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Monte Carlo simulation of hydrogen diffusion in C15 Laves phase intermetallic compounds

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Abstract

We present preliminary results from Monte Carlo simulations of hydrogen diffusion in C15 Laves phase compounds. The incoherent quasi-elastic neutron scattering function, $S_{\mathrm{inc}}(\mathbf{Q}, \omega)$, is evaluated for the case of non-interacting particles diffusing on g-sites and is compared to the analytical model proposed by Rowe et al. [J.M. Rowe, K. Sköld, H.E. Flotow, J. Phys. Chem. Solids 32 (1971) 41–54]. A good level of agreement, at low **Q**, is obtained when the tracer correlation factor is accounted for. A value of 0.00238 Å^2 per Monte Carlo cycle is obtained for the tracer diffusion coefficient. A brief discussion of the extension of this simple model to include metal hydrogen interactions is also given.

Keywords: Monte-Carlo; IQENS; Laves phase; Diffusion

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1. Introduction

Recent interest in cubic C15 Laves phase intermetallic compounds has been stimulated by their ability to absorb large amounts of hydrogen at ambient temperatures, making them ideal candidates for hydrogen storage compounds. A detailed knowledge of the diffusion mechanism at a microscopic level is essential for an understanding of the absorption properties and hydrogen capacities. Incoherent quasi-elastic neutron scattering (IQENS) provides a means of simultaneously probing the temporal and spatial evolution of the microscopic tracer diffusion. Several metal hydride systems have previously been studied via Monte Carlo simulation of the IQENS, for example NbH_x [2]. The general method involves extracting the self correlation function, $G_s(\mathbf{r}, t)$, from simulation. $G_s(\mathbf{r}, t)$ is the probability of finding an atom at a distance **r** from an arbitrary origin at time *t*, given that the same atom commenced its diffusion from that origin. $G_s(\mathbf{r}, t)$ is then Fourier transformed in both time and space to give the IQENS function, $S_{\mathrm{inc}}(\mathbf{Q}, \omega)$. This model is then used in conjunction with an experimentally obtained scattering function to yield values for the jump lengths, residence times, diffusion coefficient and so on. $S_{\mathrm{inc}}(\mathbf{Q}, \omega)$ is, in general, Lorenzian in form and is usually evaluated by examining the variation of the full width at half maximum (FWHM) as a function of **Q**. We have extended these ideas to the case of C15 Laves phase materials, where both the site energies and the shape of the potential along the diffusion paths are modelled as parameters.

2. C15 Laves phase compounds

C15 Laves phase intermetallic compounds have the space group Fd3m and, in general, the atomic formula AB_2, where A and B are early transition metals. In these materials, there are three types of tetrahedrally co-ordinated interstitial site available for hydrogen occupation, namely, in Wycoff notation, the 96g site (formed by 2A and 2B atoms), the 32e site (1A and 3B) and the 8b site (4B). In the materials considered in this work, the g sites have the lowest energy, and are the first to be occupied upon hydrogenation; at higher concentrations it is possible for e sites to become populated. The b sites are not considered here, since it is believed that they remain unoccupied at the concentrations and temperatures under consideration. Ref. [3] contains a comprehensive review of the site occupancies in cubic C15 materials.

In the C15 structure, the g sites are arranged into groups of six, each forming a hexagon. A hydrogen atom in a g site has four possible diffusion paths: Two lead to g sites on the same hexagon (g–g) at a distance of 0.153*a* (*a* being the lattice parameter), one to a g site on a neigh-

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bouring hexagon (g–g′) at 0.1768*a* and one to an e site (g–e) at 0.1624*a*. Hydrogen at an e site is able to diffuse to its three nearest neighbour g sites. The shape of the potential along the g–g and g–g′ paths is, in general, different. This can result in localised diffusion of hydrogen around g sites on a hexagon at low temperature [4].

