

## Original Paper

# Quantitative Interpretation of Isotope Correlation Coefficient Ratios in Solid Diffusion

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Received: November 18, 2022 Accepted: November 23, 2022 Online Published: November 23, 2022  
doi:10.22158/asir.v6n4p124 URL: <http://doi.org/10.22158/asir.v6n4p124>

### **Abstract**

*The correlation coefficient  $f$  is crucial in the calculation of the absolute diffusion coefficient  $D$ , especially for the vacancy mechanism. The current study for  $f$  is complex and contains many approximations and assumptions. However,  $f$  can be ignored when considering the isotope effect, which has only been stated qualitatively by previous authors and not explained from a quantitative perspective. In this paper, we will explain the reason why  $f$  can be neglected in the isotope diffusion effect by finding the most essential formula and source of  $f$ , as a way to save the most troublesome step in the calculation of the isotope diffusion effect.*

### **Keywords**

*Correlation coefficient, Solid diffusion, Isotope effect*

### **1. Introduction**

The correlation coefficient  $f$  is important in the solid state diffusion of crystalline materials. Diffusion is mediated by diffusion carriers, such as vacancies, vacancy pairs, etc. An equivalent statement is that at least three identifiable “species” must be involved in the diffusion process. For example, when an impurity atom diffusion through a vacancy in a crystal, the three “species” involved are the vacancy, the solvent atom and the impurity atom. There is no correlation between two successive jumps of atoms in interstitial diffusion because no diffusion carriers are involved, but there is a correlation between two successive jumps of atoms in the vacancy diffusion mechanism. The correlation effect refers to the fact that the successive jumps of particles are usually interdependent for the motion caused by defects. For example, for the vacancy mechanism, each particle can only jump by exchanging positions with its neighboring vacancies. After each successful exchange of a particle with a vacancy, the vacancy still be next to the particle, thus increasing the probability of the particle jumping in the opposite direction; in

other words, the probability of the particle jumping back to the vacancy again is maximized. If there is no correlation effect, as in the case of the interstitial mechanism, and the particle makes a random walk involving a series of independent jumps, each of which occurs independent of the previous jump, then the probability of the particle jumping toward any of the interstitial positions should be the same.

Therefore Bardeen and Herring (1952) introduced the correlation factor into the theory of solid diffusion. The correlation factor was defined as the ratio between the actual impurity diffusion coefficient ( $D_{act}$ ) and the diffusion coefficient resulting from uncorrelated random walk ( $D_{random}$ ).

$$f \equiv \frac{D_{act}}{D_{random}} \quad (1)$$

A very simple expression for the correlation factor was obtained under the assumption that only successive jumps of impurity particles are correlated and based on the simplified assumption of the particle jumps types in the lattice and symmetry of lattice. The expression is as follows (Compaan & Haven, 1956),

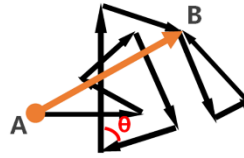
$$f = \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle} \quad (2)$$

Where  $\langle \cos \theta \rangle$  is the average angle between two consecutive jumps of the impurity atom. Equation (2) is usually applied to self-diffusion in metals and is satisfied for small vacancy concentrations and most common lattice types. Although we know that the correlation coefficient  $f$  is crucial for the study of the diffusion coefficient  $D$ , trying to calculate  $f$  exactly is complex and difficult because it is closely related to the lattice structure, with different crystal types cannot be described by a general formula. Therefore, previous authors have made approximations and assumptions based on equation (2), relying on the jump frequencies of various types of atoms in various crystal structures involved in the diffusion process to calculate it, such as the five-frequency model (Manning, 1959, 1962, 1964; Lidiard, 1955), the eight-frequency model (Manning, 1964), and the nine-frequency model (Manning, 1959).

