# Small Isotope Effect of Diffusion in Disordered Structures

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The isotope effect $E$ of a single jump vacancy diffusion mechanism in statically disordered lattices is investigated by Monte Carlo simulation. It is found that $E$ decreases significantly with increasing disorder. This effect is attributed to percolation processes and ensuing reduction of the effective dimension of space for the diffusing particle.

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Isotope-effect measurements are an important touchstone used to identify a diffusion mechanism in crystalline solids [1]. Such measurements are of major importance also in exploring the mechanism of diffusion in amorphous alloys which is still an intriguing question [2].

The isotope effect is expressed by the relation [3]

$$E = (D_{A^*}/D_A - 1)/(\sqrt{m_A/m_{A^*}} - 1), \qquad (1)$$

where $m_A$ and $m_{A^*}$ are the masses of the isotopes and $D_A$ and $D_{A^*}$ are their diffusion coefficients. These are given by [4]

$$D_j = g f_j W_j, \qquad j = A, A^*,$$

where $g$ is the factor dependent on lattice geometry and defect concentration, $W_j$ are the jump rates, and $f_j$ are the correlation factors of isotopes. According to the classical theory of reaction rates the jump rates $W_j$ are proportional to $1/\sqrt{m_j}$ [5]. In the absence of correlations of atomic jumps ($f_j = 1$), the diffusion coefficients $D_j$ simply coincide with $gW_j$ and the isotope effect is equal to 1. Such a situation can occur for interstitial impurity diffusion in a crystal by the direct jump mechanism.

It has been shown that the isotope effect $E_{\mathrm{cryst}}$ for self-diffusion in crystals by a vacancy mechanism is proportional to the tracer correlation factor $f_{\mathrm{tr}}$ as $E_{\mathrm{cryst}} = f_{\mathrm{tr}} \Delta K$, where $\Delta K$ is the fraction of the translational energy which is possessed by the solute atom as it crosses the saddle point [6]. Since $\Delta K$ for the vacancy mechanism in crystals is about unity [6] in this case the isotope effect is close to the correlation factor $f_{\mathrm{tr}}$ which ranges from 0.653 in simple cubic lattice to 0.782 in face-centered crystal [4]. Contrary to diffusion in crystals it was found that the isotope effect, $E_{\mathrm{am}}$, in amorphous solids is very small, for instance $E_{\mathrm{am}} = 0.1 \pm 0.01$ was reported for Co diffusion in a CoFeNbB glass [7], $E_{\mathrm{am}} \leq 0.06$ for Co diffusion in a FeNiB glass [8], and $E_{\mathrm{am}} \leq 0.06$ for Co diffusion in a Co rich CoZr glass [9]. The similar behavior was obtained for Co diffusion in the supercooled melt of bulk metallic glass [10]. These results are usually explained by cooperative motion of atoms [2]. Simple estimations show that if an elementary act of atomic movement simultaneously involves $n$ atoms, then the magnitude of the single jump isotope effect $E$ is reduced by a factor of $1/n$ [6,11]. However, the cooperative motion of atoms is not the only possible reason for a small isotope effect.

The aim of this Letter is to show that a low isotope effect can be expected also for the ordinary single jump vacancy mechanism in statically disordered lattices which serve as models for the structure of amorphous alloys [12]. For this purpose we restrict our investigation to the calculation of the isotope effect based on a Monte Carlo (MC) simulation of the atomic jump processes. A more detailed discussion of various aspects of diffusion in disordered structures is not attempted here and can be found, i.e., in [12,13], and references therein.

We consider diffusion by means of vacancies in structures where atomic jump rates are different for various diffusion paths. For the sake of simplicity we assume a direct superposition of two models: Manning's model of diffusion in alloys [4] and a random lattice model with randomly independent atomic jump rates [12]. This disordered structure is characterized by the site coordinates $\vec{r}_{\vec{n}}$, where $\vec{n}$ enumerates the sites, and by the effective potential relief with energy levels of the atoms in sites, $G^s_{\vec{n}}$, and at the saddle points, $G^b_{\vec{n}\vec{m}}$, between sites $\vec{n}$ and $\vec{m}$. Atoms can jump only to a vacant neighboring site in their first coordination sphere. Any site contains at the most one atom. We assume that atomic jumps are thermally activated and the jump rates $W_{\vec{n}\vec{m}}$ from site $\vec{n}$ to a neighboring vacant site $\vec{m}$ have the Arrhenius form

$$W_{\vec{n}\vec{m}} = \Gamma_j \exp[-(G^b_{\vec{n}\vec{m}} - G^s_{\vec{n}})/kT], \qquad j = A, A^*. \qquad (2)$$

