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Abstract
An exact algebraic expression is derived for the diffusivity for diffusion between interstitial e and g sites in the cubic C15 Laves phase AB$_2$ in terms of four rates of jumping between the interstitial sites. The result is for the low concentration limit of diffusing atoms and is valid for arbitrary positions of the e and g sites. The expression reduces to simple forms in some special cases. Some examples of diffusion of H in C15 intermetallic compounds are discussed.

1. Introduction

The diffusion of H in cubic C15 Laves phase intermetallic compounds AB$_2$ has been studied extensively (Skripov 2004). The H diffuses between interstitial e and g sites which are located in irregular tetrahedra of metal atoms. The diffusivity of the H can be measured by a pulsed-field-gradient nuclear magnetic resonance technique (see for example Majer *et al* 1995), and an aim in these studies is to relate the diffusivity D to the microscopic details of the H jumps. A limitation in this procedure has been the lack of a suitable theory relating the diffusivity to the rates of H jumps between the interstitial sites.

The relationship between the diffusivity and the jump rates is complicated because the structure formed by the interstitial sites is not a Bravais lattice and because there are four different rates of jumping between the sites. Some Monte Carlo simulations of the diffusivity in the C15 structure have been undertaken by Herrmann *et al* (1997), but in the absence of any rigorous theoretical framework, analysis of the experimental diffusivities of H in C15 Laves phase intermetallic compounds has used simple phenomenological models (see for example Skripov 2004). An exact expression for the diffusivity D in terms of the rates of jumping between the e and g interstitial sites in the low concentration limit is derived in this paper. The low concentration limit is often relevant to H in intermetallic compounds.

The details of the structure formed by the e and g sites is discussed in the following section. This is followed by the derivation of the general expression for the diffusivity. This expression simplifies considerably in special cases and examples of these are described and discussed in section 4.

2. Structure and jump parameters

The C15 AB_2 structure has eight formula units per cubic unit cell. The interstitial e sites are within AB_3 tetrahedra and the g sites are within A_2B_2 tetrahedra. There are also interstitial b sites within B_4 tetrahedra, but these do not appear to be occupied by H in intermetallic compounds and will not be considered. There are twelve g sites and four e sites per formula unit. It is convenient in the theory in the next section to use a primitive unit cell that contains 2 formula units, 8 e sites and 24 g sites.

The positions of the e sites involve a parameter X_e and the positions of the g sites involve parameters X_g and Z_g (Hahn 1989, space group no. 227). There are ideal values of these parameters which correspond to the close packing of spheres: $X_e = 1/4$, $X_g = 1/16$ and $Z_g = 7/8$. The e sites form a face-centred-cubic structure with half the AB_2 lattice parameter for the ideal value of X_e.

The g sites form linked hexagonal structures. Each g site has two neighbours on a hexagon and one g site neighbour on an adjacent hexagon. A g site also has one neighbouring e site. An e site has three neighbouring g sites which are each on different hexagons. A diagram of the structure of the e and g sites for the ideal structural parameters has been given by Eberle *et al* (2002) and reproduced by Skripov (2004).

Diffusing atoms have jump frequencies Γ_1 from an e site to a particular neighbouring g site, Γ_2 from a g site to a neighbouring e site, Γ_3 from a g site to a particular neighbouring g site within a hexagon and Γ_4 from a g site to a neighbouring g site on an adjacent hexagon. The probabilities c_e and c_g of occupation of e and g sites are determined by the principle of detailed balance and the rates of jumping Γ_1 and Γ_2 between the e and g sites so that $c_e\Gamma_1 = c_g\Gamma_2$. It will be assumed that the occupation probabilities are normalized to one atom per unit cell so that $8(c_e + 3c_g) = 1$ and therefore

$$c_e = \frac{\Gamma_2}{8(3\Gamma_1 + \Gamma_2)} \qquad c_g = \frac{\Gamma_1}{8(3\Gamma_1 + \Gamma_2)}. \tag{1}$$

Direct atom jumps between neighbouring e sites do not appear to occur (Skripov 2004) and have not been included in the diffusion model.

