Correlation Factor for the Diffusion of Charged Impurities in the Diamond Structure*

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The correlation factor for impurity diffusion by a vacancy-mechanism is a function of the vacancy-jump frequencies in the surroundings of the diffusing atom. Since in Si and Ge the vacancy can act as an acceptor, a long-range Coulomb interaction between donor atoms and vacancies exists. The usual assumption, that only a few vacancy-jump frequencies in the immediate surroundings of the vacancy are different from the jump frequency in the pure matrix, is not justified in this case.

A very general expression for the correlation factor of impurity-diffusion in the diamond structure is deduced. Vacancy-jump frequencies for jumps which originate from first-, second-, and third-nearest neighbours are treated explicitely. For more remote jumps the Coulomb force is taken into account as a drift force operating on the migrating vacancy. After specializing the general expression it is compared with the well-known ,,four-frequency-model'' of Manning.

1. Introduction

Many impurities in silicon and germanium diffuse by a vacancy mechanism (see e.g. [1]). This means that a diffusor pursues a correlated and not a random walk in the lattice and introduces the so-called correlation factor into the Einstein-Smoluchowski relation of the diffusion coefficient [2].

The correlation factor is a function of the vacancy-jump frequencies in the surroundings of the diffusor [3–5]. If one neglects the small difference between the mass of the tracer atom and the mass of the matrix atoms in the case of self-diffusion all vacancy jump frequencies are equal. The correlation factor is then merely a geometrical quantity. Compaan and Haven [6] have calculated geometrical correlation factors for various coordination lattices including the diamond structure.

In the case of impurity diffusion the vacancy-jump frequencies in the solvent depend on position and jump direction of the migrating vacancy with respect to the impurity atom. This is due to the interaction of vacancy and impurity. Often this interaction is only poorly known. The usual procedure is to assume that the interaction is short-ranged and that only a few vacancy-jump frequencies in the neighbourhood of the impurity are altered. Manning has proposed a four-frequency-model for the correlation factor of impurity diffusion in the diamond structure [7, 8]. In his model frequencies for vacancy-jumps which originate from third-nearest or more remote neighbours are not influenced by the presence of the impurity.

Group V impurities in silicon and germanium behave as donors. A vacancy can act as an acceptor. Therefore, under certain conditions, a long-range interaction between charged vacancies and charged impurities exists. We shall discuss in Section 5 that there is strong experimental evidence that this interaction can be well described by a Coulomb potential.

The present paper attempts to include the Coulomb interaction into the calculation of the correlation factor. The calculation, which is based on a method recently proposed by Bakker [9], takes into account different vacancy-jump frequencies for each different vacancy-jump. Vacancy-jumps which ori-

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[1] A. Seeger and K. P. Chik, Phys. Stat. Sol. **29**, 455 [1968].

[2] J. Bardeen and C. Herring, Imperfections in Nearly Perfect Crystals. Eds. W. Shockley, J. H. Hollomon, R. Maurer, and F. Seitz, J. Wiley and Sons Inc., New York 1952.

[3] A. D. le Claire and A. B. Lidiard, Phil. Mag. **1**, 518 [1956].

[4] J. R. Manning, Diffusion Kinetics of Atoms in Crystals, Van Norstrand, Princeton 1968.

[5] A. D. Le Claire, Correlation Effects in Diffusion in Solids. Solid State, Vol. X, Chap. 6, Physical Chemistry — An Advanced Treatise, Academic Press, New York, to be published.

[6] K. Compaan and Y. Haven, Trans. Faraday Soc. **52**, 796 [1956].

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[8] J. R. Manning, Phys. Rev. **136**, A 1758 [1964].

[9] H. Bakker, Phys. Stat. Sol. **38**, 167 [1970].

ginate from first-, second-, and third-nearest neighbours of the impurity are treated in detail. For more remote jumps the Coulomb force is taken into account as a drift force acting on the migrating vacancy.

2. Classification of Sites. Notation of Vacancy-jump Frequencies

The correlation factor f for diffusion of impurity (tracer)-atoms (abbreviated by T) by a monovacancy mechanism in cubic crystals is given by

$$f = (1+t)/(1-t)\,. \qquad (2.1)$$

According to MULLEN[10] t equals the probability that after a T-jump the next T-jump has the same x-component minus the probability that the next T-jump has the opposite x-component. If the plane $x=0$ is a mirror plane of the lattice structure t may be interpreted even simpler. As outlined by BAKKER[9] in this case t equals the probability that the vacancy causes the next „minus" T-jump without ever having been on the plane $x=0$. In other words: it suffices to take into account in the calculation of t vacancy trajectories with positive x-coordinates.

We choose the $(\bar{1}10)$-symmetry-plane of the lattice as the plane $x=0$. After having just exchanged its position with a vacancy, T is situated at the origin of the coordinate system. We classify the lattice sites with respect to T in the way shown in Fig. 1. Sites which can be reached in at least one, two, three, four etc. jumps are called A-, B-, C-, D-, etc. "shells". In the present case the A-shell consists of only one site. Therefore this site will be occupied by the vacancy immediately after the initial jump of T. With the exception of the A-shell we recognize within each shell different "sets of equivalent sites", for which the probabilities of being occupied by the vacancy are the same.