Here $\Gamma_j$ are the jump attempt frequencies which are different for the atoms of types $A$ and $A^*$, and $k$ and $T$ are the Boltzmann factor and the temperature, respectively. The relation (2) implies that the probability of the atom jump from the specified site depends only on the type of the atom itself and does not depend on the other neighboring atoms. We assume that magnitudes of the energy levels $G^b_{\vec{n}\vec{m}}$ and $G^s_{\vec{n}}$ are independent random variables with definite distribution densities $\rho(G)$, which we take in the form of a Gaussian distribution

$$\rho(G) = \frac{1}{\sqrt{2\pi}\,\Delta}\exp[-(G - G_0)^2/2\Delta^2], \qquad (3)$$

where $\Delta$ is the variance of the distribution and $G_0$ is the mean. The site coordinates $\vec{r}_{\vec{n}}$ and potential relief do not depend on time, i.e., it is assumed that the structure is static or "frozen."

The given definition of the diffusion problem contains three inherently different types of disorders: compositional ($\Gamma_j$), energetic ($G^b_{\vec{n}\vec{m}}, G^s_{\vec{n}}$), and dynamic ("blocking" effect). A discussion of how these affect the diffusion is given by means of an analytical bond coherent potential approximation in [14].

The main parameters of the model of a disordered structure are as follows: (1) The type of the lattice: here we consider face-centered-cubic (fcc), body-centered-cubic (bcc), and simple cubic lattices (sc). (2) The ratio $\Gamma_{A^*}/\Gamma_A$ of jump rates of the atoms of type $A^*$ and $A$: this is related to the mass ratio of atoms $A^*$ and $A$ as $(\Gamma_{A^*}/\Gamma_A - 1) = \Delta K(\sqrt{m_A/m_{A^*}} - 1)$ [1,6]. (3) The dispersion of the site energies, $\sigma_s = \Delta_s/kT$, and saddle point energies, $\sigma_b = \Delta_b/kT$. We refer to the parameters $\sigma_s$ and $\sigma_b$ as the values of random trap type disorder (RT) and random barrier type disorder (RB), respectively, according to conventional classification [12].

We calculate the random trajectories, $\vec{x}(t)$, of the atoms and the vacancy as a function of time $t$ by Monte Carlo simulation. Details of this technique are described elsewhere [15]. Time dependent diffusion coefficients, $D(t)$, of the different species are derived from

$$D(t) = \frac{1}{6}\frac{\partial}{\partial t}\langle \vec{x}^2(t)\rangle, \qquad (4)$$

where $\langle\cdots\rangle$ means ensemble averaging of trajectories. Long time asymptotic of (4) at $t \to \infty$ gives the diffusion coefficient $D$ in usual meaning.

