

Limits of the ratios of tracer diffusivities for diffusion by vacancy pairs: Application to compound semiconductors

I. V. Belova,¹ D. Shaw,² and G. E. Murch^{1,a)}

¹University Centre for Mass and Thermal Transport in Engineering Materials, Priority Research Centre in Geotechnical and Materials Modelling, School of Engineering, The University of Newcastle, Callaghan, New South Wales 2308, Australia

²Department of Physics, University of Hull, Cottingham Road, Kingston-upon-Hull HU6 7RX, United Kingdom

(Received 20 July 2009; accepted 24 October 2009; published online 4 December 2009)

In this paper, the vacancy-pair diffusion mechanism in cubic materials is revisited with emphasis on the limits of the ratio of the tracer diffusion coefficients to demonstrate the operation of this mechanism. The vacancy-pair mechanism puts very strict upper and lower bounds on this ratio. Extensive high precision Monte Carlo simulation is used to calculate tracer correlation factor, ratios of tracer diffusivities, and percolation effects (in mixed compounds). The three major cubic lattices—NaCl, CsCl, and zinc blende structures—are analyzed, and correct limits for the ratio of the tracer diffusivities are found to be 5.6, 11.2, and 2.6, respectively. For the case of the CsCl structure correlation factors are redetermined using the matrix method to obtain good agreement with the Monte Carlo results. Self-diffusion in the compound semiconductors PbSe (NaCl structure) InSb, GaSb, CdTe, and HgCdTe (zinc blende structure) is reanalyzed. It is shown that the vacancy-pair mechanism is unlikely to contribute to self-diffusion in CdTe and HgCdTe but it remains a valid possibility for self-diffusion in PbSe, InSb, and GaSb. © 2009 American Institute of Physics. [doi:10.1063/1.3264719]

I. INTRODUCTION

Many years ago, it was demonstrated convincingly that vacancy pairs make a significant contribution to self-diffusion in alkali halides.¹ However, the contribution of vacancy pairs to self-diffusion in other materials where separate sublattices exist is still largely unknown.

From a measurement of the tracer diffusion coefficient of a component alone it is generally not possible to determine the role of vacancy pairs vis à vis the role of monovacancies, although a curvature of an Arrhenius plot could in principle be in evidence because the overall activation energies for component tracer diffusion by vacancy pairs are quite different from that for diffusion via monovacancies.² There are, however, a number of experimental diffusion strategies that can possibly demonstrate the contribution of vacancy pairs to self-diffusion.

The first strategy is to make use of the very different tracer correlation behavior of vacancy pairs and monovacancies by carrying out the diffusion isotope effect experiment.³ Such a strategy has been used to demonstrate, reasonably convincingly, the significant diffusion role of divacancies in sodium at high temperatures⁴ but was less successful in its application to demonstrate the role of vacancy pairs in alkali halides.⁵

A second strategy is to dope the material (if it has an ionic character) with aliovalent ions to emphasize the role of vacancy pairs. For example, doping NaCl with a divalent cation will, via the Schottky defect product, greatly suppress the anion monovacancy concentration and expose the contri-

bution of the vacancy pair for anion diffusion.¹ Similarly, doping with a divalent anion will suppress the cation monovacancy concentration and expose the contribution of the vacancy pair for cation diffusion.¹ This strategy was used with quite some success in the alkali halides¹ but has not been attempted for other ionic materials.

A third strategy is to compare the tracer diffusion coefficient (via the Nernst–Einstein relation) with the collective diffusion quantity, the ionic conductivity, since vacancy pairs may contribute to the tracer diffusion but, being electrically neutral, do not contribute to the ionic conductivity.^{2,6} However, if cations and anions have comparable mobilities, it is unfortunately difficult to separate the individual contributions to the ionic conductivity. It should be mentioned in passing that in the case of another closely related collective diffusion quantity, the chemical interdiffusion coefficient on one sublattice, both monovacancies and vacancy pairs behave in very much the same way and such experiments are unlikely to distinguish between the two mechanisms.^{7,8}

Finally, a fourth strategy is to measure the ratio of the tracer diffusion coefficients of the two atomic components assuming that diffusion is carried almost exclusively by vacancy pairs. The vacancy-pair mechanism puts very strict upper and lower bounds on this ratio. This strategy made the triple-defect mechanism, which is very closely related to the vacancy-pair mechanism, to be preferred over the six-jump-cycle mechanism as the vehicle for self-diffusion at the stoichiometric composition in the B2 intermetallics formed from group VIII B metals and group III A metals.⁹ We mention here also the discussion of the role of vacancy pairs as the vehicle for self-diffusion in group III–group V and group II–group

^{a)}Electronic mail: graeme.murch@newcastle.edu.au.

VI compound semiconductors taking the zinc blende (sphalerite) structure.^{10,11} We will return to this below.

The numerical limits for the ratio of the tracer diffusivities for diffusion via vacancy pairs have not been as accurately determined as they should be. The difficulty in their determination is that the tracer correlation effects associated with the vacancy-pair mechanism are much more prominent than for probably any other known diffusion mechanism. Indeed, it is the tracer correlation effects inherent in the vacancy-pair mechanism that lead to the very strong coupling between the tracer diffusivities of the two components. Small approximations in the calculation of the tracer correlation factors can lead to very large errors in the determination of the limits of the ratio of the diffusivities.

In the present study, we revisit the correlation effects associated with the vacancy-pair mechanism in the three major cubic lattices (NaCl, CsCl, and zinc blende structures) with the intention of determining accurate limits for the ratio of the tracer diffusivities. We employ high precision Monte Carlo methods to determine the correlation factors. Where there is a discrepancy with existing analytical results, we use the matrix method to calculate new correlation factors. We also investigate the effect on the ratio of the diffusivities of introducing a third atomic component on one of the sublattices. Finally, we provide an extended discussion on the possible role of vacancy pairs in diffusion in compound semiconductors.