We use a classification of sites which is slightly different from Bakker's paper. His classification would introduce a D-site instead of B_2 and E-sites instead of C_2 and C_3. Notwithstanding we use Bakker's formalism. This procedure will be justified by the results (see Section 7) and has the advantage that vacancy-jump frequencies near T do not enter the $\boldsymbol{P}$ (CC)-matrix of Section 5 and therefore enables a rather straight-forward treatment of the Coulomb interaction.

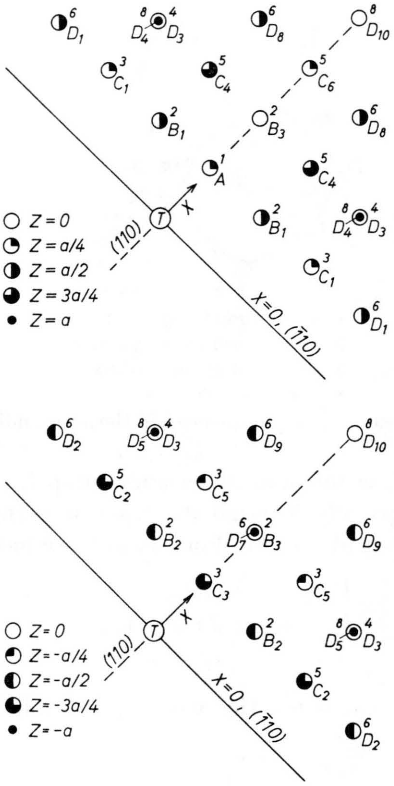

Fig. 1. Classification of sites around an impurity (tracer) atom T in the diamond lattice. Only the A-, B-, C-, and D-shells have been represented. The numbers denote i-th nearest neighbours. a) Sites with z-coordinates $\geqq 0$, b) Sites with z-coordinates $\leqq 0$.

As mentioned in the Introduction in the presence of T-atoms the vacancy-jump frequency in the solvent depends on the position of the vacancy before and after the jump. We denote by ν_{ij} the jump frequency for a vacancy-jump from an i-th nearest neighbour site of T to a j-th nearest neighbour site of T[11]. Some of the vacancy-jump frequencies in the neighbourhood of T have been indicated in Fig. 2.

The probability that a vacancy at site i will jump to site j is

$$p_{ij} = (\nu_{ij}/\Gamma_i)\,, \qquad (2.2)$$

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[10] J. G. MULLEN, Phys. Rev. **121**, 1649 [1961].

[11] We use a notation for the vacancy-jump frequencies which is different from the usual one (e. g. in MANNINGS [7,8] calculations) but which has the advantage of being systematic.

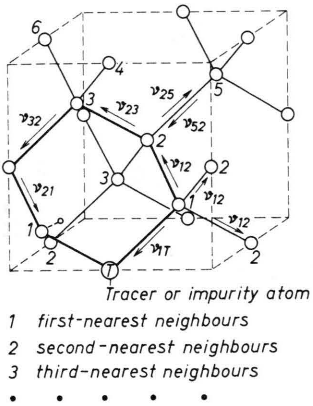

Fig. 2. Vacancy-jump frequencies in the surroundings of T.

where Γ_i is the sum of vacancy-jump frequencies for jumps which originate from a certain i-th nearest neighbour site. For example we have

$$\begin{aligned} \Gamma_1 &= \nu_{1T} + 3\,\nu_{12}\,, \\ \Gamma_2 &= \nu_{21} + 2\,\nu_{23} + \nu_{25} \\ &\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot \end{aligned} \tag{2.3}$$

where ν_{1T} denotes the vacancy-T exchange frequency.

3. General Equation for the Correlation Factor

In order to calculate t we use the formalism developed by BAKKER[9]. Applying his Eq. (2.3) to our problem we obtain

$$t = -\frac{p_{1T}}{1 - \boldsymbol{q}(A\,B)\,\boldsymbol{P}(B\,B)\,\boldsymbol{q}(BA)} \tag{3.1}$$

where $\boldsymbol{q}(A\,B)$ and $\boldsymbol{q}(\,BA)$ denote row and column matrices

$$\boldsymbol{q}(A\,B) = (p_{12}\,, 0, p_{12})\,, \quad \boldsymbol{q}(BA) = \begin{pmatrix} 2\,p_{21} \\ 0 \\ p_{21} \end{pmatrix} \tag{3.2}$$

and $\boldsymbol{P}(BB)$ denotes the square matrix

$$\boldsymbol{P}(BB) = \begin{pmatrix} P(B_1\,B_1) & P(B_1\,B_2) & P(B_1\,B_3) \\ P(B_2\,B_1) & P(B_2\,B_2) & P(B_2\,B_3) \\ P(B_3\,B_1) & P(B_3\,B_2) & P(B_3\,B_3) \end{pmatrix}. \tag{3.3}$$

The elements $P\,(B_i\,B_j)$ of $\boldsymbol{P}(B\,B)$ are the sums of the probabilities that a vacancy arrives once, twice, ... at a certain site of the set B_j avoiding the A-site and provided that set B_i is completely occupied at the beginning.