The calculations were performed in an elementary box containing $10^5$ to $10^6$ atoms. Periodic boundary conditions were used. Every atom in the box made usually $10^4$ to $10^6$ jumps, and each run was repeated 2 to 30 times for different realizations of the energies $G^s_{\vec{n}}$ and $G^b_{\vec{n}\vec{m}}$. The overall number of atomic jumps was at least $10^9$, and at some runs exceeded $10^{12}$, yielding typical statistical errors for the diffusion coefficients of <1% at the most disordered system. Figures 1 and 2 show the dependencies of long time diffusion coefficients, $D_A$, of $A$ atoms and vacancies, $D_V$, on the values of $\sigma_b$ and $\sigma_s$ in an fcc lattice. These diffusion coefficients are normalized to the vacancy diffusion coefficient, $D_V$, at $\sigma_b = \sigma_s = 0$. For comparison the corresponding dependence of the diffusion coefficient of vacancies at small times, $D_V(t \to 0)$, is also given. These figures indicate that the correlation factor, $f_{\mathrm{corr}} = D(t \to \infty)/D(t \to 0)$ [12,13], decreases rapidly with increasing disorder $\sigma$. Since the total number of atomic jumps in a MC simulation is limited at around $10^{12}$ for practical reasons a small correlation factor poses a limit also on the magnitude of disorder, $\sigma_b$ or $\sigma_s$, to be investigated in the present simulations in order to make a statistically sound estimate. From Figs. 1 and 2 it is noted that at large $\sigma$ the long range atomic diffusion coefficients behave approximately as $D(\sigma) \sim \exp(\alpha\sigma)$, with $\alpha_b \simeq 0.7$ and $\alpha_s \simeq -0.7$ for RB and RT, respectively. On the other hand, the short range vacancy diffusion coefficient is approximately $D_V(t \to 0) \sim \exp(\sigma^2/2)$. Consequently, with increasing $\sigma$ the correlation factors decrease rapidly as $f_{\mathrm{corr}} \sim \exp(\alpha\sigma - \sigma^2/2)$. To have every atom displaced on average by more than one interatomic distance, it is therefore required that it makes more than $\exp(\sigma^2/2 - \alpha\sigma)$ jumps. Moreover, the minimum number of sites in the elementary box should be larger than $\exp(\sigma^2/2)$. Thus the total number of jumps in a MC simulation is approximately $\exp(\sigma^2) \sim 10^{12}$ which limits the values of achievable $\sigma$ to less than about 5. In the present simulations $\sigma_b \leq 5$ for RB and $\sigma_s \leq 4$ for RT were chosen.

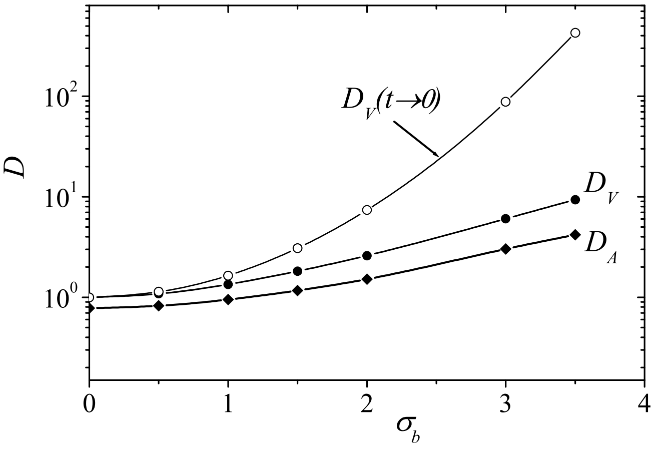

FIG. 1. Diffusion as a function of RB disorder. The diffusion coefficients are normalized to the long time diffusion coefficient $D_V$ at $\sigma = 0$.

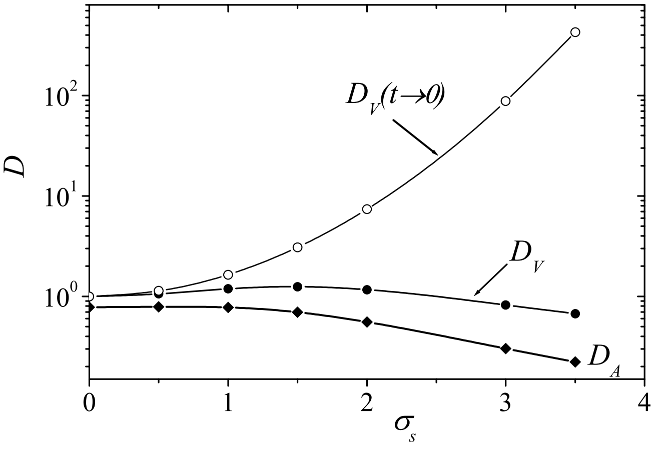

FIG. 2. Diffusion as a function of RT disorder. The diffusion coefficients are normalized in the same way as in Fig. 1.

Using the long time asymptotics of the diffusion coefficients of $A$ and $A^*$ type tracers the isotope effect was derived from the relation

$$\tilde{E} = (D_{A^*}/D_A - 1)/(\Gamma_{A^*}/\Gamma_A - 1), \qquad (5)$$

which according to $\tilde{E} = E/\Delta K$ is an upper limit to the true value $E$ of Eq. (1), since $\Delta K \leq 1$. In order to calculate the isotope effect with accuracy of better than $10^{-1}$ the ratio $\Gamma_{A^*}/\Gamma_A = 1.4$ was chosen here in accordance with earlier work [16]. Varying this ratio between 1.1 to 1.4 did not change the overall picture.

