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Comparison of theory with quenching experiments for the entropy and enthalpy of vacancy formation in Si and Ge

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In the preceding paper the authors have argued that the entropy of ionization of a vacancy in a semiconductor should be closely approximated by the entropy of the forbidden band gap; $\Delta S_{cv} = \Delta S_I(V^+) = \Delta S_I(V^-)$. Here this hypothesis is combined with the hypothesis that the entropy of formation of the neutral vacancy, $\Delta S(V^x)$, is only the entropy of its Jahn-Teller distortion. Thus $\Delta S_I(V^{\pm}) \gg \Delta S(V^x) = k\ln 3$ for Si and Ge. Empirical values for the enthalpy of ionization at low temperature, $\Delta H_I(V^{\pm})$, are combined with the values for $\Delta H(V^x)$ predicted by the macroscopic theory of Phillips and Van Vechten in order to predict the result of quenching experiments taking proper account of the charge states of the vacancies. Agreement with the experiments of Logan, Hiraki, and Elstner and Kamprath is quite satisfactory.

I. INTRODUCTION

Thermal-quenching experiments of the sort conducted by Logan[1] and by Hiraki[2] on Ge and by Elstner and Kamprath[3] on Si are effectively the only probe of the thermodynamic parameters of single vacancies in elemental semiconductors. It is a common practice to report the result of such experiments in terms of effective enthalpy and entropy parameters, $\Delta H_{\exp}$ and $\Delta S_{\exp}$, obtained by fitting the data with a van't Hoff equation,

$$\ln[C] = \ln n_H + \Delta S_{\exp}/k - \Delta H_{\exp}/kT_h. \tag{1}$$

In Eq. (1) n_H is the concentration of host lattice sites, $n_H = 8/a^3$ (a is the lattice constant), k is Boltzmann's constant, and T_h is the high temperature near the melting point from which the sample was quenched. We use the brackets, [ ], to denote concentrations of the species within and C to denote the complex of multiple vacancies or vacancies with impurities obtained at room temperature from the equilibrium concentration of vacancies at T_h by the quench. The values of $[C]$ is determined in a Hall-effect experiment at room temperature or below by detecting the change in carrier concentration of lightly doped samples resulting from the heat treatment.

The analysis of these experiments to determine the enthalpy and entropy of formation, $\Delta H(V^x)$ and $\Delta S(V^x)$, of single neutral vacancies, V^x, is not straightforward, and, in general

$$\Delta H_{\exp} \neq \Delta H(V^x), \quad \Delta S_{\exp} \neq \Delta S(V^x), \tag{2}$$

for two reasons.

First, as Kröger has noted,[4] one must take account of the various ionization states of the vacancies that are present in equilibrium at T_h. From electron-irradiation experiments at low temperature, it is known that single vacancies in Si and Ge occur in four ionization states—V^+, V^x, V^-, and V^{2-}.[3,5-7]

Second, as noted above, the species observed in the Hall-effect experiment at low temperatures is not a single vacancy V, but some complex C formed during the quench. As the time required for a single vacancy created by electron irradiation to migrate to and complex with an impurity in the purest available material is of order 10^3 sec at $T = 100$ K,[8,9] the time required for a single vacancy to complex with an impurity at room temperature is of order 10^{-3} sec or less. Therefore, no feasible quenching procedure can prevent the single vacancies which were present in their equilibrium concentration at T_h from forming complexes during the quench and before Hall-effect measurements can be performed. Consequently, one should not take the observed ionization spectrum of C to be that for V and one should investigate the relation between $[C]$ at low temperature and $[V]$, where

$$[V] \equiv [V^+] + [V^x] + [V^-] + [V^{2-}], \tag{3}$$

at T_h.