Inserting Eq. (3.2), (3.3) and (2.2) into (3.1) we obtain

$$t = -\,\nu_{1T}/(\nu_{1T} + 3\,\nu_{12}\,F_3) \tag{3.4}$$

where

$$F_3 = 1 - \frac{\nu_{21}}{3\,\Gamma_2}\,\cdot \tag{3.5}$$
$$[2\,P(B_1\,B_1) + P(B_3\,B_3) + 2\,P(B_3\,B_1) + P(B_1\,B_3)].$$

F_3 is a function of all vacancy-jump frequencies in the solvent with the exception of ν_{12}. The quantity $\nu_{12}F_3$ may be considered as an effective escape frequency of the vacancy. With (3.4) the correlation factor (2.1) can be written as

$$f = 3\,\nu_{12}\,F_3/(2\,\nu_{1T} + 3\,\nu_{12}\,F_3)\,. \tag{3.6}$$

4. Calculation of $\boldsymbol{P}(B\,B)$

The calculation of F_3 requires the determination of the matrix $\boldsymbol{P}(B\,B)$ which may be obtained from

$$\boldsymbol{P}(B\,B) = [1 - \boldsymbol{p}_1(B\,B)]^{-1}\,. \tag{4.1}$$

An element $p_1\,(B_i\,B_j)$ of the matrix $\boldsymbol{p}_1\,(B\,B)$ denotes the probability that a vacancy arrives once at a certain site of set B_j starting from an occupied set B_i and avoiding the A-shell.

In the diamond structure direct vacancy-jumps between B-sites are not possible if only jumps between nearest-neighbour sites can occur. The vacancy can therefore arrive at B_j only by trajectories which cross the C-shell. Thus we obtain

$$\boldsymbol{p}_1\,(B_i\,B_j) = \boldsymbol{q}\,(B_i\,C)\,\boldsymbol{P}(C\,C)\,\boldsymbol{q}\,(C\,B_j)\,. \tag{4.2}$$

In the present case $\boldsymbol{P}(C\,C)$ is a 6 times 6 square matrix. An element $P\,(C_k\,C_l)$ denotes the sum of probabilities that a vacancy arrives once, twice, ... at a certain site of set C_l starting from an occupied set C_k and avoiding the A- and B-shells.

The $\boldsymbol{q}$'s denote the following row and column matrices:

$$\begin{aligned} \boldsymbol{q}\,(B_1\,C) &= (p_{23}\,, & 0, && 0, && p_{25}\,, & 0, && 0\;\;) \\ \boldsymbol{q}\,(B_2\,C) &= (0, & p_{25}\,, && 2\,p_{23}\,, && 0, & p_{23}\,, && 0\;\;) \\ \boldsymbol{q}\,(B_3\,C) &= (0, & 0, && 0, && 0, & p_{23}\,, && p_{25}) \end{aligned} \tag{4.3}$$

$$\boldsymbol{q}(C\,B_1) = \begin{pmatrix} p_{32} \\ 0 \\ 0 \\ p_{52} \\ 0 \\ 0 \end{pmatrix}, \quad \boldsymbol{q}(C\,B_2) = \begin{pmatrix} 0 \\ p_{52} \\ p_{32} \\ 0 \\ p_{32} \\ 0 \end{pmatrix}, \quad \boldsymbol{q}(C\,B_3) = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 2\,p_{32} \\ p_{52} \end{pmatrix} \tag{4.4}$$

Table 1. The $\boldsymbol{P}_1$ (BB)-matrix for the diamond lattice.

	B_1	B_2	B_3
B_1	$Q_1 P(C_1 C_1)$ $+ Q_2 P(C_4 C_4)$ $+ Q_3 P(C_1 C_4)$ $+ Q_4 P(C_4 C_1)$	$Q_1[P(C_1 C_3) + P(C_1 C_5)]$ $+ Q_2 P(C_4 C_2)$ $+ Q_3 P(C_1 C_2)$ $+ Q_4[P(C_4 C_3) + P(C_4 C_5)]$	$2 Q_1 P(C_1 C_5)$ $+ Q_2 P(C_4 C_6)$ $+ Q_3 P(C_1 C_6)$ $+ 2 Q_4 P(C_4 C_5)$
B_2	$Q_1[2 P(C_3 C_1) + P(C_5 C_1)]$ $+ Q_2 P(C_2 C_4)$ $+ Q_3[2 P(C_3 C_4) + P(C_5 C_4)]$ $+ Q_4 P(C_2 C_1)$	$Q_1[2 P(C_3 C_3) + P(C_5 C_3)$ $+ 2 P(C_3 C_5) + P(C_5 C_5)]$ $+ Q_2 P(C_2 C_2)$ $+ Q_3[2 P(C_3 C_2) + P(C_5 C_2)]$ $+ Q_4[P(C_2 C_3) + P(C_2 C_5)]$	$2 Q_1[2 P(C_3 C_5) + P(C_5 C_5)]$ $+ Q_2 P(C_2 C_6)$ $+ Q_3[2 P(C_3 C_6) + P(C_5 C_6)]$ $+ 2 Q_4 P(C_2 C_5)$
B_3	$Q_1 P(C_5 C_1)$ $+ Q_2 P(C_6 C_4)$ $+ Q_3 P(C_5 C_4)$ $+ Q_4 P(C_6 C_1)$	$Q_1[P(C_3 C_5) + P(C_5 C_5)]$ $+ Q_2 P(C_2 C_6)$ $+ Q_3 P(C_5 C_2)$ $+ Q_4[P(C_6 C_3) + P(C_6 C_5)]$	$2 Q_1 P(C_5 C_5)$ $+ Q_2 P(C_6 C_6)$ $+ Q_3 P(C_5 C_6)$ $+ 2 Q_4 P(C_6 C_5)$