The divergence of $D_A(\sigma)$ and $D_V(\sigma)$ with increasing disorder seen in Figs. 1 and 2 indicates not only a correspondingly decreasing correlation factor but at the same time also a decreasing isotope effect. Figures 3 and 4 show the results of MC simulations of the isotope effect $\tilde{E}$ [cf. Eq. (5)] in different lattices. The isotope effect is seen to decrease faster than linear with increasing disorder $\sigma$, both for RB and RT disorders. The decrease with RT disorder appears to be stronger than with RB disorder. The isotope effect at fixed disorder is always lower in lattices with the smaller coordination number but curves for all lattices tend to converge for large $\sigma$. For RT disorder at $\sigma_s = 4$ the isotope effect of about 0.2 is found.

The decrease of the isotope effect with increasing disorder can be discussed in terms of a percolation process. By examining diffusion in a lattice with barrier disorder we note that, while the magnitude of $\sigma_b$ is growing, more and more barriers become so high that some of the diffusion paths are practically blocked forcing the long range diffusing atoms to use paths of quick diffusion which obviously form a percolation network [17,18]. The topological properties of percolation clusters are such that the number of the nearest neighboring sites available for diffusion, i.e., belonging to this cluster, is strongly reduced at the percolation threshold. The quick diffusion paths form a complete tree structure with a large number of dead-end branches. These do not contribute to long range diffusion which proceeds only along the so-called backbone [19] leading to a decrease of the effective dimensionality of the diffusion paths compared with the dimensionality of the lattice. The same reasoning as for the barrier disorder applies also for the trap disorder, since in this case the deep traps are not accessible by the vacancy and are therefore practically blocked for the diffusing atoms. Consequently, the evolution of a percolating network with increasing disorder and the related reduction of the effective dimensionality of the diffusion paths can be assumed to be the main reason of isotope effect decrease in disordered structures. Indeed, in the limit of one-dimensional diffusion via vacancy all atoms have identical diffusivities and the isotope effect equals zero.

In order to demonstrate the role of percolation in isotope effect reduction at vacancy diffusion in random structures we investigate the behavior of the isotope effect in a lattice containing sites of concentration $C_{\mathrm{trap}}$, which are considered inaccessible for vacancies, i.e., which are effectively blocked and therefore are completely excluded out of the diffusion process [13]. The distribution function $\rho(G^s)$ of energy levels is assumed to read

$$\rho(G^s) = (1 - C_{\mathrm{trap}})\delta(G^s - G_0) + C_{\mathrm{trap}}\delta(G^s - G_{\mathrm{trap}}), \qquad (6)$$

where $G_0$ is the regular energy level in site, and $G_{\mathrm{trap}} \to -\infty$ is the energy level in deep traps. Figure 5 shows the isotope effect as a function of concentration of the inaccessible sites. As is expected the isotope effect vanishes at the percolation threshold, $p_c$, of the nontrapped sites, $1 - C_{\mathrm{trap}} = p_c$, where $p_c = 0.31$, 0.25, 0.18 for sc, bcc, and fcc lattices, respectively [19]. Diffusion with a higher than $1 - p_c$ trap concentration can only occur for finite values of $(G_0 - G_{\mathrm{trap}})/kT$, when atoms in deep traps also contribute to diffusion and the second term on the right-hand side of Eq. (6) matters. Because of prohibitively long MC simulation times in this case only few data

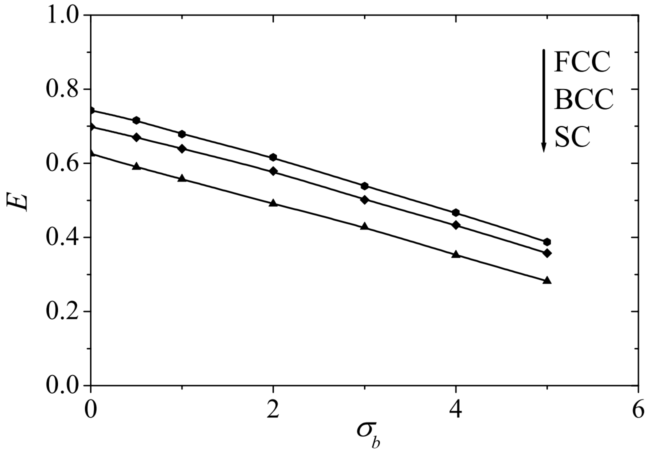

FIG. 3. Isotope effect for RB disorder in various types of lattices.

