge states of the vacancy. The basic equation is (7), which in more explicit form reads

$$D^T = D_x^0 \exp(-Q_x^{\mathrm{SD}}/k_B T) + D_-^0 \exp(-Q_-^{\mathrm{SD}}/k_B T) . \tag{14}$$

D_x^0 and D_-^0 denote preexponential factors and Q_x^{SD} and Q_-^{SD} denote activation enthalpies of the indicated defect states. The following set of values was obtained from the fit of Eq. (14) to the measured diffusivities: $D_x^0 = 3\times10^{-3}$ $\mathrm{m^2\,s^{-1}}$ and $Q_x^{\mathrm{SD}} = 3.23$ eV, $D_-^0 = 1\times10^{-4}$ $\mathrm{m^2\,s^{-1}}$ and $Q_-^{\mathrm{SD}} = 2.87$ eV.

For reasons of completeness we mention that other similar combinations of parameters yield also fits of the data with very similar values of the mean-square deviation. From the chosen values we get, for the relative con-

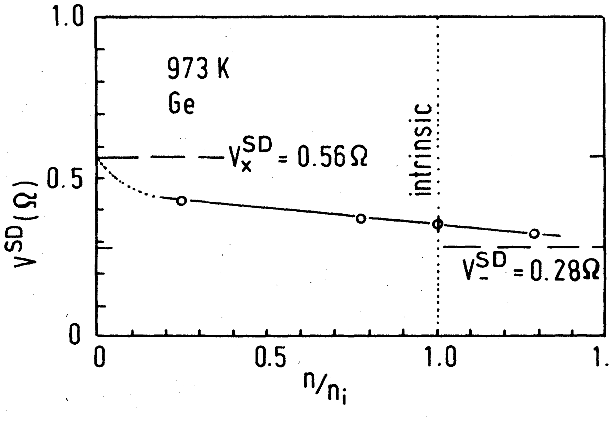

FIG. 7. Activation volume of self-diffusion in Ge at 973 K as a function of n/n_i.

tributions to the total diffusivities, $D_x^T/D^T=29\%$ at 973 K, in good agreement with the fraction deduced in Sec. IV A from the doping dependence.

Since we know that $V_x^{\mathrm{SD}} > V_-^{\mathrm{SD}}$, we expect an increase of the effective activation volume V^{SD} with temperature. The solid line also shown in Fig. 6 is calculated from Eq. (13a) using the values for V_x^{SD} and V_-^{SD} from Sec. IV B and the fractions D_x^T/D^T and D_-^T/D^T according to (14).

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