The matrix $\boldsymbol{p}_1(B B)$, which is obtained by inserting (4.3) and (4.4) into (4.2), is tabulated in Table 1 using the following abbreviations:

$$Q_1 = p_{23}\, p_{32}\,, \quad Q_3 = p_{23}\, p_{52}\,, \qquad (4.5)$$
$$Q_2 = p_{25}\, p_{52}\,, \quad Q_4 = p_{25}\, p_{32}\,.$$

Up to this point our calculation is completely general with respect to the vacancy-jump frequencies in the solvent. The $P(C_k C_l)$ contain all transition probabilities for vacancy-jumps which originate from the D-shell and more remote shells and also the transition probabilities for jumps which connect the C-shell with the D-shell.

5. Calculation of $\boldsymbol{P}(C\,C)$ including a Long-range Coulomb-interaction of Vacancy and Impurity

Long-range diffusion of an impurity (tracer) in the diamond structure is possible only if the vacancy, after having exchanged its position with T, dissociates to at least a third-nearest neighbour site of T and that it afterwards approaches T from a different direction. Otherwise the correlation factor would be zero. Such a „minimal" vacancy-trajectory is characterized by the jump sequence

$$\nu_{12} \to \nu_{23} \to \nu_{32} \to \nu_{21}$$

and a typical one has been illustrated in Fig. 2. In Sections 2, 3, and 4 we have treated explicitely the vacancy-jumps between the A-, B-, and C-shell which include the above mentioned jump frequencies.

The usual procedure in calculating impurity correlation factors is to treat more remote jumps as a self-diffusion problem, i. e. to assume that all frequencies for remote vacancy-jumps are equal to the vacancy-jump frequency ν_0 in the pure solvent. This assumption fails to be a good approximation if a long-range interaction between T and the vacancy exists.

The interaction between a charged vacancy and a charged impurity contains an elastic and an electrostatic contribution. Both interactions influence the vacancy-jump frequencies in the solvent. Although the elastic interaction may be complicated in its details, it is short-ranged and therefore affects only those frequencies in the very vicinity of T.

The electrostatic interaction between charged impurities in semiconductors can be studied in considerable detail in the so-called „pair spectra" (see e. g. [12, 13]). These spectra originate in the radiative recombination of electrons and holes at donor-acceptor pairs. The energy of the luminescence radiation depends on the electrostatic interaction energy and hence on the pair distance. Numerous experimental investigations especially in the case of GaP (see e. g. [14]) have shown that the electrostatic interaction can be represented to a good approximation by the Coulomb potential if the pair-distance exceeds a few lattice constants. It appears therefore justified to expect a long-range Coulomb interaction

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[12] F. Williams, Phys. Stat. Sol. **125**, 493 [1968].

[13] M. Gershenzon, Physics of III-V Compounds, Vol. 2, Chap. 13, Eds. R. K. Williardson and A. C. Beer, Academic Press, New York 1966.

[14] D. G. Thomas, M. Gershenzon, and F. Trumbore, Phys. Rev. **133**, A 269 [1964].

also between charged vacancy-impurity pairs in silicon and germanium, although in these cases experimental studies are not available.

In Fig. 3 a division of the surroundings of T into an inner region and a „Coulomb-region“ has been indicated schematically. We take the C-shell as the boundary between these two regions and we assume that a vacancy which migrates within the Coulomb-region is attracted only by the Coulomb force of T. We denote by $\boldsymbol{r}_i$ the position of the vacancy before the jump and by $\boldsymbol{s}_{ij}$ the jump vector of the vacancy. The coulomb force is given by

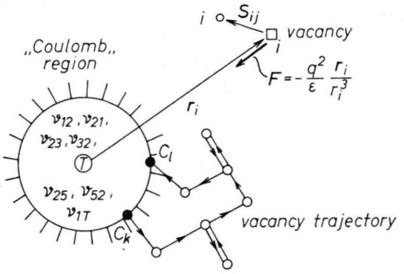

Fig. 3. Division of the surroundings of T into an inner region and into a Coulomb region.

$$\boldsymbol{F}_i = -\frac{q^2}{\varepsilon}\frac{\boldsymbol{r}_i}{r_i^3} \tag{5.1}$$

where ε denotes the dielectric constant of the material and $\pm q$ the charges of impurity and vacancy.

The Coulomb force $\boldsymbol{F}_i$ operates as a drift force on the migrating vacancy and favours vacancy-jumps which lower the Coulomb energy. The barrier height of the saddle point pertaining to the jump vector $\boldsymbol{s}_{ij}$ is altered by

$$\Delta E_{ij} = c\,\xi_{ij} \tag{5.2}$$

where c is an abbreviation for

$$c = (q^2/2\,\varepsilon\, a) \tag{5.3}$$

and

$$\xi_{ij} = a\,(\boldsymbol{s}_{ij}\cdot \boldsymbol{r}_i/r_i^3) \tag{5.4}$$

is a geometrical factor, which is characteristic for each jump. a denotes the cubic lattice constant. Some of the quantities ξ_{ij} have been tabulated in Table 2. In (5.4) we have assumed that the force on the vacancy is constant during the jump and is given by (5.1). This is probably a very reasonable approximation, since the net effect of the Coulomb interaction on the correlation factor will turn out to be small.

