A further Consideration of the Correlation Factor for Impurity Diffusion in the Diamond Structure

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The correlation factor for impurity diffusion by single vacancies in the diamond structure is calculated taking into account eight distinct vacancy-atom exchange rates. Arguments are given that such a model is physically more realistic than the usual four frequency model. It turns out that the difference from the results obtained by the latter model can become large.

A long range Coulombic impurity-vacancy interaction is also included.

Introduction

In a previous paper[1] (to be referred to as paper I), we have calculated the correlation factor f for impurity diffusion by means of single vacancies in the diamond structure. We also included the effect of a long range Coulombic interaction between an impurity and a vacancy as proposed by Mehrer[2].

We calculated f as a function of five distinct atom-vacancy exchange rates: w_{1T} for exchange of a vacancy with the tracer, w_{12} for a jump of a vacancy neighbouring the tracer to a second nearest neighbour of the tracer and by similar definitions w_{21}, w_{23} and w_{25}. All other exchange rates were assumed to be equal to w_0, the exchange rate for self-diffusion.

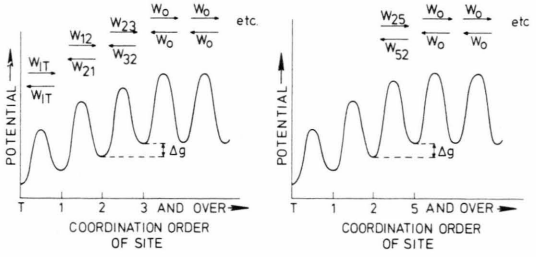

Fig. 1. Schematic diagram of vacancy potential.
On the left: the potential in a first, second, third, etc. nearest neighbour position.
On the right: the potential in a first, second, fifth etc. nearest neighbour position.

Consequently, in the absence of a long range electrostatic interaction, the potential barriers for the various jumps to overcome will have a form as drawn in Fig. 1. We get

$$\frac{w_{23}}{w_{32}} = \frac{\nu_{23}^*}{\nu_{32}^*} \exp(\Delta g/kT) \tag{1}$$

and

$$\frac{w_{25}}{w_{52}} = \frac{\nu_{25}^*}{\nu_{52}^*} \exp(\Delta g/kT) \tag{2}$$

where Δg is the difference in Gibbs free energy for the vacancy in both potential wells and the quantities ν^* for a crystal containing N atoms (3N degrees of freedom) are following Vineyard[3] given by

$$\nu^* = \frac{\prod_1^{3N} \nu_i}{\prod_1^{3N-1} \nu_i'} . \tag{3}$$

The ν_i are the $3N$ normal frequencies of lattice modes, when the atom neighbouring a vacancy is in its initial position, the ν_i' are the $3N$-1 frequencies of normal modes when the crystal is considered to vibrate around the saddle point configuration. When we assume the product of frequencies of normal modes to be the same for the vacancy in a third and in a fifth nearest neighbour position (the wells for those positions have the same depth), it turns out that (cf. Lidiard[4])

$$w_{23}/w_{32} = w_{25}/w_{52} \tag{4}$$

or

$$w_{23}/w_{25} = w_{32}/w_{52} . \tag{5}$$

So, in absence of long range electrostatic interaction the model used in paper I is not quite consistent and one has to choose at least eight distinct jump frequencies. Therefore we will calculate f as a function of exchange rates $w_{1T}, w_{12}, w_{21}, w_{23}, w_{25}, w_{32}, w_{52}$ and w_0. Moreover such a model may physically be more realistic than Manning' sfour frequencies model[5], because one of the six non-jumping atoms involved in the saddle-point configuration for w_{23}-, w_{25}-, w_{32}- and w_{52}- jumps is a nearest neighbour of the tracer.

Calculation of the correlation factor

The calculation is based on the same classification of lattice sites and uses the same formalism as in paper I.