In order to study the isotope diffusion coefficient ratio ( $D^*/D$ ), we had to firstly study the isotope correlation coefficient ratio ( $f^*/f$ ). The previous works (Van Orman & Krawczynski, 2015) can only qualitatively assume that the isotope correlation coefficient ratio can be neglected (except for H, He, where quantum effects exist), but there is no quantitative explanation. Moreover, the previous theoretical studies of correlation coefficients have too many approximates and assumptions to prove that the ratio of isotope correlation coefficients  $f^*/f$  can be neglected, so this study will search for the most essential relation of correlation coefficients from scratch to explain this phenomenon. This work saves a great deal of trouble in studying the isotope diffusion effect and lays the foundation for the subsequent work.

## 2. Quantitative Interpretation

In crystals, diffusion is the transformation process of atoms or defects (interstitial or vacancy) by thermal motion from one equilibrium position to another one, atom in the micro world can achieve macroscopic atomic migration through step by step successive jumps in the lattice (Figure 1).



**Figure 1. Schematic Diagram of the Net Displacement of the Diffusing Particle after n Disorderly Jumps in Time t**

Based on the random walk theory and the impurity atom diffusion with single vacancy mechanism, the microscopic expression of  $D$  (Mehrer, 2007) is:

$$D = a^2 \Gamma f \quad (3)$$

$a$  is lattice parameters,  $f$  is correlation coefficient, indicates the degree of atomic diffusion process deviation from pure random walk. In interstitial diffusion mechanism, there is no correlation between successive jumps,  $f = 1$ ; for vacancy diffusion mechanism, there is usually a correlation between them,  $f < 1$  (Mehrer, 2007). This study only focuses on vacancy diffusion.  $\Gamma$  is the jump rate (the impurity atom jump to the adjacent vacancy), represents the number of atom jumps ( $n$ ) per unit time ( $t$ ). For different isotopes,  $a$  are the same, so  $f$  and  $\Gamma$  are the main influencing factors of isotope diffusion coefficient ratio. The isotope diffusion coefficient ratio can be expressed as,

$$\frac{D^*}{D} = \frac{\Gamma^* f^*}{\Gamma f} \quad (4)$$

Previous study (Van Orman & Krawczynski, 2015) qualitatively believed that the effect of  $f$  for two isotopes on isotope effect was negligible (except H, He). However, there is no quantitative explanation, and in the following we will start from the initial derivation of the diffusion coefficient and give a specific expression for  $f$  in an attempt to give quantitatively its effect on the isotope effect.

Einstein (1906) and Smoluchowski (1906) almost simultaneously proposed that  $D$  is directly proportional to the mean square displacement ( $\overline{R_n^2}$ ) of the number of atom jumps ( $n$ ) in a cubic lattice (Figure 1), and inversely proportional to the diffusion time ( $t$ ).

$$D = \alpha \frac{\overline{R_n^2}}{t} \quad (5)$$

$\alpha$  is geometric correction factor. In random walk theory (Mehrer, 2007),  $\overline{R_n^2}$  can be expressed as,

$$\overline{R_n^2} = nr^2 \left( 1 + \frac{2}{n} \overline{\sum_{i=1}^{n-1} \sum_{j=1}^{n-i} \cos \theta_{i,i+j}} \right) \quad (6)$$

$r$  is the distance of each jump, and  $\theta_{i,i+j}$  is the angle between two consecutive jumps (Fig.1). Therefore,  $D$  can be expressed as,

$$D = \alpha r^2 \Gamma \left( 1 + \frac{2}{n} \overline{\sum_{i=1}^{n-1} \sum_{j=1}^{n-i} \cos \theta_{i,i+j}} \right) \quad (7)$$

When completely random,  $\overline{\sum_{i=1}^{n-1} \sum_{j=1}^{n-i} \cos \theta_{i,i+j}} = 0$ , each jump of an atom in a lattice is independent of the previous step, and

