diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Diffusion between interstitial sites in the hexagonal C14 AB_2 structure

C A Sholl

Physics and Electronics, University of New England
Armidale, NSW 2351, Australia
Email: csholl@metz.une.edu.au

Abstract

An exact algebraic expression is derived for the diffusivity of H between interstitial sites in the hexagonal C14 AB_2 structure in terms of the jump rates between the sites. The expression is valid in the low concentration limit. The theory is applied to obtaining H jump rates from diffusivity data for $ZrCr_2H_x$.

Keywords: Diffusion, diffusivity, hydrogen, C14 structure.

1. Introduction

Measurements of the diffusivity D of H between interstitial sites in metals requires a theory that relates D to the jump rates between sites in order to deduce microscopic details of the jumps from the measured D. An analytic expression for D in terms of the jump rates has recently been obtained, in the low concentration limit, for diffusion between the e and g interstitial sites in the cubic C15 Laves phase AB_2 structure [1]. The method used was a matrix procedure which requires the solution of a set of linear equations [2]. The number of equations in the set is equal to the number of interstitial sites in the unit cell, which is 24 for the C15 structure. The large amount of algebra involved can be solved by using a computer algebra package.

The present work applies this method to diffusion between interstitial sites in the more complicated hexagonal C14 AB_2 structure for which there are 48 interstitial sites per unit cell and eight jump rates between the sites.

2. Diffusivity

It is assumed that H occupy interstitial h (two sets), k and l sites which together form two types of linked hexagons [3]. The spatial arrangement of these sites in the C14 structure is shown in reference [3]. The jump rates between these sites are defined as: Γ_1 (h_1 to h_2 within type I hexagons), Γ_2 (h_2 to h_1 within type I hexagons), Γ_3 (l to l within type II hexagons), Γ_4 (k to l within type II hexagons), Γ_5 (l to k within type II hexagons), Γ_6 (h_1 to k between type I and type II hexagons), Γ_7 (k to h_1 between type I and type II hexagons) and Γ_8 (l to l between type II hexagons). The principle of detailed balance is used to calculate the relative probabilities of occupation of the h_1, h_2, k and l sites. Using the methods of references [1] and [2], the components of the diffusion tensor perpendicular and parallel to the c axis are given by the expressions

$$D_{xx} = \frac{a^2\Gamma_2\Gamma_4\Gamma_5\Gamma_6\left\{\Gamma_8\left[\Gamma_1\Gamma_7(3\Gamma_5 + 2\Gamma_3) + \Gamma_3\Gamma_4(3\Gamma_1 + 4\Gamma_6)\right] + \Gamma_1\Gamma_3\Gamma_5\Gamma_7\right\}}{XY}$$

$$D_{zz} = \frac{c^2\Gamma_2\Gamma_3\Gamma_4\Gamma_5\Gamma_6\Gamma_7}{2A\left[4\Gamma_3\Gamma_4 + \Gamma_5\Gamma_7 + 2\Gamma_3\Gamma_7)\right]}$$

where a and c are the hexagonal lattice parameters, and X and Y are

$$X = \Gamma_5\Gamma_7(\Gamma_1 + \Gamma_2) + 2\Gamma_2\Gamma_6(\Gamma_5 + 2\Gamma_4)$$

$$Y = \Gamma_4(3\Gamma_1 + 4\Gamma_6)(2\Gamma_3\Gamma_8 + 4\Gamma_3\Gamma_5 + 3\Gamma_5\Gamma_8) + 3\Gamma_1\Gamma_7\left\{\Gamma_8(\Gamma_3 + 2\Gamma_5) + \Gamma_5(2\Gamma_3 + \Gamma_5)\right\}.$$

The location of the h, k and l sites in the unit cell involve positional parameters but the above expressions are independent of these values as described in [1].

