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Correlation of Diffusivities of Various Elements in Silicon

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In a recent review of thermodynamics of point defects in solids Varotsos and Alexopoulos /1/ have considered the case of various (foreign) atoms (i), diffusing in the same bulk material (ref). The diffusion coefficient D^i is usually written in the following form:

$$D^i = D_o^i \exp(-\frac{h^i}{kT}) \ ,$$

where h^i denotes the activation enthalpy, k the Boltzmann constant, and D_o^i the pre-exponential factor from which the value of the activation entropy s^i can be estimated. Varotsos and Alexopoulos /1/ have suggested that the values of the pairs (D_o^i, h^i) are not fortuitously distributed but they are interconnected so that a plot of $\ln\left[D_o^i\sqrt{\frac{m^i}{m^{ref}}}\right]$ versus h^i - for various diffusing elements - should be a straight line. Furthermore they suggested that the slope of this straight line is solely predetermined by the elastic and expansivity data of the host material. More precisely this slope should be equal to F/k where F is given by the formula

$$F = -\frac{\beta B + \left.\frac{dB}{dT}\right|_P}{B - T\beta B - T\left.\frac{dB}{dT}\right|_P} \ , \qquad (1)$$

where β denotes the (volume) thermal expansion coefficient and B the isothermal bulk modulus. At high temperatures ($T \geq \Theta_D$, where Θ_D denotes the Debye temperature), the bulk modulus decreases almost linearly with temperature and hence $\left.\frac{dB}{dT}\right|_P$ can be practically considered as constant. Furthermore Tallon /2/ indicated that, for various solids, the quantity βB is temperature independent. Therefore the quantity F is practically independent of temperature.

In the case of silicon the diffusivities of a significant number of various elements have been studied and it was found that, among them, the values of h^i

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Table 1

Diffusion coefficents in silicon

	D_o^i ($cm^2 s^{-1}$)	h^i (eV)	ref.
Au[a]	2.4×10^{-4}	0.38	/7/
Au[b]	1.78×10^{-2}	1.13	/8/
Cu	4.7×10^{-3}	0.43	/9/
Ni	2×10^{-3}	0.47	/10/
Mn	$(6.9\pm2.2)\times10^{-4}$	0.63 ± 0.03	/11/
Li	2.5×10^{-3}	0.66	/12/
Fe[a]	1.3×10^{-3}	0.68	/3/
Fe[b]	6.2×10^{-3}	0.87	/13/
Cr	10^{-2}	1	/14/
Ir	4×10^{-2}	1.3	/15/
Ti	2×10^{-5}	1.5	/16/
Be	1×10^{-2}	2	/17/
S	0.92	2.2	/18/
Se[a]	0.11	2.42 ± 0.05	/19/
Se[b]	2.47	2.84	/20/
O[a]	0.07	2.44	/21/
O[b]	0.17	2.54	/22/
O[c]	0.23	2.56 ± 0.005	/23/
O[d]	3.2	2.92	/24/
Te[a]	1.1×10^{-2}	2.6 ± 0.2	/25/
Te[b]	$0.50^{+1.5}_{-0.38}$	3.34 ± 0.16	/26/
Ga[a]	0.005 ± 0.001	2.70 ± 0.02	/27/
Ga[b]	3.6 ± 1.44	3.51	/28/
C	1.9	3.1 ± 0.2	/29/
N	0.87	3.29	/30/
Al	8 ± 3.2	3.47	/28/
Sb[a]	0.214	3.65	/31/
Sb[b]	5.6 ± 2.24	3.94	/28/
P[a]	10.5 ± 4.2	3.69	/28/
P[b]	5.3	3.69	/32/
B	5.1	3.70	/33/
Bi[a]	1080	3.85	/31/
Bi[b]	1030	4.63	/28/
In	15.6 ± 6.6	3.91	/28/
As	60	4.20	/34/
Si[a]	20	4.4	/35/
Si[b]	154	4.65	/36/
Si[c]	1460	5.02	/37/
Ge[a]	0.2505×10^{4}	4.966	/38/
Ge[b]	$10.3^{+5.2}_{-3.4}\times10^{4}$	5.355 ± 0.047	/4/