Table 2. Some of the geometrical factors ξ_{ij} which characterize the Coulomb interaction.

Jumps from i-th nearest neighbours of T	$\xi_{i,j}$	
$i = 3$	$\xi_{3,4} = 0.1096$	$\xi_{3,6} = 0.3289$
$i = 4$	$\xi_{4,3} = -0.25$	$\xi_{4,7} = 0.25$
$i = 5$	$\xi_{5,6} = 0.0483$	$\xi_{5,8} = 0.2415$
$i = 6$	$\xi_{6,3} = -0.2722$ $\xi_{6,7} = 0$ $\xi_{6,11} = 0.2722$	$\xi_{6,5} = -0.1361$ $\xi_{6,9} = 0.1361$
$i = 7$	$\xi_{7,4} = -0.1996$ $\xi_{7,10} = 0.1426$	$\xi_{7,6} = -0.0855$ $\xi_{7,12} = 0.2566$
$i = 8$	$\xi_{8,5} = -0.1768$ $\xi_{8,13} = 0.1768$	$\xi_{8,9} = 0$
$i = 9$	$\xi_{9,6} = -0.1352$ $\xi_{9,10} = -0.0193$	$\xi_{9,8} = -0.0580$ $\xi_{9,14} = 0.1739$
$i = 10$ etc.	$\xi_{10,7} = -0.1265$ $\xi_{10,13} = 0.0632$	$\xi_{10,9} = -0.0632$ $\xi_{10,15} = 0.1265$

For elevated temperatures T we have

$$|\Delta E_{ij}/k\,T| < 1\,. \tag{5.5}$$

k denotes Boltzmann's constant. In the case of silicon ($\varepsilon = 14$, $a = 5.43$ Å, $q = e$) we obtain from (5.3): $c = 0.09$ eV. We conclude from Table 2 that even for the biggest value of ξ_{ij} (ξ_{36}) the inequality (5.5) is satisfied for temperatures above room temperature. For most other jumps $|\Delta E_{ij}|$ is even much less than $k\,T$. Since diffusion is usually investigated at high temperatures, (5.5) appears to be no serious limitation.

To first order we obtain for the vacancy-jumps frequencies

$$\nu_{ij} = \nu_0\,(1 - \xi_{ij}\,(c/k\,T)) \tag{5.6}$$

where ν_0 denotes the vacancy-jumps frequency in the pure solvent.

From Eq. (2.2) we obtain for the vacancy-jump probabilities:

$$p_{ij} = \tfrac{1}{4}\,(1 - \xi_{ij}(c/k\,T))\,. \tag{5.7}$$

In order to calculate $\boldsymbol{P}(C\,C)$ we have to invert the $(\mathbf{1} - \boldsymbol{T})$ matrix and to pick out those elements which are needed for $\boldsymbol{P}(CC)$. $\boldsymbol{T}$ denotes the one-jump transition matrix for the Coulomb region. The elements T_{mn} are the vacancy-jump probabilities of Eq. (5.7) which carry numerical factors given by the number of sites of set m that are nearest neighbours of a certain site of set n. A small part of the matrix $(\mathbf{1} - \boldsymbol{T})$, which, in principle, is infinite, has been tabulated in Table 3.

Table 3. Part of the $(\mathbf{1}-\boldsymbol{T})$-matrix for the diamond structure. (Only matrix elements which are not equal zero have been printed).

	C_1	C_2	C_3	C_4	C_5	C_6	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}
C_1	1						$-p_{36}$		$-p_{34}$							
C_2		1						$-p_{56}$			$-p_{58}$					
C_3			1										$-p_{36}$			
C_4				1						$-p_{58}$		$-2\,p_{56}$		$-p_{56}$		
C_5					1				$-p_{34}$						$-p_{36}$	
C_6						1								$-p_{56}$		$-p_{58}$
D_1	$-p_{63}$						1									
D_2		$-p_{65}$						1								
D_3	$-p_{43}$				$-p_{43}$				1							
D_4				$-p_{85}$						1						
D_5		$-p_{85}$									1					
D_6				$-p_{65}$								1				
D_7			$-p_{63}$										1			
D_8				$-p_{65}$		$-2\,p_{65}$								1		
D_9					$-p_{63}$										1	
D_{10}						$-p_{85}$										1

Since in a numerical calculation only finite matrices can be handled, we can take into account only vacancy trajectories over a limited region of the crystal. If a vacancy wanders away beyond a certain boundary we shall assume that it returns randomly to T and hence gives zero contribution to the correlation factor. Actually we neglect all vacancy trajectories which go outside the G-shell. The choice of this boundary is determined by the storage capacity of the computer available. (We then have to handle 86×86 matrices.) The error introduced by this boundary is very small.