The above complicated expressions for the diffusivity can simplify appreciably in particular cases. For example, if all jumps within hexagons are assumed to be the same ($\Gamma_1 = \Gamma_2 = \Gamma_3 = \Gamma_4 = \Gamma_5$) and all jumps between hexagons are assumed to be the same ($\Gamma_6 = \Gamma_7 = \Gamma_8$), then

$$D_{xx} = \frac{a^2\Gamma_1\Gamma_6(4\Gamma_1 + 9\Gamma_6)}{8\left(12\Gamma_1^2 + 40\Gamma_1\Gamma_1 + 29\Gamma_6^2\right)}, \quad D_{zz} = \frac{c^2\Gamma_1\Gamma_6}{16\left(4\Gamma_1 + 3\Gamma_6\right)}.$$

If, in addition, jumps within hexagons are much faster than jumps between hexagons ($\Gamma_1 >> \Gamma_6$) then the diffusion is limited by the slower jumps between hexagons and $D_{xx} = a^2\Gamma_6/24$ and $D_{zz} = c^2\Gamma_6/64$. For the ideal axial ratio $c^2/a^2 = 8/3$ these diffusivity components are identical and the diffusion is isotropic. The reverse case of $\Gamma_1 << \Gamma_6$ gives $D_{xx} = 9a^2\Gamma_1/232$ and $D_{zz} = c^2\Gamma_1/48$ with the diffusion limited by the slower jumps within hexagons. The diffusion is not isotropic for the ideal axial ratio in this case.

An example of diffusion in the C14 structure is the diffusion of H in $ZrCr_2H_x$. The diffusivity of H in hexagonal C14 $ZrCr_2H_{0.4}$ has been measured by pulsed-field-gradient nuclear magnetic resonance for temperatures between 131 and 445K [4,5]. Departure from high temperature Arrhenius behaviour was observed below about 200K. The H diffusion has also been studied by quasielastic neutron scattering [3]. The diffusion data was analysed in references [3] and [4] in terms of rapid jumps of H within hexagons (Γ_1), and slower jumps between hexagons (Γ_6) and by using a simple diffusion model. The present theory provides a more rigorous approach. Fitting the high temperature diffusivity data [5] using the two frequency model (Γ_1 and Γ_6) and the above expressions for D for $\Gamma_1 >> \Gamma_6$, and assuming Γ_6 is of Arrhenius form, gives a prefactor for Γ_6 of 2.7×10^{12} s^{-1} and an activation energy of 0.174 eV.

The low temperature diffusivity data shows a departure from Arrhenius form and so the low temperature region cannot be analysed in a similar manner. The curvature in the Arrhenius plot has been attributed to quantum diffusion effects at low temperatures [4]. This is supported by recent theoretical calculations, using Density Functional Theory, of H jump rates and diffusion in the cubic phase C15 $ZrCr_2Hx$ [6]. The diffusivity in the C15 phase also shows non-Arrhenius behaviour at low temperatures and the calculations in [6] show clearly that this is a result of quantum effects.

3. Conclusion

The anisotropic diffusivity tensor for diffusion between interstitial sites in the hexagonal C14 structure has been calculated in terms of the jump rates by the matrix method of [2] combined with a computer algebra package. The method can provide exact analytic results for *D* in the low concentration limit for quite complicated structures. The approach could also be applied to other systems and provides rigorous analytic expressions that can be used to relate diffusivity data to the microscopic details of the jump rates between interstitial sites.

References

[1] C.A. Sholl, J. Phys.: Condens. Matter **17** (2005) 1-6.

[2] O.M. Braun and C.A. Sholl, Phys. Rev. B**58** (1998) 14870-14879.

[3] A.V. Skripov, M. Pionke, O. Randl and R. Hempelmann, J. Phys.: Condens. Matter **11** (1999) 1489-1502.

[4] W. Renz, G. Majer, A.V. Skripov and A. Seeger, J. Phys.: Condens. Matter **6** (1994) 6367-6374.

[5] G. Majer, W. Renz, A. Seeger, R.G. Barnes, J. Shinar and A.V. Skripov, J. Alloys and Componds **231** (1995) 220-225.

[6] Bhatia B and Sholl D S, Phys. Rev. B (2005) (submitted for publication)