The starting equation for the correlation factor is

$$f = (1 + t)/(1 - t) . \tag{6}$$

After the initial jump the tracer is situated in the origin of the coordinate system and the vacancy occupies one of the A_2-sites (See Fig. 1 of paper I).
We found

$$t = -\frac{1}{1 - p_1(A_2A_2) + p_1(A_2A_1)} \cdot \frac{w_{1T}}{w_{1T} + 3w_{12}}; \quad (7)$$

$p_1(A_2A_2) - p_1(A_2A_1)$ can be calculated from

$$p_1(A_2A_2) - p_1(A_2A_1) \quad (8)$$
$$= [q(A_2B)]\,(\mathbf{I} - \mathbf{p}_1(BB))^{-1}\,\{q(BA_2) - q(BA_1)\},$$

but this relation can be simplified using the symmetry equations

$$q(B_3A_2) = q(B_1A_1), \quad q(B_4A_2) = q(B_2A_1). \quad (9)$$

Substituting these relations into Eq. (8) one can easily prove that

$$p_1(A_2A_2) - p_1(A_2A_1)$$
$$= [q^*(A_2B)]\,(\mathbf{I} - \mathbf{p}_1^*(BB))^{-1}\{q^*(BA_2)\} \quad (10)$$

with

$$[q^*(A_2B)] = (q(A_2B_3),\, q(A_2B_4)), \quad (11)$$

$$\{q^*(BA_2)\} = \begin{pmatrix} q(B_3A_2) \\ q(B_4A_2) \end{pmatrix} \quad (12)$$

and (13)

$$\mathbf{p}_1^*(BB) = \begin{pmatrix} p_1(B_3B_3) - p_1(B_3B_1) & p_1(B_3B_4) - p_1(B_3B_2) \\ p_1(B_4B_3) - p_1(B_4B_1) & p_1(B_4B_4) - p_1(B_4B_2) \end{pmatrix}.$$

So, contrary to $\mathbf{p}_1(BB)$, which is a 4×4 matrix, $\mathbf{p}_1^*(BB)$ is a 2×2 matrix, the inversion of which is much easier to perform.

In a similar way, writing down symmetry relations for the elements of $\mathbf{p}_1(CC)$, $\mathbf{p}_1^*(BB)$ is obtained from a 4×4 matrix $\mathbf{p}_1^*(CC)$ by

$$p_1^*(B_kB_l) = [q^*(B_kC)]\,(\mathbf{I} - \mathbf{p}_1^*(CC))^{-1}\,\{q^*(CB_l)\}. \quad (14)$$

This is a simplification found by MANNING[5] and translated into our formalism.

Up to now, $\mathbf{P}(CC)$ was calculated using the equation

$$\mathbf{P}(CC) = (\mathbf{I} - \boldsymbol{\Gamma})^{-1} \quad (15)$$

where $\boldsymbol{\Gamma}$ is the one-jump transition probability matrix. To get an accurate result this method implies the building of a big crystal model — in order to classify lattice sites into sets and to find the transition probabilities by inspection — and the numerical inversion of a very large matrix. Therefore we have decided to perform this classification as well as the calculation of the transition probabilities by an electronic computer and to avoid the inversion of $\mathbf{I} - \boldsymbol{\Gamma}$.

We take into account 9 shells, choosing the I-shell as a boundary. The expressions for the elements $p_1(H_kH_l)$ are now written as

$$p_1(H_kH_j) = [q(H_kI)]\,(\mathbf{I} - \mathbf{p}_1(II))^{-1}\,\{q(IH_l)\}, \quad (16)$$

while $p_1(I_iI_j) = 0$ for all i and j, because no transitions within the I-shell are possible and the vacancy is considered as being lost when migrating beyond the I-shell.

The elements of $\mathbf{p}_1(GG)$ are calculated by

$$p_1(G_kG_l) = [q(G_kH)]\,(\mathbf{I} - \mathbf{p}_1(HH))^{-1}\,\{q(HG_l)\} \quad (17)$$

and the elements of $\mathbf{p}_1(FF)$, etc. by similar relations.