Probably because this analysis is rather complicated and requires an estimate of the entropy of ionization for the various states of V, $\Delta S_I(V^+)$, $\Delta S_I(V^-)$, and $\Delta S_I(V^{2-})$, it has not been attempted by experimentalists. As a result, $\Delta H_{\exp}$ and $\Delta S_{\exp}$ have often been confused with $\Delta H(V^x)$ and $\Delta S(V^x)$. As $\Delta S_{\exp}$ is much greater than the entropy resulting from the threefold degenerate Jahn-Teller distortion of V^x,[10]

$$\Delta S_{\mathrm{JT}}(V^x) = k\ln 3 = 1.1k, \tag{4}$$

the assumption that $\Delta S_{\exp} = \Delta S(V^x)$ forces one to conclude that the contribution due to the shift in lattice mode frequencies from ν^0 to ν'

$$\Delta S_L(V^x) = \sum_i k \ln(\nu_i^0/\nu_i') \tag{5}$$

is implausibly large, i.e., about $2k$ or more. [In fact, recent infrared and Raman measurements of defect zinc-blende-structure semiconductors, such as In_2Te_3, lead to the conclusion that neutral vacancies (in those materials) produce a negligible shift in mode frequencies about the vacancies.[11] Thus,

$$\nu_i^0 \cong \nu_i' \rightarrow S_L(V^x) \cong 0\,, \tag{6}$$

and it would seem that a similar situation should obtain about V^x in Si, Ge, or the III-V compounds.] This discrepancy has lead to some speculation that the predominate defect at T_h is more complicated than the single vacancy.[12] We contend that the large values of $\Delta S_{\rm exp}$ observed result from the fact that most of the single vacancies are ionized at T_h, so that this speculation about a more complex species is not supported by the quenching data.

Due to the problem of retaining a detectable concentration of single vacancies long enough to make a measurement at a practical temperature, it is extremely difficult to measure $\Delta S_I(V^+)$ or $\Delta S_I(V^-)$ directly. At T_h, where the equilibrium concentration is significant the measurements of the ionization energy are obscured by thermal broadening. If the vacancies are produced by irradiation, the temperature must be kept low enough to make the measurement before the $V \rightarrow C$ reaction occurs. At such temperatures, less than about 150 K, the phonon density is so small that ΔS_I cannot be large enough for $T\Delta S_I$ to be measured with any accuracy.

Therefore, the theoretical values for ΔS_I and the relative concentrations of V^+, V^x, V^-, and V^{2-} that the authors have estimated from simple theoretical considerations[13] are the most reliable, indeed almost the only, estimates available. The theoretical conclusion is that

$$\Delta S_I(V^+) = \Delta S_I(V^-) = \Delta S_I(V^{2-}) = \Delta S_{cv} \tag{7}$$

to within an accuracy of about 10%, where ΔS_{cv} is the entropy of the forbidden band gap (the standard entropy of formation of pairs of free electrons and holes)

$$0 = e^+ + e^-, \quad \Delta H_{cv}, \quad \Delta S_{cv}\,. \tag{8}$$

In Fig. 1 we show the relative concentrations as a function of Fermi level of the four ionization states of single vacancies in Si at room temperature and at $T_h = 1400$ K calculated from the assumption of Eq. (7) and the empirical values of $\Delta H_I(V^+)$, $\Delta H_I(V^-)$, and $\Delta H_I(V^{2-})$ at $T=0$ shown in Fig. 2.[3,4,6] Although the empirical values for ΔH_I in Ge are rather uncertain, it seems clear that the corresponding figures for Ge are qualitatively similar.[7]

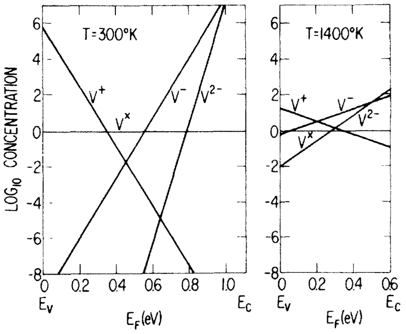

FIG. 1. Relative concentration of the charge states V^+, V^x, V^-, and V^{2-} for the single vacancy in Si as a function of the Fermi level E_F at $T = 300$ K and $T = 1400$ K. E_v and E_c denote the valence- and conduction-band-edge free energies, respectively.