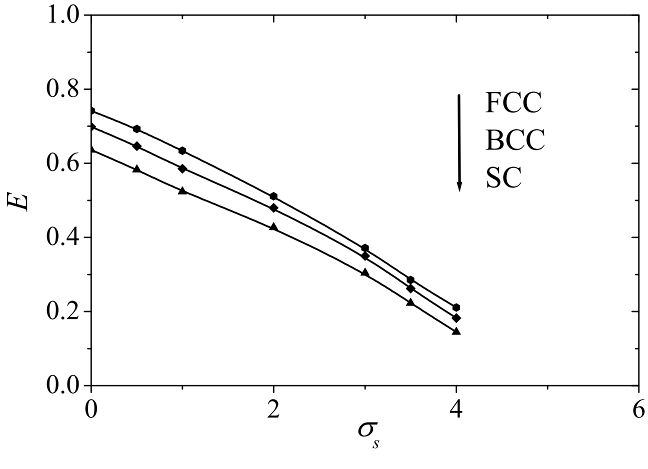

FIG. 4. Isotope effect for RT disorder in various types of lattices.

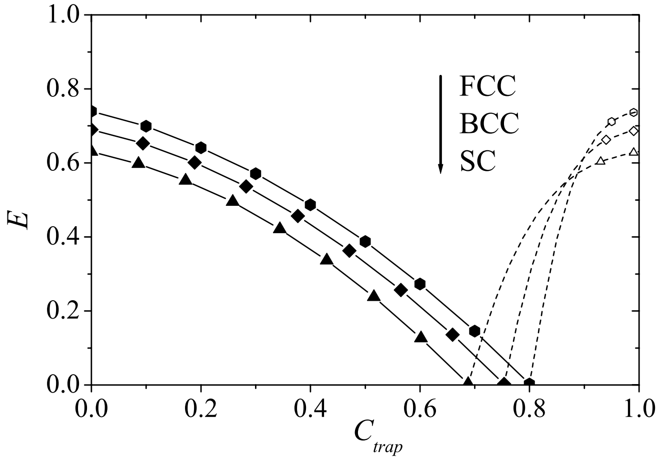

FIG. 5. Isotope effect as function of concentration of deep traps in different lattices.

points of a more surveying character were obtained. These are also given in Fig. 5 and reproduce the expected behavior for percolating systems [13].

In conclusion the present MC simulations of a single jump vacancy mechanism on a random lattice indicate that both the correlation factor and the isotope effect can become very small, depending on the degree of structural disorder. In particular for the random trap model with a Gaussian distribution of site energies it was shown that a negligible small isotope effect is observed if the dispersion of energies reaches $\sigma_s \sim 5$. We suggest that the physical reason for the low isotope effect is based on reducing the effective dimension of the space for diffusion by site blocking. The result may be described as a percolation process. In order to interpret in terms of MC simulation the isotope effects obtained experimentally in amorphous alloys, a detailed knowledge of the energy distribution of sites and saddle points in these materials is necessary which, however, is presently not available. Only as an estimate the dispersion of about 0.2 eV was deduced from measurements of the internal friction in CuZr and FeB metallic glasses [20]. According to the molecular dynamics simulation of amorphous solids, the energy distribution is close to Gaussian with variance of about 0.05–0.2 eV [21]. For this the present results would predict an isotope effect near zero at temperatures below about 500 K.

Finally we note that a heterogeneous structure, for instance the polycluster model of the amorphous solid [22], comprises low-dimensional diffusion paths so that in these structures also small correlation factors and isotope effects are expected. The stringlike atomic motions observed in the recent molecular dynamics simulations both in glass state [23,24] and in supercooled liquid state [25] confirm further the significance of low-dimensionality for diffusion in disordered media.

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