II. THEORY AND COMPUTER SIMULATIONS

A. Previous calculations

There have been a number of analytical calculations of the tracer correlation factors for the NaCl and CsCl structures. Compaan and Haven¹² and Howard¹³ calculated the component tracer correlation factors for various values of the ratio of the end vacancy-atom exchange frequencies. The values provided by Howard¹³ are a little larger than those of the more accurate calculations of Compaan and Haven.¹² This is almost certainly because of limitations of the size of the return boundary region used by Howard.¹³ Howard¹³ was able to give the limits for the ratio of the tracer diffusion coefficients D_A/D_B in the NaCl structure as

$$6.1^{-1} < (D_A/D_B)^{\text{NaCl}} < 6.1, \quad (1)$$

and in the CsCl structure (as interpolated by Le Claire¹⁴) as

$$12.1^{-1} < (D_A/D_B)^{\text{CsCl}} < 12.1. \quad (2)$$

An early and limited Monte Carlo study of self-diffusion via vacancy pairs in the NaCl structure¹⁵ gave results for the correlation factors that were somewhat lower than the analytical results of Compaan and Haven,¹² but no limits of the diffusivity ratios were provided. Using a modified matrix method Bakker and co-workers¹⁶ also determined correlation factors for self-diffusion via vacancy pairs in the CsCl structure. They found the following limits of the ratio of the diffusion coefficients:

$$13.3^{-1} < (D_A/D_B)^{\text{CsCl}} < 13.3. \quad (3)$$

Later, Belova and Murch¹⁷ adapted Manning's well-known diffusion kinetics theory for the random alloy¹⁸ to derive the first *closed-form* expressions for the tracer correlation factors for both the NaCl and CsCl structures. The absolute values for the correlation factors were in reasonable agreement with new Monte Carlo results provided by Belova and Murch¹⁷ but probably no better than the previously derived ones by Compaan and Haven,¹² Howard,¹³ and Bakker *et al.*¹⁶ The following limits of the ratio of the diffusion coefficients for the NaCl and CsCl structures can be easily obtained from the expressions given by Belova and Murch¹⁷ as follows:

$$7.76^{-1} < (D_A/D_B)^{\text{NaCl}} < 7.76, \quad 5.84^{-1} < (D_A/D_B)^{\text{CsCl}} < 5.84. \quad (4)$$

Belova and Murch¹⁷ later extended Manning's kinetics theory arguments in order to determine tracer correlation factors via vacancy pairs in mixed sublattice materials such as (Na,K)Cl and Na(Cl,Br).¹⁸ These results were also in reasonable agreement with their Monte Carlo results.

Two analytical studies have addressed the calculation of tracer correlation factors for diffusion via vacancy pairs in the zinc blende structure. Weiler and colleagues¹⁹ calculated the tracer correlation factors using a modified matrix method. They found that the limits for the ratio of the tracer diffusion coefficients are given by

$$2.59^{-1} < (D_A/D_B)^{\text{zinc blende}} < 2.59. \quad (5)$$

Vorob'ev and colleagues²⁰ calculated the tracer correlation factors using a set of Bogolubov kinetic equations for the probability distribution functions of the atomic configurations of interest. They found that the limits for the ratio of the tracer diffusion coefficients are given by

$$2.92^{-1} < (D_A/D_B)^{\text{zinc blende}} < 2.92. \quad (6)$$

There have been no Monte Carlo calculations of the tracer correlation factors in the zinc blende structure. Furthermore, no limits generally of the ratios of the diffusivities obtained by Monte Carlo have ever been published.

B. Models used in the present study

The vacancy pair consists of tightly bound anion and cation vacancies at a nearest-neighbor separation. In the CsCl structure, the anion and cation sublattices are simple cubic, whereas in the NaCl and zinc blende structures the anion and cation sublattices are fcc. In the CsCl structure, the number of possible jumps of an end vacancy that retains the integrity of the vacancy pair is three. On the other hand, in the NaCl and zinc blende structures the number of possible jumps of an end vacancy that retains the integrity of the vacancy pair is four. For the binary ionic crystal AB, we can identify two ion-vacancy exchange frequencies w_A and w_B for the A (anions) and B (cations) respectively. For the ternary (AC)B consisting of mixed cation (A and C cations) sublattice and single anion element sublattice we identify

three ion-vacancy exchange frequencies w_A , w_C , and w_B . In the present study the A and C cations are assumed to be randomly mixed on their sublattice.

The vacancy-pair diffusion mechanism puts strong geometric restrictions on the displacements of the ions at each end of the vacancy pair. ‘‘Sum-rule relations’’²¹ between the phenomenological coefficients have been shown to be exact for these structures as well.⁸ Because of these relations, collective correlation factors (the correlated parts of the phenomenological coefficients) can be calculated analytically in a relatively straightforward way for the binary AB system and, with a little more difficulty, for the ternary (AC)B system, assuming a random distribution of A and C.

On the other hand, tracer correlation effects as embodied in the tracer correlation factor (the correlated part of the tracer diffusivity) are much more complicated and require special effort. For the binary system, the use of analytical methods, such as the matrix method,²² can give an accurate result for the limits on the ratio of the tracer diffusivities with the use of a large enough matrix.

C. Monte Carlo simulations

In conventional random walk theory of isotropic solid-state diffusion, the tracer diffusion coefficient for the vacancy-pair mechanism is given by

$$D_i = f_i^{2v} c_{2v} w_i a^2, \quad (7)$$

where $c_{2v} = N_{2v}/N$, N_{2v} is the number of vacancy pairs, N is the total number of atoms, w_i is the atom i -vacancy-pair exchange frequency, a is the lattice parameter, and f_i^{2v} is the correlation factor of the tracer i atomic species.

We made use of standard Monte Carlo computer simulation techniques²³ to calculate tracer correlation factors and the ratios of the tracer diffusivities in all three structures: CsCl, NaCl, and zinc blende (as functions of the ratio of the exchange frequencies w_A/w_B).

The tracer correlation factors were calculated from a form of the Einstein equation

$$f_i^{2v} = \frac{\langle \Delta r_i^2 \rangle}{\langle n_i \rangle \bar{a}^2}, \quad (8)$$

where $\langle \Delta r_i^2 \rangle$ is the mean square displacement of a tracer i atom in the time of the simulation with the average to be taken over a large number of tracer atoms (see below), $\langle n_i \rangle$ is the average of number of jumps per i atom (see below), and \bar{a} is the jump distance. For the CsCl structure the jump distance $\bar{a} = a$, the lattice parameter, whereas for the NaCl and zinc blende structures $\bar{a} = a/\sqrt{2}$.