3. Results

Simulations have been performed for a system of non-interacting particles, with diffusion limited to g sites. This case corresponds to low concentration in systems such as $ZrCr_2H_x$ and HfV_2H_x, where only g sites are occupied [3]. At ambient temperatures, there is believed to be an indiscernible difference in the jump rates along g–g and g–g′ paths, so in our model we have used equal transition probabilities. Fig. 1a shows the FWHM, $\Gamma(\mathbf{Q})$, of the scattering function along the [100] direction, for $c=0.1$. Chudley and Elliott [5] proposed a model for the IQENS from atoms diffusing by jumps to nearest neighbours on a Bravais lattice. This was based on a system of partial differential equations which describe the time evolution of $G_s(\mathbf{r}, t)$. Rowe et al. [1] extended this formalism to deal with jumps on a non-Bravais lattice and with equal residence times on each site (as is the case here). We have applied this method to the case of diffusion on g sites in C15, the details of which will be published at a later date. The resulting curve is shown in Fig. 1a. The model is only valid in the limit $c \rightarrow 0$; for finite concentrations, the tracer correlation factor, f_t, has to be accounted for (see Ref. [6] for a discussion of f_t). In practice, the only way of obtaining values for f_t is by Monte Carlo simulation. We have evaluated f_t for $c=0.1$ and obtained a value of 0.78.

As can bee seen from Fig. 1a, there is a good level of agreement between $\Gamma(\mathbf{Q})$ from Monte Carlo and the model of Rowe, at low **Q**, when the tracer correlation factor is taken into account. This region corresponds to length scales which are large compared with the individual jump distances, i.e. long-range diffusion is being probed. The two expressions diverge slightly at higher values of **Q**, in the regime of the discrete jump lengths. The results follow the expected D_tQ^2 relationship at low Q (D_t is the tracer diffusion coefficient), as can be seen from Fig. 1b. From the gradient of the line of best fit, a value for D_t of 0.00238 $Å^2$ per Monte Carlo cycle is obtained. As an example of the kind of comparison that can be made with experimentally observed data, this can be compared with a value of $D_t=8.06\times10^{-12}$ m^2 s^{-1} obtained for $HfV_2H_{0.3}$ at 295 K [7]. The lattice parameter of this intermetallic hydride is 7.389 Å. If we apply this to the Monte Carlo results (which were simulated for $a=1$ Å) a value of $D_t=1.2994\times10^{-21}$ m^2 per Monte Carlo cycle is obtained. A Monte Carlo cycle is completed when each atom in the system has attempted to jump once, on average. This can be related to the classical attempt frequency, and yields a value $\Gamma=6.2\times10^9$ s^{-1}.