As the H-shell contains 49 sets, the largest matrix the computer has to invert is a 49×49 matrix, whereas the former method would have demanded the impracticable inversion of a 218×218 matrix!

As a consequence of the model the elements of $\mathbf{p}_1^*(CC)$ are functions of the jump frequency ratios

$$u \equiv w_{32}/w_0 \quad \text{and} \quad v \equiv w_{52}/w_0 \quad (18)$$

As follows from Eq. (14) the elements of $\mathbf{p}_1^*(BB)$ are now functions of u, v and the jump frequency ratios

$$x \equiv w_{23}/w_{21} \quad \text{and} \quad y \equiv w_{25}/w_{21}, \quad (19)$$

while in the absence of long range Coulombic interaction Eq. (5) holds, so

$$u/v = x/y \quad (5')$$

After substitution of $\mathbf{p}_1^*(BB)$,

$$[q^*(A_2B)] = \left(\frac{w_{12}}{w_{1T} + 3w_{12}},\ \frac{w_{12}}{w_{1T} + 3w_{12}}\right) \quad (20)$$

and

$$\{q^*(BA_2)\} = \begin{pmatrix} \dfrac{w_{21}}{w_{21} + 2w_{23} + w_{25}} \\ \dfrac{2w_{21}}{w_{21} + 2w_{23} + w_{25}} \end{pmatrix} \quad (21)$$

into Eq. (10) we obtain from Eq. (7)

$$t = -w_{1T}/(w_{1T} + 3Fw_{12}) \quad (22)$$

with

$$3F = \frac{F_1x + F_2y + 3(F_5x^2 + F_6xy + F_7y^2)}{1 + F_3x + F_4y + F_5x^2 + F_6xy + F_7y^2}. \quad (23)$$

The coefficients F_i, which are functions of u and v, can be found by means of the relations

$$\begin{aligned} F_1 &= 6 - g_1 - 2g_3 - g_5 - 2g_7, \\ F_2 &= 3 - g_2 - 2g_4 - g_6 - 2g_8, \\ F_3 &= 4 - g_1 - g_7, \\ F_4 &= 2 - g_2 - g_8, \\ F_5 &= 4 - 2g_1 - 2g_7 + g_1g_7 - g_3g_5, \\ F_6 &= 4 - g_1 - g_7 - 2g_2 - 2g_8 + g_1g_8 \\ &\quad + g_2g_7 - g_3g_6 - g_4g_5, \\ F_7 &= 1 - g_2 - g_8 + g_2g_8 - g_4g_6. \end{aligned} \quad (24)$$

Tab. 1. The coefficient γ_{ij} from Eq. 25 for various values of c/kT. Nine shells for $c/kT = 0$ and seven shell for $c/kT \neq 0$ were taken into account.