3. Diffusivity

The diffusivity D is defined by

$$D = \frac{\langle R^2 \rangle}{6t} \tag{2}$$

where $\langle R^2 \rangle$ is the mean square displacement of an atom in a long time t. One approach to evaluating D is to write the displacement $\mathbf{R}$ of an atom as $\mathbf{R} = \mathbf{R}_1 + \mathbf{R}_2 + \cdots + \mathbf{R}_n$ for a sequence of n steps in a time t (see for example Allnatt and Lidiard 1993). If the cross-terms $\mathbf{R}_i \cdot \mathbf{R}_j$ $(i \neq j)$ in $\langle R^2 \rangle$ average to zero, the diffusivity can be written as

$$D_{av} = \frac{1}{6} \sum_k r_k^2 c_k \Gamma_k n_k \tag{3}$$

where r_k is the length of a jump of type k, c_k is the probability of an atom at a site of type k, Γ_k is a rate of jumping from a site of type k and n_k is the number of these jump paths from the site. For diffusion between the e and g sites for the ideal e and g parameters in the C15 structure, equation (3) has the simple form

$$D_{av} = \frac{a^2}{128} \frac{\Gamma_1(3\Gamma_2 + 3\Gamma_3 + 2\Gamma_4)}{3\Gamma_1 + \Gamma_2}, \tag{4}$$

where a is the cubic lattice parameter and the expressions for c_e and c_g in equation (1) have been used. The cross-terms average to zero, however, only if there is sufficient symmetry and this is not the case for diffusion between the e and g sites in general.

A general practical method for calculating D for diffusion between sites in complex unit cells has been described by Braun and Sholl (1998). The following is an outline of the procedure. The sites within a unit cell are labelled $\alpha = 1, \ldots, s$ and $\gamma_{\mathbf{l},\alpha;\mathbf{l}_0,\alpha_0}$ are the rates of jumping from site α_0 in the unit cell $\mathbf{l}_0$ to site α in the unit cell $\mathbf{l}$. A square matrix $\mathbf{\Lambda}(\mathbf{k})$ of dimension s is defined by

$$\Lambda_{\alpha,\alpha_0}(\mathbf{k}) = (c_{\alpha_0}/c_\alpha)^{1/2} \sum_{\mathbf{l}} \exp[\mathrm{i}\mathbf{k} \cdot (\mathbf{l} - \mathbf{l}_0)] \left[\delta_{\mathbf{l},\mathbf{l}_0}\delta_{\alpha,\alpha_0} \sum_{\mathbf{l}',\alpha'} \gamma_{\mathbf{l}',\alpha';\mathbf{l}_0,\alpha_0} - \gamma_{\mathbf{l},\alpha;\mathbf{l}_0,\alpha_0} \right] \tag{5}$$

where c_α is the equilibrium occupation probability of site α normalized to one atom per unit cell. The site $\mathbf{l}_0$ may be chosen arbitrarily because of translational symmetry. Matrices $\mathbf{\Lambda}_0$, $\mathbf{\Lambda}_1$ and $\mathbf{\Lambda}_2$ are then constructed which are defined by

$$\mathbf{\Lambda}_0 = \lim_{\mathbf{k}\to 0} \mathbf{\Lambda}(\mathbf{k}), \qquad \mathbf{\Lambda}_1 = \lim_{\mathbf{k}\to 0} \frac{\partial}{\partial k_x}\mathbf{\Lambda}(\mathbf{k}), \qquad \mathbf{\Lambda}_2(\mathbf{k}) = \lim_{\mathbf{k}\to 0} \frac{\partial^2}{\partial k_x^2}\mathbf{\Lambda}(\mathbf{k}). \tag{6}$$

An s-dimensional vector $\mathbf{v}_0$ is defined by $(\mathbf{v}_0)_\alpha = c_\alpha^{1/2}$ and a vector $\mathbf{v}_1$ is the solution of the set of s linear equations

$$\mathbf{\Lambda}_0 \mathbf{v}_1 = -\mathbf{\Lambda}_1 \mathbf{v}_0. \tag{7}$$

The determinant of $\mathbf{\Lambda}_0$ is zero so that one of the components of $\mathbf{v}_1$ may be chosen arbitrarily and $s - 1$ of the equations (7) solved for the other linearly independent components. For isotropic diffusion the diffusivity D is finally calculated from

$$D = \mathbf{v}_0^* \mathbf{\Lambda}_1 \mathbf{v}_1 + \tfrac{1}{2}\mathbf{v}_0^* \mathbf{\Lambda}_2 \mathbf{v}_0. \tag{8}$$