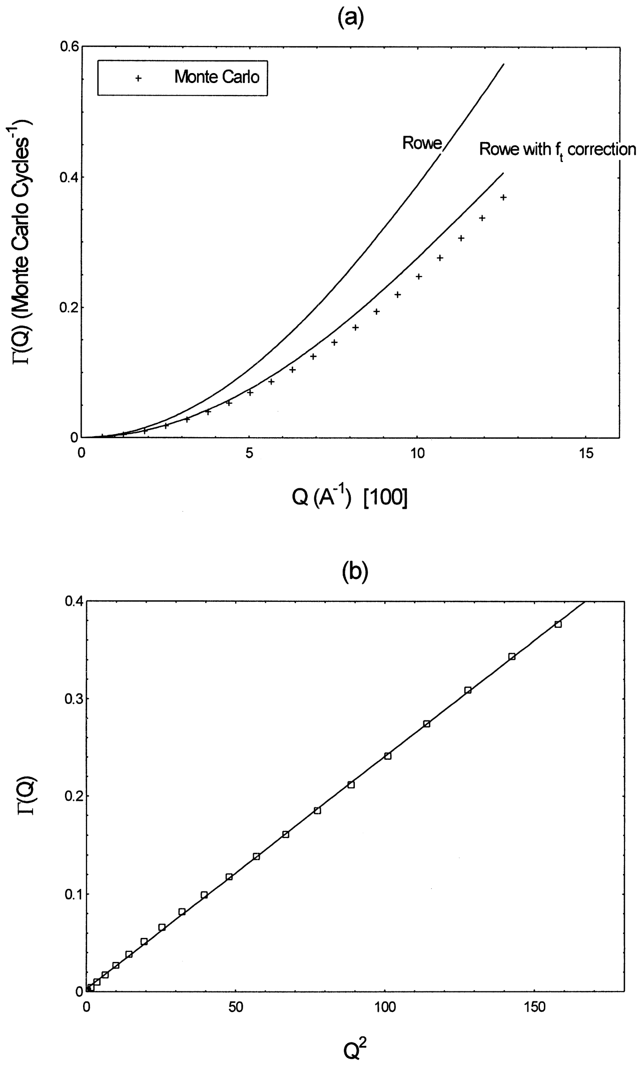

Fig. 1. (a) The FWHM of the scattering function, calculated by Monte Carlo and the model of Rowe et al. [1], with and without a correction for the tracer correlation factor. (b) The variation of the FWHM as a function of $\mathbf{Q}^2$, from which a value for the tracer diffusion coefficient can be extracted.

4. Extending the model to include interactions

We are currently in the process of extending the model presented in the previous sections to include both hydrogen–metal (H–M) and hydrogen–hydrogen (H–H) interactions. The H–H interactions are accounted for by a hard sphere radius of 2.1 Å [3]; this is a reasonable assumption at low concentrations. The H–M interactions are important, since they define the site energies and barrier heights along the various diffusion paths. We have chosen to model these interactions by a Born–Mayer potential, of the form

$$V(\mathrm{r}) = \sum_i C_i \exp\left(-\frac{\mathrm{r}}{\rho_i}\right) \tag{1}$$

where the sum is over the four metal atoms forming the tetrahedron. The parameters have been obtained for several compounds by fitting to the hydrogen vibrational frequencies, obtained from inelastic neutron scattering (INS) measurements (J.F. Fernandez, M. Kemali, D.K. Ross and C. Sanchez, to be published). We have used these values to locate the positions of the potential minima numerically. For $ZrCr_2H_{0.3}$, the g-site lies at $x=0.3123$, $z=0.1246$ with an energy of 0.7332eV; the e-site is at $x=0.2718$ with an energy of 0.8509eV. The potentials along the various diffusion paths are shown in Fig. 2.

In our Monte Carlo model, we define the jump probability from site i to j as

$$P(i \rightarrow j) = \Gamma \exp(-V_{ij}/k_B T) \tag{2}$$

where $V_{ij} = \Delta E_{ij} + E_{ij}$ is the sum of the energy required to surmount the potential barrier and the energy difference between the sites. The former is introduced so that a distinction can be made between g–g and g–g′ jumps. The latter is the standard energy difference used in Monte Carlo simulations of equilibrium thermodynamic properties. It ensures that only the configurations which contribute most to the integral of the thermal average are considered. From the INS data, we have calculated the values $V_{gg} = 0.148$ eV, $V_{gg'} = 0.28$ eV and $V_{ge} = 0.406$ eV. The zero point energies at the potential minimum and saddle point have been accounted for in calculating these values. The essential difference between this model and previous ones is that we have accounted for the classical energy required to overcome the energy barrier.