In Sec. II we discuss the problem of the various ionization states of V. We calculate the result of a "perfect quench" experiment, i.e., one in which all the equilibrium concentration of vacancies present at T_h $[V(T_h)]$, are trapped within the sample in complexes C which have one ionization state for each vacancy. In this case the Hall measurement gives exactly the correct result:

$$[C] \equiv |\Delta([e^+] - [e^-])| = [V(T_h)]\,. \tag{9}$$

In making this calculation we shall assume the values for the enthalpy of neutral vacancy formation $\Delta H(V^x)$ calculated from theory using the macroscopic model of Phillips and Van Vechten,[14,15]

$$\Delta H(V_{\rm Si}^x) = 2.66 \text{ eV}, \quad \Delta H(V_{\rm Ge}^x) = 2.21 \text{ eV}. \tag{10}$$

(No empirical adjustment is made although one

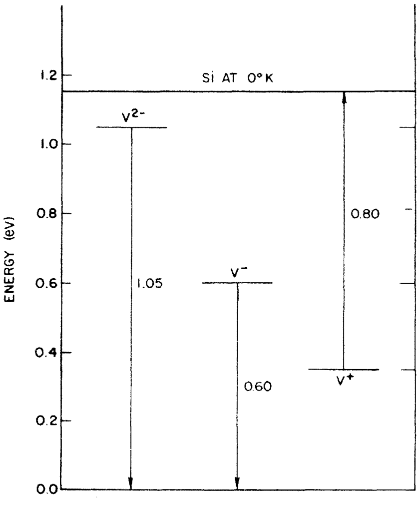

FIG. 2. Vacancy-charge-state energy levels for Si at $T = 0$ K as assumed by the authors. Energy values are uncertain to about ±0.2 eV and represent the author's judgment of a reasonable compromise between the empirical determinations of Refs. 3, 5, and 6.

should expect a slight overestimate.) Furthermore, we shall assume that, as discussed at Eq. (6), the lattice modes are not shifted by V^x so that

$$\Delta S_L(V^x_{\rm Si}) = \Delta S_L(V^x_{\rm Ge}) = 0 \,, \tag{11}$$

and thus the standard entropy of formation of the neutral vacancy $\Delta S(V^x)$, is

$$\Delta S(V^x) = \Delta S_{\rm JT}(V^x) = k \ln 3 \tag{12}$$

for both Si and Ge.

In Sec. III we consider the question of the validity of Eq. (9). It is noted that although imperfect quenching produces measured values of $\Delta H_{\rm exp}$ and $\Delta S_{\rm exp}$ which are less than those which would result from a perfect quench, $\Delta H^{\rm PQ}_{\rm exp}$ and $\Delta S^{\rm PQ}_{\rm exp}$,[16] comparison of diffusion and annealing experiments show that the difference in enthalpy is not more than about 10% and the difference in entropy not more than about 50% for the particular experiments reported in Refs. 1–3.

In Sec. IV the agreement between the theoretical and empirical parameters is discussed.

II. EFFECT OF THE MULTIPLE CHARGE STATES OF THE SINGLE VACANCY

Kröger has noted the importance of a proper account of the ionization state of the vacancy if one is to determine $\Delta H(V^x)$ and $\Delta S(V^x)$ from $\Delta H_{\rm exp}$ and $\Delta S_{\rm exp}$.[4] (In this section we shall assume perfect quenching, $\Delta H_{\rm exp} = \Delta H^{\rm PQ}_{\rm exp}$ and $\Delta S_{\rm exp} = \Delta S^{\rm PQ}_{\rm exp}$.) Kröger assumed that V^- was the only significant species at T_h in the Ge quenching experiment.[1] The samples were intrinsic with the Fermi level at midgap at T_h. In such a case

$$\Delta H(V^x) = \Delta H^{\rm PQ}_{\rm exp} - \Delta H_I(V^-) + \tfrac{1}{2}\Delta H_{cv} + 3kT_h^2\, d[\ln(m_n^*/m_p^*)]/4dT_h \tag{13}$$

and

$$\Delta S(V^x) = \Delta S^{\rm PQ}_{\rm exp} - \Delta S_I(V^-) + \tfrac{1}{2}\Delta S_{cv} + \tfrac{3}{4}k \ln(m_n^*/m_p^*) + 3kT_h\, d[\ln(m_n^*/m_p^*)]\,/4dT_h \,. \tag{14}$$

In Eqs. (13) and (14) m_n^* and m_p^* are the density-of-states effective masses of the conduction and valence bands, respectively, including the factors which result from the degeneracy of the conduction band minima in Si and Ge.

The analysis which Kröger gave is equivalent to these formulas except for the last term in each. These last terms arise from the temperature dependence of the effective masses,[17-22] which Kröger implicitly assumed to be negligible.