The evaluation of the second term in equation (8) is straightforward, but an analytic solution of the linear equations (7) can be formidable for a large number s of sites per unit cell. For e and g sites in the C15 structure $s = 32$ and so it is necessary to solve a system of 31 linear equations involving the jump rates Γ_α ($\alpha = 1, 4$) if the occupation probabilities c_α are expressed in terms of Γ_1 and Γ_2 using equation (1). An analytic solution of these equations was achieved with the assistance of a computer algebra package. The final result is

$$\begin{aligned}
D = \frac{a^2\Gamma_1}{32(\Gamma_2 + 3\Gamma_1)} \Bigg\{ & 4\Gamma_4(1 - \Gamma_1/\Gamma_2) + 3\Gamma_2 - 5\Gamma_1 \\
& + \frac{[\Gamma_2(\Gamma_3 + \Gamma_1) + 3\Gamma_3\Gamma_1](4\Gamma_4 + 5\Gamma_2) + \Gamma_2^2(2\Gamma_4 - 10\Gamma_3 - 3\Gamma_2)}{\Gamma_2(\Gamma_2 + 3\Gamma_3)} \\
& - \frac{2\Gamma_4(8\Gamma_3\Gamma_4 + 5\Gamma_3^2 + 2\Gamma_2\Gamma_3 + 3\Gamma_2\Gamma_4)}{(\Gamma_2 + 3\Gamma_3)(\Gamma_3 + \Gamma_4)} \Bigg\}.
\end{aligned} \tag{9}$$

This expression is valid for arbitrary values of the positional parameters that determine the location of the e and g sites within the unit cell. This is because the input to the above calculations involves only the lattice parameter a and the rates of jumping between the sites. The distances between the interstitial sites are not used. The distances between the sites will physically influence the jump rates, but it is the jump rates and the network connections within the system and between unit cells that determine the diffusivity. The expression (3) for D_{av} does depend on the distances between the sites, as does the contribution to D from the cross-terms in this method. The combination of these terms would be independent of the relative distances between the sites.

In cases such as diffusion of H in intermetallic compounds the complicated expression (9) is likely to simplify because of significant differences in the magnitudes of some of the jump rates. Some special cases are considered in the following section.

4. Special cases

4.1. No jumps within hexagons

If $\Gamma_3 = 0$ jumps within hexagons are excluded. In this limit, expression (9) gives $D = 0$ and long range diffusion cannot occur. In this case, jumps can occur between adjacent hexagons and back and forth between neighbouring e and g sites, but jumps within hexagons are necessary for an atom to escape its local environment.

4.2. Only g site occupation

In the limit $\Gamma_2 \to 0$ the rate of jumping from g to e sites becomes negligible, $c_e \to 0$, and the diffusion occurs only between g sites. Taking this limit in the expression (9) gives

$$D = \frac{a^2}{48} \frac{1}{\Gamma_3^{-1} + \Gamma_4^{-1}}. \tag{10}$$

This result is similar in form to the diffusivity for a one-dimensional lattice (Kehr *et al* 1978, Braun and Sholl 1998) for which $D = a^2\Gamma$ where Γ^{-1} is the residence time averaged over all of the sites. In these cases the diffusivity becomes zero if any of the jump rates are zero. For diffusion between the g sites this corresponds physically to long range diffusion requiring jumps both within and between hexagons and the slower of these jump rates is the rate limiting step for diffusion.

The results of the low concentration Monte Carlo simulations of Herrmann *et al* (1997) for diffusion between g sites are consistent with equation (10). These authors analysed their Monte Carlo data in terms of an expression for D that is equivalent to equation (4) multiplied by a factor they called a 'correlation factor' g. Equating this form for D to equation (10) enables their factor g to be obtained. The results as a function of Γ_3/Γ_4 agree with their graphical values of g.