The sublattice size used was 30 000 and the average number of jumps per atom of the slower moving species was 100. This provided full convergence of the correlation factors. The Monte Carlo results for the ratio of the tracer diffusion coefficients are shown in Fig. 1. These results act as a reference point for all of the analytical calculations.

It is quite clear that the Monte Carlo results for the ratio of the diffusivities show a plateau for $w_A/w_B < 10^{-3}$ and that the limits of the ratios of the tracer diffusivities are the following.

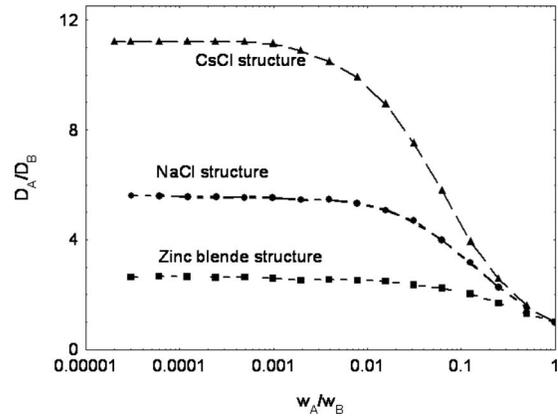


FIG. 1. Monte Carlo simulation results for the ratio of the tracer diffusivities for diffusion via vacancy pairs in the NaCl, CsCl, and zinc blende crystal structures as a function of the ratio of the vacancy-pair end exchange frequencies.

For the CsCl structure,

$$11.2^{-1} < (D_A/D_B)^{\text{CsCl}} < 11.2. \quad (9)$$

For the NaCl structure,

$$5.6^{-1} < (D_A/D_B)^{\text{NaCl}} < 5.6. \quad (10)$$

For the zinc blende structure,

$$2.6^{-1} < (D_A/D_B)^{\text{zinc blende}} < 2.6. \quad (11)$$

We see that the Monte Carlo simulation results agree very well with the matrix method results given above for the zinc blende structure¹⁹ and deviate slightly from those for the NaCl structure.^{12,13} On the other hand, the simulation results for the limits deviate quite significantly from those for the CsCl structure (11.2 compared with 13.3 given in Ref. 16). The matrix method is normally relatively accurate provided a sufficiently large number of jumps are counted. For the zinc blende structure, where the agreement is good, calculations were done with a maximum of four jumps counted¹⁹ but for the CsCl structure¹⁶ only a maximum of three jumps was counted. The approximate Manning approach,¹⁷ while giving a reasonable estimate of the correlation factors themselves as mentioned above, does not provide an accurate estimate of the ratio of the tracer diffusivities in either the NaCl or CsCl structures, with the latter being quite poor.

D. Analytical calculation of the tracer correlation factor for the CsCl structure

Because of the deviation observed above for the CsCl structure, we redetermined the tracer correlation factors for that structure using the matrix method²² but using up to five jumps counted.

The CsCl structure consists of two simple-cubic interpenetrating sublattices, one of which is occupied by A atoms and the other by B atoms. The two vacancies are located at the nearest-neighbor positions. The vacancy pair is assumed not to dissociate, with possible atomic jumps occurring within the sublattices, resulting in the next-nearest-neighbor positions. Therefore three A atoms and three B atoms are able to jump into the vacancy pair at any moment. A atoms

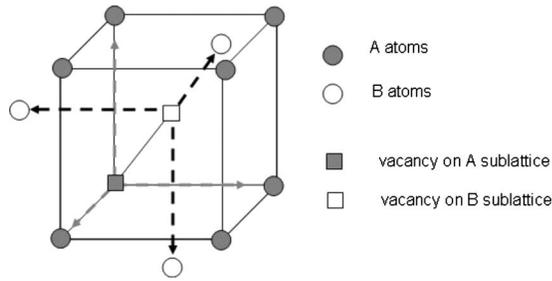


FIG. 2. Schematic presentation of the possible vacancy pair jumps (shown by dashed arrows) in the case of CsCl structure.

jump with a vacancy-exchange rate w_A , and B atoms with w_B . In Fig. 2 we present a schematic illustration for the possible jumps of the vacancy pair. The diffusion coefficient of, for example, B atoms is given by [Eq. (7)]

$$D_B = f_B^{2v} c_{2v} w_B a^2.$$

Following Howard¹³ the correlation factor f_B^{2v} can be written in the matrix form

$$f_B^{2v} = 1 + 2\mathbf{bT}(\mathbf{I} - \mathbf{T})^{-1}\mathbf{d}, \quad (12)$$

where \mathbf{b} and \mathbf{d} are row and column vectors, \mathbf{b} being the vector of *a priori* probabilities for the B atom jumps [which is simply $w_B/(3w_B + 3w_A)$] multiplied by the corresponding cosines of these jumps with the diffusion direction, \mathbf{d} is simply a vector of the starting position of the B (tracer) atom, \mathbf{I} is the identity matrix, and \mathbf{T} is the square matrix containing transition probabilities between neighboring defect positions. Vectors \mathbf{b} and \mathbf{d} are easy to compute. The main difficulty in the use of this method is in constructing the matrix \mathbf{T} with its elements T_{ij} as the probability that when a vacancy pair (initially located at a site i) jumps, it does so to a site j (and j cannot be the site where the tracer ion is located after the first tracer-vacancy pair exchange). In computing the \mathbf{T} matrix we extensively exploited the symmetry of the crystal structure in such a way that with the chosen initial jump all the crystal sites are classified according to the distance to the vacancy pair (shells). This step of the calculation can be successfully completed with the use of MATHEMATICA[®] software to incorporate any number of shells. Matrix conversion then can be done using the same software.