In fact, $d[\ln(m_n^*/m_p^*)]\,/dT$ is not large in Si (Ref. 17) and probably negligibly small in Ge. However, this situation results from a cancellation between the effects of intraband scattering, which cause both band masses to increase with temperature,[18-20] and the effects of interband scattering, which cause both band masses to decrease with temperature.[21,22] The former effects dominate in wide-band-gap semiconductors while the latter dominate in narrow-gap semiconductors. For Si intraband scattering is only slightly more effective than intraband scattering so that measurements show $dm^*/dT \gtrsim 0$ from $T = 0$ to 600 K.[17] As the gap is slightly smaller in Ge than in Si, the cancellation is even closer.

The approximation of neglecting the last term in both Eqs. (13) and (14) for the particular cases of Si and Ge is further supported by the observation that only the logarithm of the ratio m_n^*/m_p^* appears and

$$\ln(m_n^*/m_p^*) \approx 0 \tag{15}$$

because $m_n^* \approx m_p^*$ in Si and Ge. (The actual values at T_h are about 0.2 for Si and 0.4 for Ge. Recall that the degeneracy factors for the four conduction-band minima in Si and six in Ge are included in the definition of m_n^*.) However, this approximation is not generally accurate and would certainly be untenable for narrow, direct-gap semiconductors, such as InSb or InAs.[21,22]

Of course, if some other ionization state, such as V^+, is the dominant species at T_h, one can derive expressions analogous to Eqs. (13) and (14). However, when two or more ionization states are present in comparable concentrations at T_h, the case for Si and Ge (Fig. 1), it is simpler to calculate equilibrium concentration of all ionization states of each species assuming a given Fermi level and then to iterate the calculation to achieve self-consistency via the condition of neutrality. We have done this for Si and Ge using the conclusions of Ref. 13 to relate ΔS_I for all vacancy states, Eq. (7), and for the impurities to ΔS_{cv}. We use the empirical formula of Varshni[23] to calculate the band-gap free energy $\Delta E_{cv}(T_h)$ and thus $\Delta S_{cv}(T_h)$ and $\Delta H_{cv}(T_h)$. We use the values of $\Delta H(V^x)$ calculated by Phillips and Van Vechten[14,15] and the empirical values of $\Delta H_I(T = 0)$ for the various states of V in Si, Fig. 2, which the authors judge to be a reasonable compromise between Refs. 3, 5, and 6. For Ge, where the empirical values of $\Delta H_I(T = 0)$ for single vacancies are not established with any accuracy,[7] we simply assume that the vacancy levels have the same relative positions within the gaps of Si and Ge:

$$\Delta H_I(V^{\pm,2-}, {\rm Ge}) = \Delta H_I(V^{\pm,2-}, {\rm Si})\Delta H_{cv}({\rm Ge}, T = 0)/\Delta H_{cv}({\rm Si}, T = 0). \tag{16}$$

{While there are numerous reports[1,2,4,12] of the

TABLE I. Parameters used in calculation. (See text.)

Property	Si	source	Ge	source
ΔH_{exp}	2.5 eV	Ref. 3	2.0 eV	Ref. 1
ΔS_{exp}	4.4 k	Ref. 3	3.4 k	Ref. 1
$\Delta H(V^x)$(calc)	2.66 eV	Refs. 14,15	2.21 eV	Refs. 14,15
$\Delta S(V^x)$(calc)	1.1 k	Eq. (12)	1.1k	Eq. (12)
$\Delta H_I(V^+, T=0)$	0.80 eV	Refs. 3,5,6	0.51 eV	Eq. (16)
$\Delta H_I(V^-, T=0)$	0.60 eV	Refs. 3,5,6	0.38 eV	Eq. (16)
$\Delta H_I(V^{2-}, T=0)$	1.05 eV	Refs. 3,5,6	0.67 eV	Eq. (16)
T_h	1050–1300 K	Ref. 1	1050–1200 K	Refs. 1,2
$\Delta S_{cv}(T_h)$	6.3 k	Ref. 23	5.2k	Ref. 23
$\Delta S_I(V^{\pm,2-})$	6.3 k	Eq. (7)	5.2k	Eq. (7)
$m_n^*(T_h)$	1.28 m_e	Ref. 17	0.554 m_e	Ref. 17
$m_p^*(T_h)$	0.92 m_e	Ref. 17	0.37 m_e	Ref. 17

ionization levels of the various complexes C which result at room temperature from $[V(T_h)]$ under various conditions, one has no justification to ascribe any of these to the single vacancy at T_h.} The values of the parameters assumed are listed in Table I. The calculation was done for light doping ($10^{15}/\text{cm}^3$) and 10% compensation both n-type and p-type (B and P for Si, Ga and As for Ge), which conditions typify the samples used in Refs. 1–3. The results for the total concentration of vacancies in all charge states at T_h, $[V(T_h)]$, are shown in Fig. 3 and Table II.