According to Eq. (5.7) the transition matrix may be written as a sum of two terms:

$$\boldsymbol{T}=\boldsymbol{T}^{(0)}-(c/k\,T)\,\boldsymbol{T}^{(1)}. \tag{5.8}$$

The second term accounts for the Coulomb interaction whereas the first term equals the transition matrix which one obtains by treating remote vacancy-jumps as a self-diffusion problem. In the validity range of the inequality (5.5) the second term is a small correction term. We are therefore justified to determine the inverse of the matrix $(\mathbf{1}-\boldsymbol{T})$ in the following way:

$$(\mathbf{1}-\boldsymbol{T})^{-1}=(\mathbf{1}-\boldsymbol{T}^{(0)})^{-1}-(c/k\,T)\,(\mathbf{1}-\boldsymbol{T}^{(0)})^{-1}\cdot\boldsymbol{T}^{(1)}\,(\mathbf{1}-\boldsymbol{T}^{(0)})^{-1}. \tag{5.9}$$

The matrix operations on the right hand side of (5.9) can be performed by a computer. Afterwards those elements of $(\mathbf{1}-\boldsymbol{T})^{-1}$ can be picked out which are needed for the matrix $\boldsymbol{P}(CC)$. Each element of this matrix can be written as

$$P(C_k\,C_l)=P^{(0)}(C_k\,C_l)-(c/k\,T)\,\eta_{kl} \tag{5.10}$$

where the numerical values of $P^{(0)}(C_k C_l)$ and η_{kl} are known after the evaluation of (5.9).

6. General Equation for F_3 including Coulomb Interaction

As we have shown in Section 3, F_3 is given by Eq. (3.6) which contains four elements of the $\boldsymbol{P}(BB)$ matrix. Their determination is described in Section 4. The main task is to invert $(\mathbf{1}-\boldsymbol{p}_1)$. We refrain from describing this laborious (compare Table 1) but uninteresting work and at once report the result. For F_3 we obtain

$$F_3=1-\frac{\nu_{21}}{3\,\Gamma_2}\,\frac{Z}{N}\,, \tag{6.1}$$

where the following abbreviations have been used:

$$Z=3+\sum_{i=1}^{4}(\alpha_i\,Q_i+\alpha_{ii}\,Q_i^2)+\sum_{\substack{i,j\\ i>j}}^{4}\alpha_{ij}\,Q_i\,Q_j\,, \tag{6.2}$$

$$\begin{aligned}N=1&+\sum_{i=1}^{4}(\beta_i\,Q_i+\beta_{ii}\,Q_i^2+\beta_{iii}\,Q_i^3)+\sum_{\substack{i,j\\ j>i}}^{4}\beta_{ij}\,Q_i\,Q_j\\&+\sum_{\substack{i,j\\ j\neq i}}^{4}\beta_{iij}\,Q_i^2\,Q_j+\sum_{\substack{i,j,k\\ j>i\\ k>j}}^{4}\beta_{ijk}\,Q_i\,Q_j\,Q_k\,.\end{aligned} \tag{6.3}$$

If only linear terms in $c/k\,T$ in accordance with (5.5) are retained the coefficients $\alpha\ldots$ and $\beta\ldots$ can be written as follows:

$$\begin{aligned}\alpha\ldots&=\alpha^{(0)}-\alpha^{(1)}\,(c/k\,T)\,,\\ \beta\ldots&=\beta^{(0)}-\beta^{(1)}\,(c/k\,T)\,.\end{aligned} \tag{6.4}$$

Table 4. The coefficients $\alpha^{(0)}$ and $\beta^{(0)}$.

i	1	2	3	4
$\alpha_i^{(0)}$	-16.02	-7.16	-0.259	-0.259
$\alpha_{ii}^{(0)}$	13.8	4.27	$2.2 \cdot 10^{-3}$	$2.2 \cdot 10^{-3}$
$\beta_i^{(0)}$	-7.1	-4.07	-0.17	-0.17
$\beta_{ii}^{(0)}$	12.35	5.44	$4.7 \cdot 10^{-3}$	$4.7 \cdot 10^{-3}$
$\beta_{iii}^{(0)}$	-6.31	-2.40	$-3.1 \cdot 10^{-5}$	$-3.1 \cdot 10^{-5}$
$\alpha_{ij}^{(0)}$	$\alpha_{12}^{(0)} = 19.1$ $\alpha_{23}^{(0)} = 0.31$	$\alpha_{13}^{(0)} = 0.37$ $\alpha_{24}^{(0)} = 0.31$	$\alpha_{14}^{(0)} = 0.37$ $\alpha_{34}^{(0)} = 4.4 \cdot 10^{-3}$	
$\beta_{ij}^{(0)}$	$\beta_{12}^{(0)} = 19.5$ $\beta_{23}^{(0)} = 0.45$	$\beta_{13}^{(0)} = 0.57$ $\beta_{24}^{(0)} = 0.45$	$\beta_{14}^{(0)} = 0.57$ $\beta_{34}^{(0)} = 8.9 \cdot 10^{-3}$	
$\beta_{iij}^{(0)}$	$\beta_{112}^{(0)} = -16.9$ $\beta_{221}^{(0)} = -13.2$ $\beta_{331}^{(0)} = -6.7 \cdot 10^{-3}$ $\beta_{441}^{(0)} = -6.7 \cdot 10^{-3}$	$\beta_{113}^{(0)} = -0.43$ $\beta_{223}^{(0)} = -0.29$ $\beta_{332}^{(0)} = -6 \cdot 10^{-3}$ $\beta_{442}^{(0)} = -6 \cdot 10^{-3}$	$\beta_{114}^{(0)} = -0.43$ $\beta_{224}^{(0)} = -0.29$ $\beta_{334}^{(0)} = -8.7 \cdot 10^{-5}$ $\beta_{443}^{(0)} = -8.7 \cdot 10^{-5}$	
$\beta_{ijk}^{(0)}$	$\beta_{123}^{(0)} = -0.74$ $\beta_{234}^{(0)} = -1.1 \cdot 10^{-2}$	$\beta_{124}^{(0)} = -0.74$	$\beta_{134}^{(0)} = -1.3 \cdot 10^{-2}$	