As was already mentioned, the building of this matrix \mathbf{T} and performing calculations are greatly automated by making extensive use of a combination of symbolic and numerical analyses available in MATHEMATICA[®] software. In Eq. (12) the exact value for the tracer correlation factor could be obtained as a limiting case with the size of matrix \mathbf{T} going to infinity. This is of course impossible in practice, but it is desirable to keep as many terms in the matrix \mathbf{T} as possible. We use the maximum size of matrix \mathbf{T} as 250×250 , where up to about five jumps of the vacancy pair were counted with the implication that other jumps of the vacancy pair do not contribute significantly into the tracer correlation factor. The inversion of the $\mathbf{I}-\mathbf{T}$ matrix was done numerically by MATHEMATICA[®] point by point. The new analytical limits for the ratio of the tracer correlation factors calculated with the matrix method are

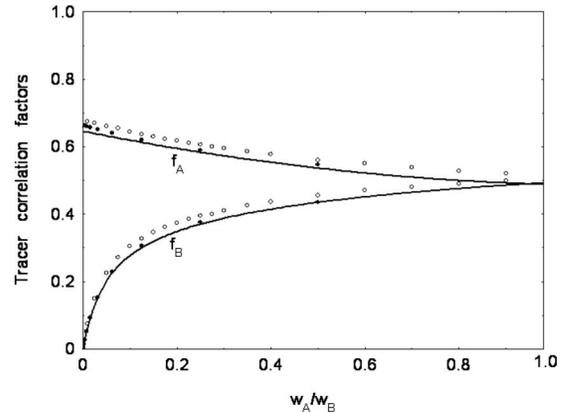


FIG. 3. Tracer correlation factors f_A and f_B for the CsCl binary (AB) structure as a function of the ratio of the end vacancy-atom exchange frequencies. Solid lines: Monte Carlo simulation results (this study); \circ : earlier matrix method results (Ref. 16); and \bullet : matrix method (present study).

$$11.259^{-1} < (D_A/D_B)^{\text{CsCl}} < 11.259. \quad (13)$$

The results of all the calculations for the tracer correlation factors in this structure are presented in Fig. 3. The new matrix method results for CsCl are clearly now in much better agreement with the Monte Carlo simulation results of the present study.

E. Role of the vacancy pair in diffusion in compound semiconductors

In the IIB-VIB, IIIB-VB, and IVB-VIB binary compound semiconductors, diffusion under thermal equilibrium conditions requires the ambient vapor pressure of one of the components to be specified and controlled. At a given temperature such control enables the level of nonstoichiometry (i.e., the deviation from stoichiometry) to be varied between the cation- and anion-rich limits. The concentrations of cation (anion) vacancies and interstitials will decrease or increase, respectively, with the cation (anion) partial vapor pressure in an electrically intrinsic material. In an electrically extrinsic material, the concentration of the cation-anion vacancy pair will be independent of the partial pressure only if the pair is electrically neutral. Observing how cation and anion self-diffusions vary with a component partial pressure is a strategy that can identify possible diffusion mechanisms as well as eliminating others.

1. Self-diffusion in InSb and GaSb

First, we consider self-diffusion in two IIIB-VB compound semiconductors: InSb and GaSb. Both take the zinc blende structure. We first discuss InSb. Kendall and Huggins²⁴ found $D_{\text{Sb}}/D_{\text{In}} \approx 1.6$ between 475 and 517 °C with D_{In} and D_{Sb} both showing no variation between In and Sb rich materials. These workers gave Arrhenius parameters with the pre-exponential factor D_0 being of the order of $3 \times 10^{13} \text{ cm}^2 \text{ s}^{-1}$, which is very high compared with typical values in solids. However, Kendall and Huggins²⁴ showed that this high value is likely to be a result of the large vibrational entropy contributions associated with the vacancy-pair

mechanism. It is clear that the observed ratio of the self-diffusion coefficients is fully consistent with the limits of the vacancy-pair mechanism found above.

Next, we consider self-diffusion in GaSb. The results for D_{Ga} and D_{Sb} between 594 and 700 °C show that D_{Ga} and D_{Sb} increase, depending on the temperature, by up to factors of 2 and 6.7, respectively, as the Sb pressure rises from the Ga rich limit to the Sb rich one.²⁵ Both D_{Ga} and D_{Sb} can be shown to comprise two terms, one independent of Sb pressure and the other increasing with Sb pressure.²⁶ The pressure-independent terms are $D_{\text{Ga}}=6.7 \exp(-3.01 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{Sb}}=13 \exp(-3.16 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$. It follows that $D_{\text{Ga}}/D_{\text{Sb}}=3.8$ and 3.1 at 600 and 700 °C, respectively. This spread of 3.1–3.8 cannot be regarded as significant and these ratios are only just outside the theoretical limits of the ratio of the tracer diffusivities for the vacancy-pair mechanism for the zinc blende structure. It is certainly possible that the differences are still within experimental uncertainties. On the other hand, the differences could be real, and the obvious candidate mechanisms to account for the pressure independence are Ga and Sb Frenkel defects. However, this would require that the tracer diffusivities by way of diffusion of the Ga and Sb defects to be almost identical. This would seem to be a most remarkable condition. Another way to resolve the differences is to assume that the pressure-independent D_{Ga} actually has two components: a vacancy pair and a Frenkel pair. This idea was proposed in Ref. 26 in order to reconcile the self-diffusion results of Ref. 27 (see below) with those of Ref. 25. This obviously reduces the $D_{\text{Ga}}/D_{\text{Sb}}$ ratio.