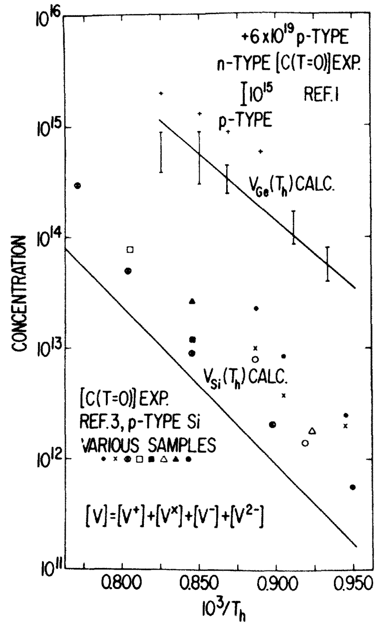

FIG. 3. Calculated values for the total concentration of vacancies in all ionization states at T_h compared with the concentration of trapped-defect complexes obtained by quenching various samples from T_h. Theoretical values have not been adjusted for the overestimate of $\Delta H(V^x)$ expected to occur with the macroscopic model of Phillips and Van Vechten.

The experimental values of $[C]$ measured at low temperature in samples quenched from various T_h in Refs. 1 and 3 are also shown in Fig. 3. Although the variation in $[V(T_h)]$ with impurity type is too slight to be detected at these doping levels and temperatures, the resultant values of $[C]$ clearly depend on the impurity type and concentration. Logan's experiment[1] in Ge shows that n-type doping results in larger values of $[C]$ than p-type doping of the same concentration. He also showed that p-type samples doped with $6\times10^{19}/\text{cm}^3$ Sn produced values of $[C]$ somewhat greater than the $10^{15}/\text{cm}^3$ As-doped n-type samples.

We may conclude from these comparisons that the parameters assumed for V^x are not the parameters that describe the total concentration $[V(T_h)]$ predicted:

$$\Delta H_{\text{exp}}^{\text{PQ}}(\text{calc}) > \Delta H(V^x)(\text{calc}) \tag{17}$$

and

$$\Delta S_{\text{exp}}^{\text{PQ}}(\text{calc}) \gg \Delta S(V^x)(\text{calc}). \tag{18}$$

The empirical values of both ΔH_{exp} *and* ΔS_{exp} *are lower than those predicted assuming perfect quenching with the discrepancy (14–18)% in enthalpy but as much as 45% in entropy:*

$$\Delta H_{\text{exp}}^{\text{PQ}}(\text{calc}) \gtrsim \Delta H_{\text{exp}}, \tag{19}$$

$$\Delta S_{\text{exp}}^{\text{PQ}}(\text{calc}) > \Delta S_{\text{exp}}. \tag{20}$$

However, the variation from sample to sample in measured values of $[C]$ is certainly sufficient to cast doubt upon the assumption of perfect quenching, Eq. (9). Thus we suspect

$$\Delta H_{\text{exp}}^{\text{PQ}} \neq \Delta H_{\text{exp}}, \quad \Delta S_{\text{exp}}^{\text{PQ}} \neq \Delta S_{\text{exp}}. \tag{21}$$

III. IMPERFECT QUENCHING

The presumption of perfect quenching, Eq. (9), may introduce errors from two sources. First, the number of vacancies trapped in the sample

TABLE II. Comparison of calculation for perfect quench, PQ, assumption with experiment.