	c/kT	γ_{00}	γ_{10}	γ_{01}	γ_{20}	γ_{11}	γ_{02}	γ_{21}	γ_{12}	γ_{22}
	0	4.9752	16.2303	5.9446	12.4423	19.2260	1.6401	14.6587	5.2694	4
	1	1.203	6.628	1.850	7.915	10.033	0.632	11.893	3.394	4
G	2.5	0.118	1.682	0.282	3.827	3.841	0.135	8.637	1.792	4
	5	0.003	0.247	0.013	1.259	1.075	0.010	5.444	0.792	4
	10	0.000	0.012	0.000	0.185	0.168	0.000	2.629	0.256	4
	∞	0	0	0	0	0	0	0	0	4
	0	0	6.1786	0.0897	12.4422	7.5717	0.0853	14.6587	2.1989	4
	1	0	2.129	0.022	7.915	3.364	0.030	11.893	1.223	4
$g_1 G$	2.5	0	0.339	0.001	3.827	0.835	0.005	8.637	0.434	4
	5	0	0.014	0.000	1.259	0.071	0.000	5.444	0.061	4
	10	0	0.000	0.000	0.185	0.000	0.000	2.629	0.001	4
	∞	0	0	0	0	0	0	0	0	4
	0	0	0.0897	2.6316	0.1968	8.6627	1.6401	6.7372	5.2694	4
	1	0	0.039	0.800	0.171	4.453	0.632	5.437	3.394	4
$g_2 G$	2.5	0	0.005	0.115	0.111	1.639	0.135	3.876	1.792	4
	5	0	0.000	0.005	0.037	0.434	0.010	2.336	0.792	4
	10	0	0.000	0.000	0.002	0.063	0.000	1.009	0.256	4
	∞	0	0	0	0	0	0	0	0	4
	0	0	−3.4070	−0.1206	−6.2211	−4.2361	−0.0733	−7.3294	−1.2396	−2
	1	0	−1.226	−0.033	−3.958	−1.951	−0.026	−5.946	−0.703	−2
$g_3 G$	2.5	0	−0.216	−0.004	−1.913	−0.528	−0.005	−4.319	−0.267	−2
	5	0	−0.010	−0.000	−0.630	−0.049	−0.000	−2.722	−0.040	−2
	10	0	−0.000	−0.000	−0.092	−0.000	−0.000	−1.315	−0.001	−2
	∞	0	0	0	0	0	0	0	0	−2
	0	0	0.0771	0.5285	0.0587	1.6505	0	1.2058	0	0
	1	0	0.072	0.198	0.082	1.033	0	1.158	0	0
$g_4 G$	2.5	0	0.061	0.040	0.131	0.525	0	1.098	0	0
	5	0	0.023	0.003	0.105	0.201	0	0.954	0	0
	10	0	0.002	0.000	0.025	0.042	0	0.650	0	0
	∞	0	0	0	0	0	0	0	0	0
	0	0	−6.8140	0.1541	−12.4423	−7.9788	−0.1084	−14.6587	−2.4056	−4
	1	0	−2.451	0.081	−7.915	−3.644	−0.042	−11.893	−1.387	−4
$g_5 G$	2.5	0	−0.431	0.029	−3.827	−0.949	−0.007	−8.637	−0.527	−4
	5	0	−0.020	0.003	−1.259	−0.084	−0.000	−5.444	−0.080	−4
	10	0	−0.000	0.000	−0.185	−0.001	−0.000	−2.629	−0.001	−4
	∞	0	0	0	0	0	0	0	0	−4
	0	0	−0.2411	1.0569	−0.3760	3.2628	0	2.3580	0	0
	1	0	−0.118	0.397	−0.295	2.049	0	2.283	0	0
$g_6 G$	2.5	0	−0.036	0.081	−0.189	1.042	0	2.168	0	0
	5	0	−0.003	0.005	−0.052	0.401	0	1.899	0	0
	10	0	−0.000	0.000	−0.002	0.085	0	1.300	0	0
	∞	0	0	0	0	0	0	0	0	0
	0	0	13.7764	0.9934	18.6633	17.5163	0.5091	21.9881	5.0927	6
	1	0	5.886	0.343	11.873	9.489	0.215	17.839	3.384	6
$g_7 G$	2.5	0	1.604	0.071	5.740	3.848	0.059	12.956	1.870	6
	5	0	0.246	0.004	1.889	1.090	0.005	8.166	0.816	6
	10	0	0.012	0.000	0.277	0.168	0.000	3.944	0.256	6
	∞	0	0	0	0	0	0	0	0	6
	0	0	0.9934	3.3130	1.2565	11.1577	1.6401	8.7399	5.2694	4
	1	0	0.611	1.049	1.107	6.016	0.632	7.354	3.394	4
$g_8 G$	2.5	0	0.299	0.167	0.888	2.471	0.135	5.735	1.792	4
	5	0	0.074	0.008	0.420	0.735	0.010	3.806	0.792	4
	10	0	0.004	0.000	0.066	0.115	0.000	1.818	0.256	4
	∞	0	0	0	0	0	0	0	0	4

The functions g_i are quotients of which both numerator and denominator are of the form

$$\sum_{i=0}^{2}\sum_{i=0}^{2}\gamma_{ij}\,u^i\,v^j \tag{25}$$

The coefficients γ_{ij} have been calculated for various strengths of Coulombic interaction and are given in Table 1, where G stands for the denominator of the g_i's (all g_i's have the same denominator). In the cases where $c/kT \neq 0$ seven shells were taken into account, while for $c/kT = 0$ this number was nine.