The expression (10) provides a straightforward method for fitting low concentration H diffusion data in C15 intermetallic compounds where only g sites are occupied. An example is provided by TaV_2H_x. The H diffusivity has been measured as a function of temperature for $x = 1.24$ and is close to the Arrhenius form in the temperature range 334–484 K (Majer *et al* 1995). A fit of the diffusion data to an Arrhenius expression gave a prefactor $D_0 = 2.75 \times 10^{-8}$ m^2 s^{-1} and an activation energy of $E = 0.267$ eV. Spin–lattice relaxation rates of H in this system show two peaks as a function of temperature and the high temperature peak has been associated with the slower jumps between the hexagons (Skripov 2004). It was deduced that the H occupy g sites only and jumps within hexagons (Γ_3) are much faster than jumps between hexagons (Γ_4) in this temperature range. Analysis of the low H concentration spin relaxation data ($x = 0.06$) gave the prefactor of these jump rates as 3.8×10^{11} s^{-1} and an activation energy of 0.22 eV (Buzlukov and Skripov 2004). These parameters can also be deduced directly from the diffusion data using equation (10). This expression becomes $D = a^2\Gamma_4/48$ since the slower jump rate will dominate when the jump rates are significantly different. Using $a = 7.160$ Å (Buzlukov and Skripov 2004) the value of Γ_4 deduced from the diffusivity fit has a prefactor 2.57×10^{12} s^{-1} and an activation energy 0.267 eV. The jump rate Γ_4 for $x = 1.24$ deduced from the diffusion data is therefore similar to the rate obtained

from the relaxation data for $x = 0.06$ and supports the interpretation of the high temperature relaxation peak as being due to the slower rate of jumping between hexagons.

4.3. All g jump rates the same

The case $\Gamma_2 = \Gamma_3 = \Gamma_4$ corresponds to the same rate of jumping from a g site to a neighbouring e site as to neighbouring g sites, both within a hexagon and on an adjacent hexagon. The expression (9) for D in this case becomes

$$D = \frac{a^2}{48} \frac{1}{\Gamma_2^{-1} + (3\Gamma_1)^{-1}}. \tag{11}$$

It is interesting that the approximate expression (4) for D_{av} for the ideal e and g structural parameters also reduces to the same result. Therefore if the rates of jumping from a g site are similar in magnitude, the expression D_{av} is likely to be a reasonable approximation.

An example is provided by H diffusion in HfTi$_2$H$_x$. The H diffusion and spin relaxation data for this system have been analysed by Bhatia *et al* (2004) to obtain the jump rates Γ_α, which were assumed to be of Arrhenius form. The diffusivity D was calculated by a numerical evaluation of equation (8) in this work. For the deduced jump rate prefactors and activation energies, the jump frequencies Γ_2, Γ_3 and Γ_4 differ by less than 50% for $1000/T \sim 2.7$. The numerical values of D from equations (8) and (11) are very similar in this temperature regime in agreement with the above theory.

4.4. Mainly e site occupation

If $\Gamma_1 \ll \Gamma_2$ the occupation probability of the e sites is much greater than for the g sites. This condition alone does not lead to a significant simplification of the general expression for D; however, if in addition $\Gamma_3 \ll \Gamma_4$, then

$$D = \frac{a^2 \Gamma_1}{48} \left(1 + \frac{\Gamma_2}{3\Gamma_3} \right)^{-1}. \tag{12}$$

A special cases of this result is that if $\Gamma_2 \ll \Gamma_3 \ll \Gamma_4$ then $D = a^2 \Gamma_1/48$ so that the diffusion is determined simply by the e to g jump rate. Another special case is that if $\Gamma_3 \ll$ both Γ_2 and Γ_4 then $D = (a^2/16)\Gamma_1\Gamma_3/\Gamma_2$. In both of these cases the diffusivity would have Arrhenius form if the individual jump rates were of Arrhenius form.

5. Conclusion

A general algebraic expression has been derived for the diffusivity D of diffusion between interstitial e and g sites in the cubic Laves phase C15 structure in the low concentration limit. The result is valid for arbitrary positions of the e and g sites.

The general result is a complicated combination of the four rates of jumping between interstitial sites. The diffusivity will not necessarily be of Arrhenius form if the individual jump rates are of Arrhenius form. There are, however, a number of special cases for which the general expression for D simplifies considerably. These results can produce a quite direct method of analysing diffusion data for H in intermetallic compounds to obtain some of the H jump rates in such cases.

Spatial correlation effects due to the blocking of some attempted jumps and consequent correlations between successive jumps will be relevant at higher concentrations of the diffusing particles. The low concentration limit results are, however, likely to be a good approximation for many cases of H in C15 intermetallic compounds.

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