	T_h (K)	$\Delta H(V^x)$ (eV)	$\Delta H_{\text{exp}}^{\text{PQ}}$ (calc) (eV)	ΔH_{exp} (eV)	$\Delta S_{\text{exp}}^{\text{PQ}}$ (calc) (k)	ΔS_{exp} (k)
Si	1075	2.66	2.80	2.5	4.50	4.4
	1175	2.66	2.82		4.71	
	1275	2.66	2.85		4.96	
Ge	1075	2.21	2.33	2.0	4.78	3.4
	1175	2.21	2.35		4.94	

may not equal the change in carrier concentration. It seems very unlikely that $[C]$ could overestimate the number of trapped vacancies by more than a factor of 2 because V^{2-} is the highest ionization state of the single vacancy. An effect of this magnitude would cause ΔS_{exp} to be greater than $\Delta S_{\text{exp}}^{\text{PQ}}$ by $k \ln 2 = 0.69k$. However, the Hall effect as a function of temperature experiments indicated only a single ionization level for the observed C,[1-3] so it seems unlikely that there is any overestimate at all. Measurements of $[C]$ may underestimate the number of trapped vacancies if each complex C contains more than one vacancy but produces only one ionization level. It seems unlikely that such an effect could be any larger than a factor of 2, corresponding to an underestimate of $\Delta S_{\text{exp}}^{\text{PQ}}$ by $0.69k$, because the concentration of vacancies is so much less than the concentration of impurities while the divacancy binding energy, about 0.9 eV,[16] is no greater than a typical vacancy-impurity binding energy.[8] Therefore, it is unreasonable to assume that the dominate complex contains several vacancies. It is more likely that measurements of $[C]$ would underestimate the number of trapped vacancies because some of the trapped vacancies were bound in other complexes C' which were so much deeper than C that they were not detected in the Hall experiments. However, this effect should not be large either. Thus ΔS_{exp} may underestimate $\Delta S_{\text{exp}}^{\text{PQ}}$ by no more than about $1k$. However, ΔH_{exp} should not be affected unless the ratio of $[C]$ to trapped vacancies varies radically with T_h, which seems improbable.

The second source of error introduced by assuming a perfect quench is that one may not succeed in trapping all the equilibrium concentration of vacancies present at T_h. As some of the vacancies will manage to diffuse to surfaces or to dislocations and thus escape from the sample during the quench, the number of trapped vacancies will generally be less than $[V(T_h)]$. This causes ΔS_{exp} to be less than $\Delta S_{\text{exp}}^{\text{PQ}}$. Because the rate of diffusion and thus the rate of escape increases with T_h, ΔH_{exp} is also less than $\Delta H_{\text{exp}}^{\text{PQ}}$.

The effect of the escape of vacancies during the quench of Ge samples was noted by Hasiguti and Motomiya (HM),[16] who programmed a computer to simulate the process. HM concluded that the magnitude of this effect might become as large as 35% in ΔH_{exp} and 300% in ΔS_{exp} if rather extreme values are assumed for the parameters of the simulation program. Thus, they suggested $\Delta H_{\text{exp}}^{\text{PQ}}$ might be as large as 2.7 eV and $\Delta S_{\text{exp}}^{\text{PQ}}$ as large as $10k$. We maintain that because the parameters applicable to the experiments of Refs. 1 to 3 are distinctly different from those assumed by HM, the magnitude of the effect in these experiments cannot be nearly as large as the extreme values suggested by HM.

The most important difference between the assumptions of HM and these experiments is that HM assumed the samples to be pure so that trapping occurred only through the formation of divacancies V_2, which they take to be relatively immobile. The samples used in these experiments were doped so that impurities were always more numerous than the vacancies. As noted at the end of Sec. II and in Fig. 3, the nature and concentration of impurities has a distinct effect on the measured values of $[C]$. Because most of the vacancies and the impurities are ionized at T_h, the Coulomb attraction can produce a larger capture radius than would obtain for two V^x's going to V_2. The binding energy of vacancies to impurities is as great as that for V_2,[8,16] and the resulting complex is certainly less mobile. The fact that donor impurities D trap more vacancies than acceptors A can be explained by noting that V^{2-} will have a particularly large capture cross section for D^+ whereas there is no V^{2+}. (Note that the equilibrium between ionization states is maintained by very rapid electronic processes so that $[V^{2-}]$ is not depleted.)