The data for self-diffusion in GaSb obtained by Bracht *et al.*²⁷ conflict with those from Ref. 25 in that (i) D_{Ga} although comparable to Ref. 25 shows no change between Ga rich and Sb rich materials, and (ii) D_{Sb} is roughly three orders of magnitude smaller than found in Ref. 25. The data from Ref. 27 thus clearly exclude a vacancy-pair mechanism but the marked discrepancy between the experimental results of Refs. 27 and 25 requires a little comment. Whereas Weiler and Mehrer²⁵ used radiotracer diffusion into a GaSb wafer, Bracht *et al.*²⁷ used interdiffusion between isotopically (stable) enriched molecular beam epitaxy (MBE) grown epilayers of GaSb. The only notable other difference in technique was the addition of H to the diffusion ampoule by Ref. 25, and this feature was suggested by Shaw²⁶ to account for the discrepancy. It was proposed that the presence of H in the wafer suppressed Sb diffusion. An attempt to validate this proposal was inconclusive.²⁸ There remains, however, the similar behavior with Ref. 25 found in InSb self-diffusion²⁴ and In diffusion in GaSb (Ref. 29) (see further below), where H was not included in the diffusion ampoule, which might suggest that the presence of H is not a factor. A common feature in Refs. 24, 25, and 29 but not in Ref. 27 is the use of acids and organic solvents in the surface preparation of their diffusion samples. Such liquids are a potential source of contamination with H so that the H ambient employed by Ref. 25 may have only a minimal effect. An aspect not referred to by Ref. 27 is the purity of their starting enriched isotopes and the resulting purity of the epilayers. The total foreign impurity level in the as-received enriched isotopes, ⁷¹Ga, ¹²¹Sb,

and ¹²³Sb, can be up to 1% atomic^{30,31} so that it is at least feasible for the discrepancy to arise from impurity contamination of the MBE epilayer structures grown by Ref. 27. It is therefore felt, mainly because of the similar behavior found by three independent investigations,^{24,25,29} that the reliability of the results from Ref. 27 needs to be established by measurement of the residual foreign impurity content of their epilayers.

2. Chemical diffusion of In in GaSb

Mathiot and Edelin²⁹ observed the chemical diffusion of In in GaSb between 520 and 706 °C. The In concentration never exceeded 3% and diffusion profiles were good fits to complementary error functions over three orders of magnitude in the In concentration. This means that D_{In} is independent of the In concentration up to at least 3% and so can be equated to D_{In} obtained by self-diffusion measurements of In in the homogenous ternary compound InGaSb (In content <3%). Depending on the temperature, D_{In} increases by up to a factor 12 with rising Sb pressure and, similar to self-diffusion in GaSb, also has two terms: The pressure-independent term in this case is $D_{\text{In}}=0.83 \exp(-2.87 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$.³² At 600 and 700 °C it follows that, for the pressure-independent terms, $D_{\text{Ga}}/D_{\text{In}}=1.3$ and 1.5, respectively. The difference between these two values cannot be regarded as significant. It is also of interest to note that $D_{\text{In}}/D_{\text{Sb}}=3.0$ and 2.0 at 600 and 700 °C, respectively.

3. Self-diffusion in CdTe and HgCdTe

Next, we consider the IIB-VIB compound semiconductors CdTe and HgCdTe, both of which take the zinc blende structure. In CdTe, it was found that D_{Te} increased with Te pressure at a given temperature and that at Te saturation $D_{\text{Te}}(\text{Te sat})=5.3 \times 10^{-4} \exp(-1.49 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$, between 500 and 800 °C, and $D_{\text{Te}}(\text{Te sat})=16.6 \exp(-2.42 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$ between 660 and 920 °C.³³ D_{Cd} is independent of component partial pressure except perhaps close to Cd saturation where there may be an increase. The ratio of the self-diffusivities $D_{\text{Cd}}(\text{Te sat})/D_{\text{Te}}(\text{Te sat})=3.1 \times 10^4 \exp(-0.93 \text{ eV/kT})$ ranges from 0.13 at 600 °C to 1.35 at 800 °C. These are minimum values and will increase by factors $\sim 10^3$ at ~ 800 °C as the Te (Cd) pressure decreases (increases) in traversing the vapor-solid phase field from Te saturation to Cd saturation. Based on this experimental evidence and the above theoretical limits of the ratio of the diffusivities it is clear that the vacancy-pair mechanism is unlikely to be a principal contributor to self-diffusion in CdTe.

In HgCdTe, Hg and Cd share the metal sublattice and Te occupies the nonmetal sublattice. For HgCdTe (20% Cd) it was found that $D_{\text{Te}}=814 \exp(-2.32 \text{ eV/kT})/P_{\text{Hg}} \text{ cm}^2 \text{ s}^{-1}$ between 450 and 550 °C where P_{Hg} is the Hg partial pressure (atm).¹⁰ At Te saturation (when P_{Hg} is least), it was found that $D_{\text{Te}}(\text{Te sat})=1.8 \times 10^{-4} \exp(-1.25 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$. The self-diffusion coefficients for Hg and Cd are considerably higher than for Te. Between 350 and 500 °C the self-diffusion coefficient of Hg is given by D_{Hg}

$=0.28 \exp(-1.51 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$ and is independent of P_{Hg} except close to Hg saturation when there is an increase.¹⁰ The behavior of Cd self-diffusion with respect to P_{Hg} is very similar to Hg with $D_{\text{Cd}}=0.057 \exp(-1.44 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$ in the interval 350–500 °C.¹⁰ Within this temperature interval $D_{\text{Hg}}/D_{\text{Cd}}$ lies between 1.3 and 1.7. Due to experimental uncertainty, the only safe conclusion is that $1 < D_{\text{Hg}}/D_{\text{Cd}} < 2$. Between 450 and 550 °C, using the pressure-independent D , the above data give the ratio $D_{\text{Hg}}/D_{\text{Te}}$ (Te sat) $=1.55 \times 10^3 \exp(-0.27 \text{ eV/kT})$, which takes values of 20 at 450 °C and 34 at 550 °C. These ratios are minimum values and will increase as P_{Hg} increases in changing the nonstoichiometry from Te rich to Hg rich. Similar to CdTe, it is clear that these ratios sit far outside of the limits for the vacancy-pair mechanism and thus this mechanism is unlikely to be a major contributor to self-diffusion in HgCdTe.