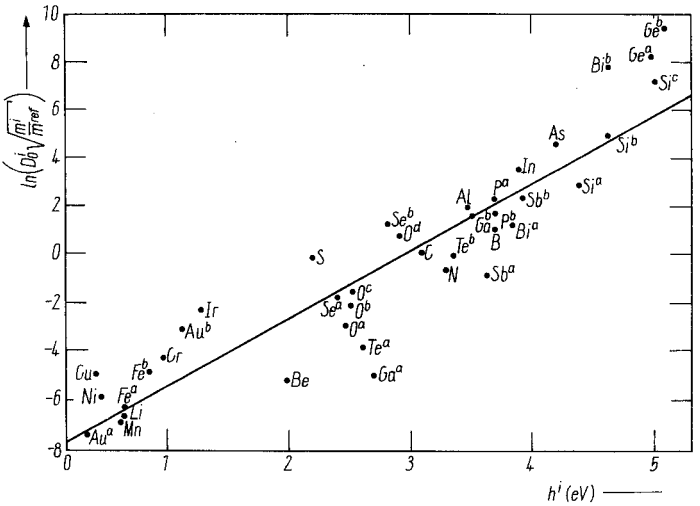

Fig. 1. Plot of $\ln\left\{\sqrt{D_o^i \frac{m^i}{m^{ref}}}\right\}$ versus h^i for various impurities in silicon. Data from Au^a: /7/; Au^b: /8/; Cu /9/; Ni: /10/; Mn /11/; Li: /12/; Fe^a :/13/; Fe^b: /13/; Cr: /14/; Ir: /15/; Be: /17/; S: /18/; Se^a: /19/; Se^b: /20/; O^a: /21/; O^b: /22/; O^c: /23/; O^d: /24/; Te^a: /25/; Te^b: /26/; Ga^a: /27/; Ga^b: /28/; C: /29/; N: /30/; Al: /28/; Sb^a: /31/; Sb^b: /28/; P^a: /28/; P^b: /32/; B: /33/; Bi^a: /31/; Bi^b: /28/; In: /28/; As: /34/; Si^a: /35/; Si^b: /36/; Si^c: /37/; Ge^a: /38/; Ge^b: /4/

vary by one order of magnitude whereas those of D_o^i change by 16 orders of magnitude. Therefore the case of silicon provides a good material for the check of the suggestion of Varotsos and Alexopoulos.

In Table 1 we have collected the diffusion constants D_o^i and h^i published by various workers /3, 7 to 38/. A least squares fitting to a straight line leads to an intercept -8.47 and a slope 2.94 eV^{-1}. This straight line has been drawn in Fig. 1. In the calculation we have not considered the point of Ti for which Weber /3/ has stated that it needs further confirmation. Note that if one deletes the point of Ge reported by Dörner et al. /4/ the slope of the straight line becomes a little bit smaller, i.e. 2.78 eV^{-1}.

We turn now to the calculation of the slope predicted from (1). For the temperature region 1400 to 1500 K the quantity B has a value around $1.2 \times 10^{-5} K^{-1}$ /5/.

Fig. 5 of Matsuo and Kagaya /6/ indicates that B has values of 743 kbar and 720 kbar for T = 1400 and 1500 K, respectively. Therefore, for T = 1450 K, we have B = 731.5 kbar and $\left.\frac{dB}{dT}\right|_P$ = -0.23 kbar/K.

By inserting the above data into (1) we have (T = 1450 K) $F \approx 2.1 \times 10^{-4}\ K^{-1}$ and hence $F/k = 2.44\ eV^{-1}$. This value differs by 20% from the slope of the straight line of Fig. 1. The difference turns only to 14% if one deletes the point (D_o^i, h^i) reported for Ge by Dorner et al. /4/.

It is well known that the experimental error in the determination of D_o is large, especially when the diffusion plot ln D versus 1/T extends over a small temperature range. This is evident from Fig. 1 if one compares the D_o values that correspond to the same diffusing element but come from different research groups. In view of this scatter we can say that the deviation of 20% or 14% between the values predicted from (1) and the slope obtained from the experimental points is remarkably small.

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