Another significant difference between the assumptions of HM and Logan's experiments[1] is that Logan's quenching rate, 10 000 K/sec, was 20 times that assumed by HM. Hiraki performed very similar experiments with a 1000 K/sec quench rate[3] and measured $\Delta H_{\text{exp}} = 1.9$ eV and $\Delta S_{\text{exp}} = 1.4k$, which are less than Logan's values, Table II, by only 0.1 eV and $2.0k$, respectively. Therefore, it is difficult to believe that an infinite quench rate could produce much greater values. For the case of Si, Elstner and Kamprath state only that their quench rate was greater than 100 K/sec.[3] However, the rate of vacancy diffusion was much less than in the Ge experiments because the range of T_h was the same while the activation energy for migration is substantially higher in Si.[15,24,25] Therefore, the error introduced by this effect was not large in the Si experiment either.

We conclude that the analysis of HM would indicate

$$\Delta H_{\text{exp}}^{\text{PQ}} \cong 1.1 \Delta H_{\text{exp}}, \quad \Delta S_{\text{exp}}^{\text{PQ}} \cong 1.4 \Delta S_{\text{exp}} \tag{22}$$

if the parameters appropriate to Refs. 1 and 3 were assumed.

However, the most convincing evidence that Eq. (22) is accurate comes from comparing the values for the rate of vacancy diffusion deduced from atomic diffusion experiments[24,25] with those obtained directly by measuring the rate at which the vacancies trapped in the quenching experiment will anneal out.[1-3] When the single-vacancy mechanism dominates atomic self-diffusion, the self-diffusivity D_s is related to the vacancy diffusivity D_V as[26]

$$D_s(T_h) = [V(T_h)] D_V(T_h)/n_H . \tag{23}$$

Taking the measured values[24] for D_s in Ge and using Logan's values[1] for $\Delta H_{\text{exp}}^{\text{PQ}}$ and $\Delta S_{\text{exp}}^{\text{PQ}}$ to estimate $[V(T_h)]$, one concludes

$$D_V = 3 \exp(-1.0 \text{ eV}/kT_h) \text{ cm}^2/\text{sec} . \tag{24}$$

This estimate may be compared with that obtained by observing the rate that trapped vacancies anneal back out,[2]

$$D_V = 2 \exp(-1.2 \text{ eV}/kT_h) \text{ cm}^2/\text{sec} . \tag{25}$$

Evaluating these expressions, one finds that Eq. (24) implies a value of D_V which is greater than that implied by Eq. (25) by a factor of 10 to 15 in the appropriate temperature range 1000–1210 K. This would imply that one had underestimated $[V(T_h)]$ by the same factor of 10 to 15 by using ΔH_{exp} and ΔS_{exp} in place of $\Delta H_{\text{exp}}^{\text{PQ}}$ and $\Delta S_{\text{exp}}^{\text{PQ}}$. One can see from the scatter of data points corresponding to different samples in Fig. 3 that this is a conservative estimate of the systematic experimental error. It corresponds to a discrepancy in entropy of about $2.5k$ and would imply $\Delta S_{\text{exp}}^{\text{PQ}}(\text{Ge}) = 5.9k$, about 20% more than the calculated value. However, the relative values of the entropy and enthalpy terms in Eqs. (24) and (25) imply that the two estimates of D_V gradually converge as T_h increases whereas the analysis shows they should gradually diverge. Thus, it is evident that part of the discrepancy is due to random, rather than systematic experimental error. Consequently, one may conclude

$$3.4k \lesssim \Delta S_{\text{exp}}^{\text{PQ}}(\text{Ge}, T_h) \lesssim 5.9k . \tag{26}$$

For Si the corresponding analysis is complicated by the fact that it has not been possible to measure self-diffusion in the absence of effects arising from free surfaces contaminated with oxygen.[27] However, by taking impurity-diffusion data together with measurements of impurity-vacancy binding energies, one can obtain values[25] of $D_V(\text{Si}, T_h)$ which agree with the values obtained by annealing out vacancies[3,15] within experimental uncertainty.