4. Self-diffusion in PbSe

PbSe is a IVB-VIB compound semiconductor and takes the NaCl structure. The self-diffusivities of Pb and Se, D_{Pb} and D_{Se} , respectively, have been measured by Guldi *et al.*³⁴ between 500 and 800 °C at the Pb and Se saturated composition limits. At Pb saturation, D_{Pb} (Pb sat) $=0.070 \exp(-2.07 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$ and D_{Se} (Pb sat) $=2.0 \exp(-2.30 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$ while at Se saturation, D_{Pb} (Se sat) $=1.78 \times 10^{-1} \times \exp(-1.73 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$ and D_{Se} (Se sat) $=1.50 \times 10^{-3} \times \exp(-1.41 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$. To within a factor of ~ 2 , D_{Pb} (Pb sat) $=D_{\text{Se}}$ (Pb sat), whereas the ratio D_{Pb} (Se sat)/ D_{Se} (Se sat) ranges from 0.01 at 500 °C to 0.037 at 800 °C. Of particular note is that at 800 °C, D_{Pb} (Pb sat) $=D_{\text{Pb}}$ (Se sat). These results show that the D_{Pb} (Pb sat)/ D_{Se} (Pb sat) lies well within the limits for the vacancy-pair mechanism in the NaCl structure. Below 800 °C, both D_{Pb} and D_{Se} increase with the Se partial pressure. This indicates additional self-diffusion mechanisms with associated diffusivities that increase with Se pressure so that the contribution of the vacancy-pair mechanism to the overall self-diffusivity becomes minimal. At 800 °C, however, D_{Pb} (Pb sat) $=D_{\text{Pb}}$ (Se sat). This suggests that contributions from additional mechanisms for Pb self-diffusion are now minimal across the PbSe composition range: For Se self-diffusion the additional mechanisms for D_{Se} remain dominant as D_{Se} (Se sat) $\gg D_{\text{Pb}}$ (Se sat). It is plausible that the vacancy pair is the primary mechanism for D_{Pb} from 800 °C to the melting point of PbSe.

5. Self-diffusion and percolation in the ternary mixed system

Since the theoretical analysis (Sec. II C) was couched only in terms of the binary system, it is appropriate to extend the analysis further in order to formally include the third component to cover the case of self-diffusion in HgCdTe. We first considered the mixed ternary compound (AC)B where nonmetal B has a very low mobility compared with the mobility of metal A and mobility of metal C. This attempts to

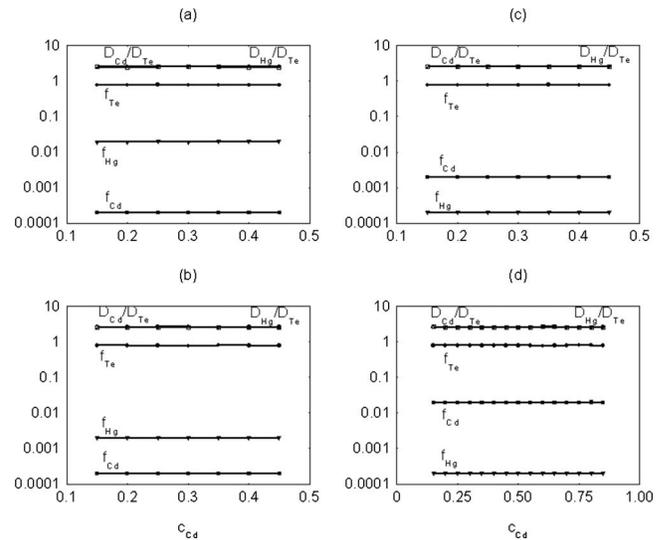


FIG. 4. Tracer correlation factors and ratios of nonmetal to metal tracer diffusion coefficients as a function of Cd composition for four cases: (a) Cd mobility two orders of magnitude lower than the Hg mobility, (b) Cd mobility an order of magnitude lower than Hg mobility, (c) Cd mobility an order of magnitude higher than the Hg mobility, and (d) Cd mobility two orders of magnitude higher than the Hg mobility. Symbols: \circ : $D_{\text{Cd}}/D_{\text{Te}}$ and \cdot : $D_{\text{Hg}}/D_{\text{Te}}$; other symbols are clearly marked.

capture the experimental situation of fast metal diffusion compared with Te diffusion in HgCdTe as discussed above. We specify that

$$(w_A, w_C) \gg w_B.$$

We consider here further two subclasses:

$$w_A > w_C, \quad w_A \approx w_C.$$

In this situation, Monte Carlo numerical simulations for all three structures show that *both* metal diffusivities D_A and D_C must follow the (upper) limiting relations with respect to the anion tracer diffusivity D_B , i.e., to be within the factor 11.2 for the CsCl structure, 5.6 for the NaCl structure, and 2.6 for the zinc blende structure. However, to further verify this, we performed a set of Monte Carlo simulations where we assigned ratios of metal mobilities from 10^{-2} to 10^2 . The ratio of the nonmetal mobility to the highest of the metal mobilities was set to be 10^{-4} . The metal sublattice composition was allowed to vary from 20% Cd to 40% Cd. The results of the computer simulations are shown in Fig. 4. We see that both ratios of metal to nonmetal tracer diffusivities are under the value of 2.6 as was predicted for the case of the binary system. The ratios of the metal self-diffusion coefficients for all cases are almost unity. This means that if the vacancy-pair mechanism operates in the zinc blende structure and the nonmetal atoms are very slow moving, then the metal atoms cannot show a self-diffusion coefficient higher than approximately double that of the nonmetal self-diffusion coefficient. It is clear that the vacancy-pair mechanism in the zinc blende structure always makes the diffusivities of metal and nonmetal extremely closely coupled.

