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Diffusion between Interstitial Sites in the Hexagonal C14 AB_2 Structure

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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 [2] combined with a computer algebra package. The present work applies this method to diffusion between interstitial sites in the hexagonal C14 AB_2 structure.

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). Using the principle of detailed balance and the methods of [1,2], the components of the diffusion tensor perpendicular and parallel to the c axis are

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

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

where a and c are the lattice parameters and

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

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

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 in [1]).

The above expressions for the diffusivity can simplify appreciably in particular cases. For example, if all jumps within hexagons are assumed to be the same (Γ_1= Γ_2= Γ_3= Γ_4= Γ_5) and all jumps between hexagons assumed to be the same (Γ_6= Γ_7= Γ_8), then

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

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 diffusion of H in $ZrCr_2H_x$. The diffusivity of H in 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 in [3,4] was analysed 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 above theory provides a more rigorous approach. Fitting the high temperature diffusivity data [5] using the two frequency model 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. It has been argued [3] that the low temperature departure from Arrhenius form for D is a consequence of quantum diffusion and so the low temperature data cannot be analysed in a similar manner.

3. Conclusion

The results obtained for the diffusivity between interstitial sites in the hexagonal C14 structure show that the method of [2] combined with a computer algebra package can provide analytic results for D in the low concentration limit for quite complicated structures. The method could also be applied to other systems and provides rigorous analytic expressions that can be used to analyse diffusion data.

References

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