IV. CONCLUSION: AGREEMENT BETWEEN THEORY AND EXPERIMENT

One may conclude from Fig. 3 that one underestimates $[V(T_h)]$ somewhat by using the theoretical values for $\Delta H(V^x)$ calculated[14,15] by Phillips and Van Vechten together with the theoretical values for the entropy parameters and the empirical values for ΔH_I indicated in Fig. 2. Moreover, from the discussion of the Sec. III, it is clear that the error is not in the entropy parameters. Indeed,

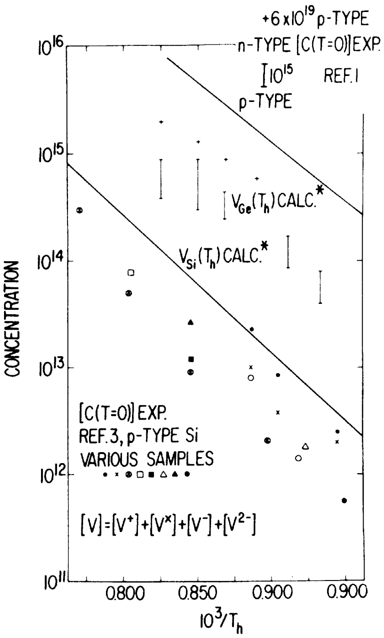

FIG. 4. Empirically adjusted calculation is compared with the same quenching data as shown in Fig. 3. Taking proper account of the effects of the ionized states of the vacancies at high temperature and of the finite rate of quenching, it is found that the empirical values of $\Delta H(V_{\text{Si}}^x) = 2.4$ eV and $\Delta H(V_{\text{Ge}}^x) = 2.0$ eV. Thus the macroscopic model of Phillips and Van Vechten overestimates $\Delta H(V^x)$ by 10% in both cases. All other calculated parameters are accurate to the limit of experimental error and have not been adjusted for this plot.

theory and experiment agree on the entropy within the fairly crude limits of experimental uncertainty,

$$\Delta S^{\mathrm{PQ}}_{\mathrm{exp}}(T_h)(\mathrm{exp}) = (4.7 \pm 1.3)k \qquad (27)$$

for both Si and Ge as compared with the calculated values in Table II, which range from 4.50 to 4.96k for either case depending on temperature. Therefore, $\Delta S(V^x)$ is indeed small[11] and is entirely accounted for by the Jahn-Teller distortion, Eq. (12).

One may test the sensitivity of the calculated values to the assumptions about $\Delta H_I(T=0)$ indicated in Fig. 2 by repeating the calculation with different values. The sensitivity is not great. For example, if we assume the V^+ level in Si is 0.25 eV lower so that $\Delta H_I(V^+, T=0) = 1.05$ eV, we calculate $\Delta H^{\mathrm{PQ}}_{\mathrm{exp}}(\mathrm{calc}) = 2.80$ eV and $\Delta S^{\mathrm{PQ}}_{\mathrm{exp}} = 4.35k$ at 1175 °K as compared with 2.82 eV and 4.71k in Table II.

Therefore, we must conclude that $\Delta H(V^x)$ has been overestimated by about 10% at Eq. (10), and that empirically (see Fig. 4)

$$\Delta H(V^x_{\mathrm{Si}}) = 2.4 \pm 0.2 \text{ eV} \qquad (28)$$

and

$$\Delta H(V^x_{\mathrm{Ge}}) = 2.0 \pm 0.2 \text{ eV}. \qquad (29)$$

As noted above one should have expected this result because the macroscopic model of Phillips and Van Vechten[14,15] will clearly not underestimate the true value of $\Delta H(V^x)$. It is gratifying that the error made by adopting such a simple model is so slight.

The reader should note that the correspondence between the values of $\Delta H(V^x)$ in Eqs. (28) and (29) and the values of ΔH_{exp} in Refs. 1 to 3 is accidental and that these are quite distinct quantities.

Finally, it is worth noting that the entropy of self-diffusion in Ge, $\Delta S_d \approx 10k$,[24] is in satisfactory agreement with the sum of Eq. (26) for $\Delta S^{\mathrm{PQ}}_{\mathrm{exp}}(\mathrm{Ge}, T_h)$ and Swalin's estimate[10] of the entropy of single-vacancy migration, $\Delta S_m = k \ln 60 = 4.1k$. As Swalin's estimate was based solely on geometrical considerations, we see that it is not necessary to invoke any large contribution due to shifts in lattice mode frequencies in order to account for self-diffusion in Ge by a simple, single-vacancy mechanism. It is only necessary to assume the vacancies are ionized. As noted, self-diffusion data in Si are confused by free surface effects,[27] but values of ΔS_m for single vacancies in Si inferred from impurity diffusion[25] are also in satisfactory agreement with Swalin's estimate.

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