Table 5. The coefficients $\alpha^{(1)}$ and $\beta^{(1)}$.

i	1	2	3	4
$\alpha_i^{(1)}$	$1.6 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	$-3.5 \cdot 10^{-2}$	$5.3 \cdot 10^{-2}$
$\alpha_{ii}^{(1)}$	$-5.6 \cdot 10^{-3}$	$-1.6 \cdot 10^{-2}$	$6.4 \cdot 10^{-4}$	$-1.7 \cdot 10^{-3}$
$\beta_i^{(1)}$	$4.3 \cdot 10^{-2}$	$6.1 \cdot 10^{-2}$	$-1.9 \cdot 10^{-2}$	$4.2 \cdot 10^{-2}$
$\beta_{ii}^{(1)}$	-0.12	-0.15	$1.5 \cdot 10^{-3}$	$-2.1 \cdot 10^{-3}$
$\beta_{iii}^{(1)}$	$8.2 \cdot 10^{-2}$	$8.9 \cdot 10^{-2}$	$-2 \cdot 10^{-5}$	$2.3 \cdot 10^{-5}$
$\alpha_{ij}^{(1)}$	$\alpha_{12}^{(1)} = -5.4 \cdot 10^{-2}$ $\alpha_{23}^{(1)} = 4.1 \cdot 10^{-2}$	$\alpha_{13}^{(1)} = 5.3 \cdot 10^{-2}$ $\alpha_{24}^{(1)} = -6.3 \cdot 10^{-2}$	$\alpha_{14}^{(1)} = -7 \cdot 10^{-2}$ $\alpha_{34}^{(1)} = -4.3 \cdot 10^{-3}$	
$\beta_{ij}^{(1)}$	$\beta_{12}^{(1)} = -0.42$ $\beta_{23}^{(1)} = 4.6 \cdot 10^{-2}$	$\beta_{13}^{(1)} = 6.7 \cdot 10^{-2}$ $\beta_{24}^{(1)} = -0.11$	$\beta_{14}^{(1)} = -0.15$ $\beta_{34}^{(1)} = -2.4 \cdot 10^{-4}$	
$\beta_{iij}^{(1)}$	$\beta_{112}^{(1)} = 0.42$ $\beta_{221}^{(1)} = 0.45$ $\beta_{331}^{(1)} = -1.8 \cdot 10^{-3}$ $\beta_{441}^{(1)} = 3 \cdot 10^{-3}$	$\beta_{113}^{(1)} = -4.9 \cdot 10^{-2}$ $\beta_{223}^{(1)} = -2.8 \cdot 10^{-2}$ $\beta_{332}^{(1)} = -1.6 \cdot 10^{-3}$ $\beta_{442}^{(1)} = 2.7 \cdot 10^{-3}$	$\beta_{114}^{(1)} = 0.11$ $\beta_{224}^{(1)} = 7.7 \cdot 10^{-2}$ $\beta_{334}^{(1)} = -8 \cdot 10^{-6}$ $\beta_{443}^{(1)} = 2.4 \cdot 10^{-5}$	
$\beta_{ijk}^{(1)}$	$\beta_{123}^{(1)} = -7.9 \cdot 10^{-2}$ $\beta_{234}^{(1)} = 9 \cdot 10^{-4}$	$\beta_{124}^{(1)} = 0.19$	$\beta_{134}^{(1)} = 9.8 \cdot 10^{-4}$	

The numerical values of the coefficients are tabulated in Tables 4 and 5. From Table 4 we recognize that the various coefficients $\alpha^{(0)}$ and $\beta^{(0)}$ cover several orders of magnitude. This property could be used if one wants to simplify Eq. (6.1).

Table 5 shows that the relative importance of the Coulomb interaction is greater for terms which contain Q_3 and/or Q_4. This is due to the fact that only vacancy trajectories with four or more vacancy-jumps within the Coulomb region can contribute to these terms whereas terms which only contain Q_1 and/or Q_2 have important contributions from vacancy trajectories with fewer jumps within the Coulomb region.