The next question is as follows: Is it possible for nonmetal atoms to diffuse only via the vacancy-pair mechanism whereas metal atoms diffuse via the vacancy-pair mechanism

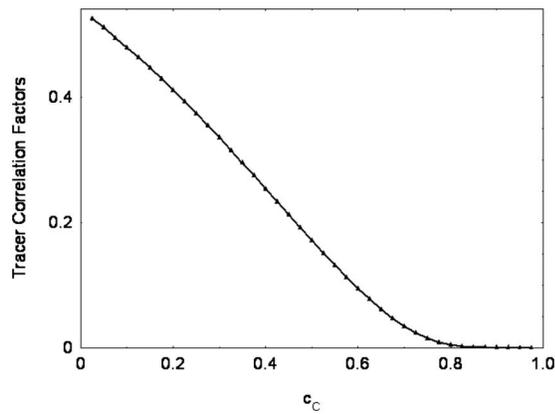


FIG. 5. Percolation behavior as reflected in the tracer correlation factor f_A for the mixed metal system in the zinc blende structure; c_C is composition of the immobile metal species. The critical value of c_C is about 0.8.

in addition to some other unrelated mechanism? (This ignores of course the experimental observation that the Te diffusivity is proportional to the inverse of the Hg partial pressure and so Te is unlikely to diffuse only via a vacancy-pair mechanism.) The answer to this question is as follows: possibly. Then for metal atoms, the contribution to the self-diffusion coefficients from the vacancy-pair mechanism will be negligible and the other mechanism will mostly contribute to the metal self-diffusion coefficients. A plausible candidate for the other mechanism is a metal interstitial-vacancy (Frenkel) pair. Detailed analysis of this diffusion mechanism is beyond the scope of the present paper.

For the sake of completeness for the mixed system, we also consider a mixed ternary compound (A,C)B where nonmetal B takes a very high mobility compared with the mobility of metal A and mobility of metal C. In this situation, we have that

$$(w_A, w_C) \ll w_B.$$

We consider further that metal A is much more mobile than metal C,

$$w_A \gg w_C.$$

In this situation, we expect a well-defined percolation behavior for metal atoms on their sublattice: There is a critical value of $c_C^c = 1 - c_A^c$ (percolation threshold) at and below which the A atoms on the metal sublattice are connected in the sense that long range diffusion (unrestricted by the smallness of w_C) of A atoms is possible. If the long range diffusion of A atoms is possible then so will the long range diffusion of B atoms. (The tracer diffusion coefficient of B, of course, must be within the range of limits defined above from the A tracer diffusion coefficient.)

In Ref. 18 it was proposed that the percolation composition thresholds c_C^c for this case will simply be the following simple geometric correlation factor f_0 for the vacancy-pair mechanism (in CsCl: $f_0 = 0.49$). Our Monte Carlo results presented in Fig. 5 (for the case of the zinc blende structure), Fig. 6 (for the case of CsCl structure), and Fig. 7 (for the case of NaCl structure) clearly show that this is not, in fact, a correct proposition. The percolation behavior (as reflected in the percolation composition thresholds c_C^c) for the

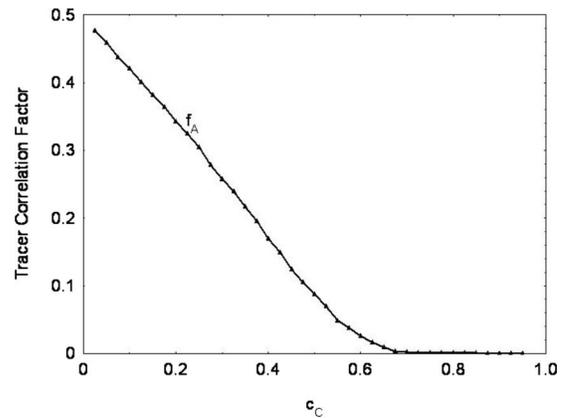


FIG. 6. Percolation behavior as reflected in the tracer correlation factor f_A for the mixed metal system in the CsCl structure; c_C is composition of the immobile metal species. The critical value of c_C is about 0.7.

vacancy-pair mechanism for the mixed metal/nonmetal compound follows f_0 for the sublattice containing the mixed atom system.

Let us further consider the results when nonmetal atoms (of one type) are very mobile (B) and one type of metal atoms (C) has a much lower mobility than the other type of metal atoms (A) (and the nonmetal atoms!): $w_C \ll w_A \ll w_B$. In this case, if the composition of the very slow moving metal atoms (C) is less than f_0 for the corresponding sublattice (fcc, fcc, and sc), there are, in fact, no limits at all for the ratio D_B/D_C ! But there will be lower limits for the ratio D_B/D_A (the factor 11.2^{-1} for the CsCl structure, 5.6^{-1} for the NaCl structure, and 2.6^{-1} for the zinc blende structure). Once the percolation threshold is reached, both ratios will have limits superimposed on them.

In Fig. 8 we present tracer correlation factors and ratios of nonmetal to metal tracer diffusion coefficients as functions of the metal atom (C) composition calculated for the case of the CsCl structure when $w_C = 10^{-2} w_A = 10^{-4} w_B$. The dashed line shows the limit of the tracer diffusion coefficients for the vacancy-pair mechanism in the CsCl structure. It is interesting to note that the ratio of D_B/D_C (the fastest diffusers to the slowest diffusers) is, in fact, outside the prescribed limits above for almost the whole range of composition c_C .

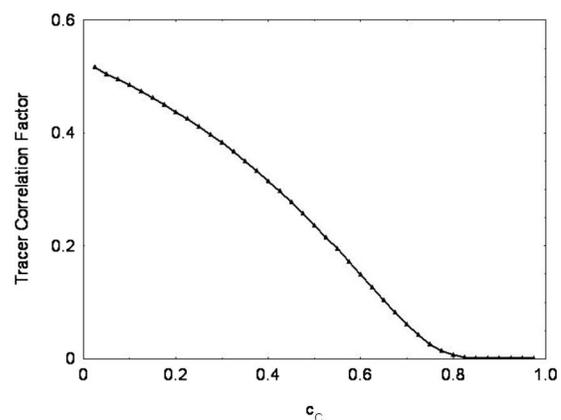


FIG. 7. Percolation behavior as reflected in the tracer correlation factor f_A for the mixed metal system in the NaCl structure; c_C is composition of the immobile metal species. The critical value of c_C is about 0.8.