In the absence of Coulombic interaction and taking $u = v = 1$ and $x = y = \alpha^{-1}$ we have to reobtain the results of the four frequency model. In the case of nine shells Eq. (23) becomes

$$3F = \frac{6.228\,\alpha + 9.470}{\alpha^2 + 3.661\,\alpha + 3.157}. \tag{26}$$

For selfdiffusion ($\alpha = 1$) we have $3F = 2.008$, which is almost equal to the exact value of 2.

By calculating also the coefficients for eight shells and considering that $3F = 2$ in case of selfdiffusion we obtain by extrapolation

$$3F = \frac{6.167\,\alpha + 9.261}{\alpha^2 + 3.627\,\alpha + 3.087}. \tag{27}$$

If we compare the coefficients in Eq. (27) with those obtained by MANNING[5] the differences appear to be at most 0.13%.

Conclusions

The modification of our former method, as given in Eqs. (16) and (17), turns out to yield far more accurate results in computing correlation factors than we were able to obtain as yet.

Moreover we were able to express $3F$ as a function of u, v, x and y (i.e. w_{32}/w_0, w_{52}/w_0, w_{23}/w_{21} and w_{25}/w_{21}, respectively).

By putting $x = y = \alpha^{-1}$, which implies $u = v$ (Eq. (5′)), we get

$$3F = \frac{(F_1 + F_2)\,\alpha + 3\,(F_5 + F_6 + F_7)}{\alpha^2 + (F_3 + F_4)\,\alpha + F_5 + F_6 + F_7}. \tag{28}$$

For $u\,(= v) = 1$ (four frequency model) we obtained nearly the same coefficients as in Manning's Eq. (32). However, for values of u not much different from 1, the coefficients deviate considerably as is shown in Table 2.

Finally, when $u \neq v$ and taking $y = (v/u)\,x$ in accordance with Eq. (5′), $3F$ can be plotted as a function of x for various values of u and v. As shown in Fig. 2

Tab. 2. Comparison of the coefficients from Eq. (18) for some cases.

	F_1+F_2	$F_5+F_6+F_7$	F_3+F_4
Eq. (27)	6.167	3.087	3.627
Ref. 5 (Eq. 32)	6.167	3.091	3.629
$u = v = 0.9$	6.351	3.375	3.771
$u = v = 0.6$	6.825	4.258	4.189
$u = v = 1.5$	5.772	2.386	3.248

the values of $3F$ can differ radically from those, obtained by use of the four frequency model, even when the differences between the activation energies of w_{32}-, w_{52}- and w_0-jumps are not too big.

It is obvious from the foregoing calculations with the aid of our physically more realistic eight frequency model, that results form the four frequency model have to be interpreted cautiously, because the correlation factor is rather sensitive for the values of the frequencies we added in our approach of the problem.

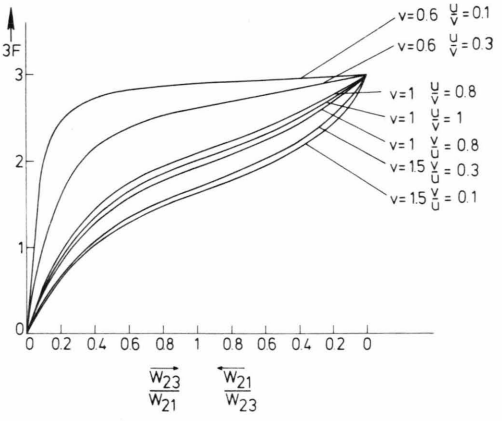

Fig. 2. Plot of $3F$ as a function of w_{23}/w_{21} for various values of u and v.

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