7. Application to the Four-Frequency Model of the Correlation Factor

Eq. (6.1) to (6.3) can be used in connection with Tables 4 and 5 to deduce simpler equations for F_3 by specializing some of the vacancy-jump frequencies. We confine ourselves to consider the well-known ,,four-frequency-model“. In Mannings notation[4, 7, 8] this model takes into account the following frequencies:

$$\begin{aligned} &(w_2 \equiv \nu_{1T})\,, \quad (w_3 \equiv \nu_{12})\,, \\ &w_4 \equiv \nu_{21}\,, \qquad w_5 \equiv \nu_{23} = \nu_{25}\,. \end{aligned} \tag{7.1}$$

All other frequencies are assumed to be equal to the vacancy-jump frequency in the pure solvent. (The two frequencies w_2 and w_3 have been mentioned for reasons of completeness. They are needed in the Eq. (3.6) for f but not in F_3.) Inspection of (4.5) shows that the four quantities Q_i are equal and we have

$$Q_i = \frac{1}{4}\,\frac{w_5}{w_4 + 3\,w_5}\,, \quad i = 1, \ldots, 4\,. \tag{7.2}$$

If we neglect for the moment the Coulomb interaction we obtain by inserting (7.2) into (6.1)

$$F_3 = \frac{23.5 + 24.9\,\alpha + 6.29\,\alpha^2}{23.5 + 36.6\,\alpha + 18.4\,\alpha^2 + 3\,\alpha^3} \tag{7.3}$$

with $\alpha \equiv w_4/w_5$. When α goes to zero $F_3 = 1$. When α goes to infinity $F_3 = 0$. In the case of self-diffusion, where all vacancy-jump frequencies are equal, F_3 deviates by $+0.8\%$ from the exact value 2/3 which follows from the value $f = 0.5$ for the correlation factor of Compaan and Haven[6]. This deviation introduces an error of less than $+0.3\%$ into the correlation factor for self-diffusion. In the case of impurity diffusion, the error is in the same order of magnitude. If even more accurate values are required one has to consider in Section 5 vacancy trajectories which extend beyond the G-shell.

Eq. (7.3) agrees in its algebraic form with the expression for F_3 derived by Manning[8]. In Fig. 4 (upper curve) $3\,F_3$ as calculated from (7.3) has been plotted. This curve practically would coincide with the corresponding curve from Mannings expression. The deviations are not greater than 0.8%.

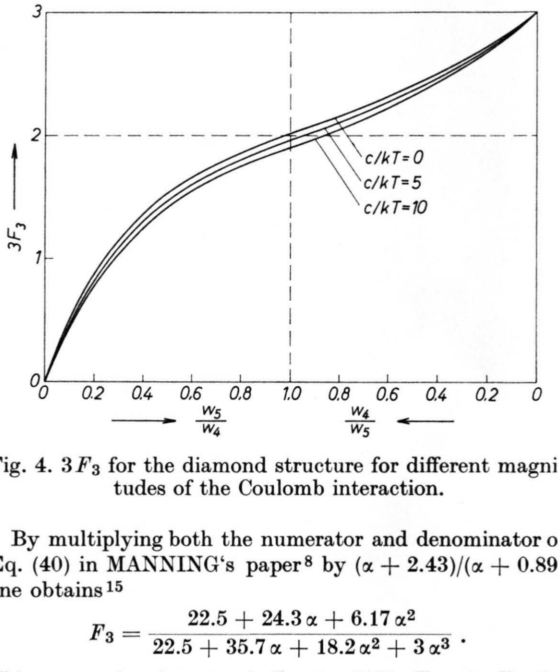

Fig. 4. $3\,F_3$ for the diamond structure for different magnitudes of the Coulomb interaction.

By multiplying both the numerator and denominator of Eq. (40) in MANNING‘s paper[8] by $(\alpha + 2.43)/(\alpha + 0.89)$ one obtains[15]

$$F_3 = \frac{22.5 + 24.3\,\alpha + 6.17\,\alpha^2}{22.5 + 35.7\,\alpha + 18.2\,\alpha^2 + 3\,\alpha^3}\,.$$

This expression is very similar to (7.3). Eventually the agreement between both expressions could be improved by taking into acconnt more shells.

Let us now include the Coulomb interaction but retain the four-frequency-model for the inner jump frequencies. We then obtain from (6.1)

$$F_3 = \sum_{i=0}^{2} \gamma_i\,\alpha^i \Big/ \sum_{i=0}^{3} \delta_i\,\alpha_i \tag{7.4}$$

where the coefficients γ_i and δ_i can be written as

$$\begin{aligned} \gamma_i &= \gamma_i^{(0)} - \frac{c}{k\,T}\,\gamma_i^{(1)}\,, \\ \delta_i &= \delta_i^{(0)} - \frac{c}{k\,T}\,\delta_i^{(1)}\,, \end{aligned} \tag{7.5}$$

and have been tabulated in Table 6. $\gamma_i{}^{(0)}$ and $\delta_i{}^{(0)}$ of course agree with the values of (7.3). The influence of the Coulomb interaction is shown in

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[15] J. R. Manning, private communication.

Table 6. The coefficients γ_i and δ_i for the four-frequency-model of the correlation factor including Coulomb interaction.

i	0	1	2	3
$\gamma_i^{(0)}$	23.5	24.9	6.29	—
$\gamma_i^{(1)}$	0.44	0.37	0.08	—
$\delta_i^{(0)}$	23.5	36.6	18.4	3
$\delta_i^{(1)}$	0.44	0.41	0.09	0

Fig. 4 for different values of c/kT. F_3 is lower by some percent and hence f is smaller than without Coulomb interaction. As already mentioned in Section 3, $\nu_{12} F_3$ can be interpreted as an effective escape frequency. It appears plausible that the Coulomb attraction diminishes the chance of a vacancy to escape the surroundings of T.

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