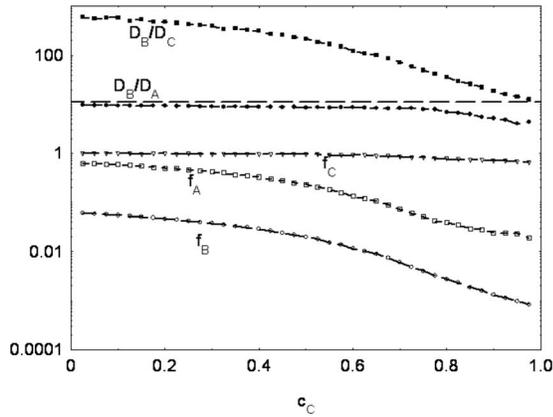


FIG. 8. Tracer correlation factors and ratios of nonmetal to metal tracer diffusion coefficients as a function of metal atom (c) composition calculated for the CsCl structure for the case when $w_A=10^{-2}w_C=10^{-4}w_B$. The dashed line shows the limit of the tracer diffusion coefficients for the vacancy-pair mechanism in the CsCl structure.

III. SUMMARY

The vacancy-pair diffusion mechanism in cubic materials was revisited with emphasis on the limits of the ratio of the tracer diffusion coefficients to demonstrate the operation of this mechanism. High precision Monte Carlo simulation was used to calculate tracer correlation factor, ratios of tracer diffusivities, and percolation effects (in mixed compounds). The three major cubic lattices—NaCl, CsCl, and zinc blende structures—were analyzed, and correct limits for the ratio of the tracer diffusivities were found to be 5.6, 11.2, and 2.6, respectively. For the case of the CsCl structure correlation factors were also redetermined using the matrix method, and good agreement with the Monte Carlo results was obtained. Self-diffusion in the compound semiconductors PbSe (NaCl structure) and InSb, GaSb, CdTe, and HgCdTe (zinc blende structure) were reanalyzed. It was shown that the vacancy-pair mechanism is unlikely to contribute to self-diffusion in CdTe and HgCdTe but it remains a valid possibility for self-diffusion in PbSe, InSb, and GaSb.

ACKNOWLEDGMENTS

This research was partially supported by the Australian Research Council.

- ¹M. Bénérière, M. Chemla, and F. Bénérière, *J. Phys. Chem. Solids* **37**, 525 (1976).
- ²F. Bénérière, *Physics of Electrolytes* (Academic, London, 1972), Chap. 6, p. 203.
- ³N. L. Peterson, *J. Nucl. Mater.* **69–70**, 3 (1978).
- ⁴J. N. Mundy, *Phys. Rev. B* **3**, 2431 (1971).
- ⁵F. Nicolas, F. Bénérière, and M. Chemla, *J. Phys. Chem. Solids* **35**, 15 (1974).
- ⁶F. Bénérière, *J. Chem. Soc., Faraday Trans.* **86**, 1151 (1990).
- ⁷I. V. Belova and G. E. Murch, *Philos. Mag.* **84**, 2139 (2004).
- ⁸I. V. Belova and G. E. Murch, *Philos. Mag.* **84**, 3637 (2004).
- ⁹H. Mehrer, *Diffusion in Solids* (Springer, New York, 2007).
- ¹⁰D. Shaw, *J. Electron. Mater.* **24**, 587 (1995).
- ¹¹D. Shaw, *J. Cryst. Growth* **86**, 778 (1988).
- ¹²K. Compaan and Y. Haven, *Trans. Faraday Soc.* **52**, 786 (1956).
- ¹³R. E. Howard, *Phys. Rev.* **144**, 650 (1966).
- ¹⁴A. D. Le Claire, in *Physical Chemistry—An Advanced Treatise*, edited by H. Eyring, D. Henderson, and W. Jost (Academic, New York, 1970), Vol. 10, p. 261.
- ¹⁵R. L. Lindström and R. Lindström, *Philos. Mag. A* **47**, 627 (1983).
- ¹⁶H. Bakker, N. A. Stolwijk, and M. A. Hoetjes-Eijkel, *Philos. Mag. A* **43**, 251 (1981).
- ¹⁷I. V. Belova and G. E. Murch, *Philos. Mag. A* **79**, 1509 (1999).
- ¹⁸I. V. Belova and G. E. Murch, *Philos. Mag. A* **79**, 2681 (1999).
- ¹⁹D. Weiler, H. Mehrer, and N. A. Stolwijk, *Philos. Mag. A* **50**, 559 (1984).
- ²⁰V. M. Vorob'ev, V. A. Murav'ev, and V. A. Panteleev, *Sov. Phys. Solid State* **23**, 653 (1981).
- ²¹A. R. Allnatt and A. B. Lidiard, *Atomic Transport in Solids* (Cambridge University Press, Cambridge, 1993).
- ²²J. Bardeen and C. Herring, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley, J. H. Hollomon, R. Maurer, and F. Seitz (Wiley, New York, 1952).
- ²³G. E. Murch, in *Diffusion in Crystalline Solids*, edited by G. E. Murch and A. S. Nowick (Academic, Orlando, FL, 1984), Chap. 7, p. 379.
- ²⁴D. L. Kendall and R. A. Huggins, *J. Appl. Phys.* **40**, 2750 (1969).
- ²⁵D. Weiler and H. Mehrer, *Philos. Mag. A* **49**, 309 (1984).
- ²⁶D. Shaw, *Semicond. Sci. Technol.* **18**, 627 (2003).
- ²⁷H. Bracht, S. P. Nichols, E. E. Haller, J. P. Siveira, and F. Briones, *J. Appl. Phys.* **89**, 5393 (2001).
- ²⁸K. Sunder and H. Bracht, *Physica B* **401–402**, 262 (2007).
- ²⁹D. Mathiot and G. Edelin, *Philos. Mag. A* **41**, 447 (1980).
- ³⁰A. V. Inyushkin, A. N. Taldenkov, A. Yu Yakubovskiy, A. V. Markov, L. Moreno-Garsia, and B. N. Sharonov, *Semicond. Sci. Technol.* **18**, 685 (2003).
- ³¹Trace Sciences International, Certificates of Analysis (2009).
- ³²D. Shaw, *J. Phys. C* **16**, L839 (1983).
- ³³D. Shaw, *Properties of Narrow Gap Cadmium-Based Compounds*, EMIS Data Review Series No. 10, edited by P. Capper (INSPEC, London, UK, 1994), p. 111.
- ³⁴R. L. Guldi, J. N. Walpole, and R. H. Rediker, *J. Appl. Phys.* **44**, 4896 (1973).