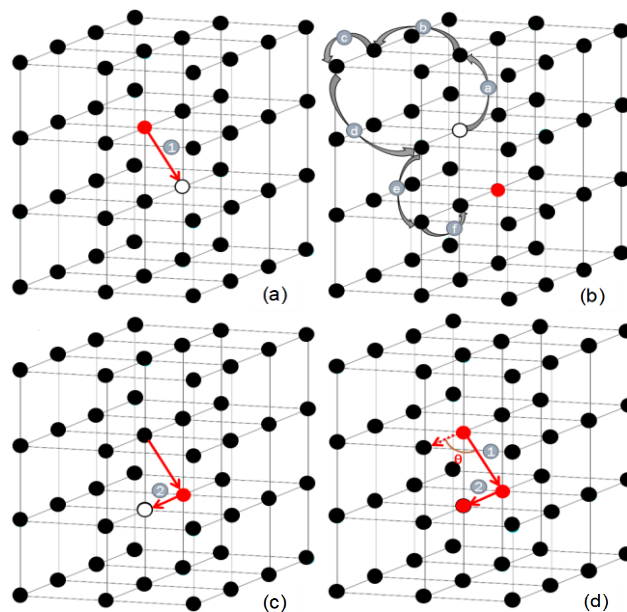
$$D = a^2 \Gamma \quad (8)$$

This is interstitial diffusion mechanism. However, successive jumps of vacancy mechanism are related,

means  $\overline{\sum_{l=1}^{n-1} \sum_{j=1}^{n-l} \cos \theta_{l,l+j}} \neq 0$ ,  $f$  can be expressed as,

$$f = 1 + \frac{2}{n} \overline{\sum_{l=1}^{n-1} \sum_{j=1}^{n-l} \cos \theta_{l,l+j}} \quad (9)$$

This is consistent with the result of Bardeen and Herring (1952). For the vacancy mechanism, when vacancy and vacancy are independent, after the impurity atom jumps into the adjacent vacancy (Figure 2a), the next jump tends to return to the original position, which means that the  $\theta$  is zero. Therefore, if the impurity atom wants to move forward it must depend on the solvent atoms exchange with the vacancy continuously and bring the vacancy adjacent to the impurity atom. There are many ways to bring the vacancy back near the impurity atom again, and only one (a~f) of them is shown in Figure 2b. When a vacancy is next to the impurity atom again, impurity can make a second jump to form a group of continuous jumps (Figure 2c, 2d).



**Figure 2. Schematic Diagram of Two Successive Jumps of an Impurity Atom in a Crystal. Black Spheres Represent Solvent Atoms, Red Spheres Represent Impurity Atom, and Hollow Spheres Represent Vacancy. (a) First Exchange of Impurity Atom with Vacancy. (b) a-f is a Possibility of Continuous Exchange of Vacancy with Solvent Atoms. (c) Second Exchange of Impurity Atom with Vacancy. (d) The Angle  $\theta$  between two Consecutive Exchanges**

Therefore, the  $\theta$  is affected by the exchange mode between the solvent atom and the vacancy, which related to the binding energy between them, which further affects the jump direction of the vacancy. However, all the above are independent of the mass of solute. So we can avoid the difficulty of calculating the absolute value of  $f$  in study of the isotope effect.

The form of solvent-vacancy exchange remains unchanged before and after impurity isotopes substitution. Neglecting the nuclear volume effect of isotopes and combining with the geometric characteristics of solids, isotopic atoms will jump into the same geometric center of mass in the

vacancy. Therefore, the  $\theta$  (Figure 2d) for isotopes are the same, the ratio  $f^*/f$  is 1 according to Eq.(9). It shows that the effect of  $f$  cannot be ignored when studying the  $D$  of vacancy diffusion, however, the effect of  $f^*/f$  is ignored when studying the isotope effect.

Thus, Equation (10) can be used to study isotope effects regardless of whether it is vacancy diffusion or interstitial diffusion.

$$\frac{D^*}{D} = \frac{\Gamma^*}{\Gamma} \quad (10)$$

This also suggests that diffusive isotope effects essentially do not change the direction of isotope diffusion, but rather greatly affect the diffusion rate, leading to isotope fractionation.

### 3. Conclusion

This paper explains that the correlation coefficient ratio  $f^*/f$  can be neglected when studying the isotope diffusion effect, either in the interstitial mechanism or vacancy mechanism, allowing us to study the isotope diffusion effect more conveniently in the next step.

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