5. Conclusion

We have demonstrated our model for the prediction of the IQENS from hydrogen diffusion in C15 Laves phase compounds. We obtained a value for D_t of 0.00238 Å per Monte Carlo cycle for the case of the 'ideal' C15 structure. However, to extract useful quantitative data it will be necessary to extend this model, using the ideas discussed in Section 4, to simulate the diffusion process more realistically. In addition, the polycrystalline average of $\Gamma(\mathbf{Q})$ will need to be evaluated, as the existence of a

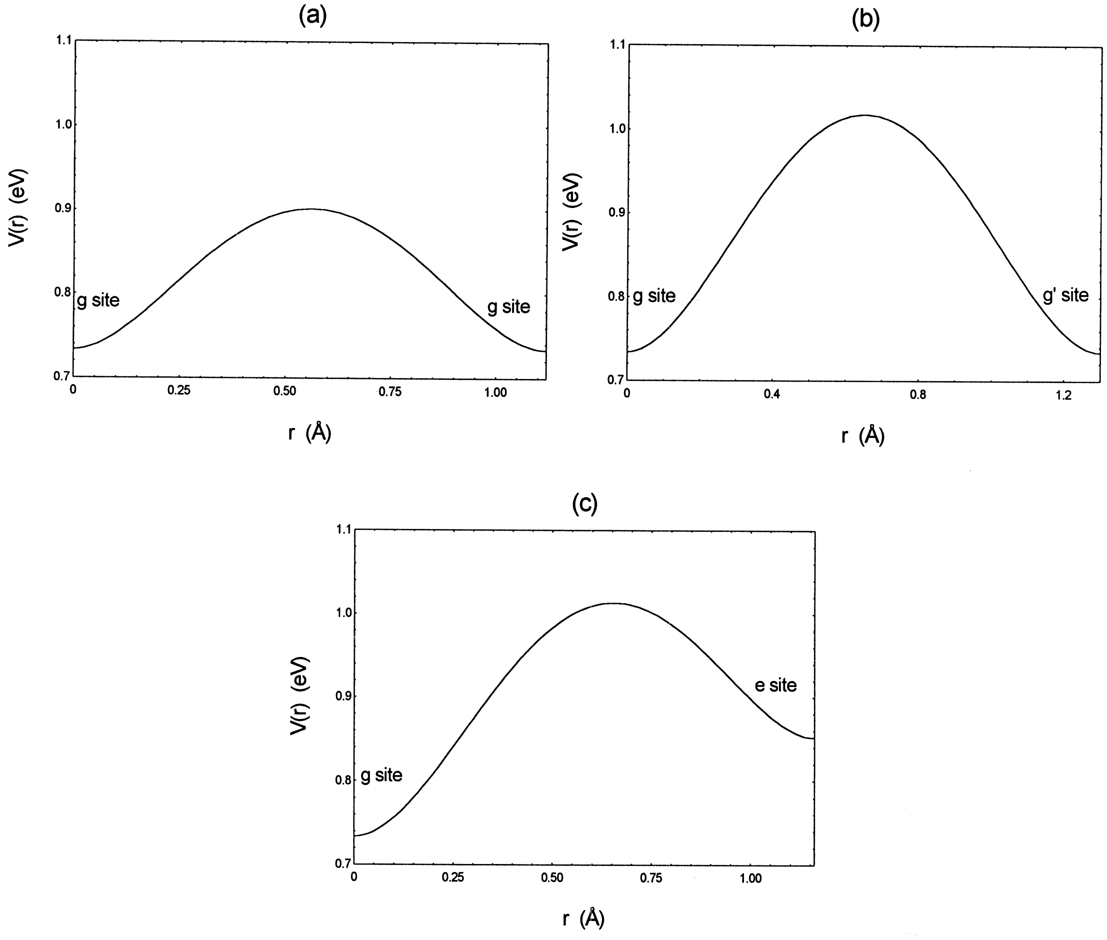

Fig. 2. The Born–Mayer potential along the diffusion paths (a) g–g, (b) g–g′ and (c) g–e for $ZrCr_2H_{0.3}$.

single-crystal C15 hydride is a virtual impossibility. Therefore, IQENS is performed on powdered samples. With the aid of these two techniques, it should be possible to elucidate the mechanism of hydrogen diffusion in these compounds.

References

[1] J.M. Rowe, K. Sköld, H.E. Flotow, J. Phys. Chem. Solids 32 (1971) 41–54.
[2] D.A. Faux, D.K. Ross, J. Less-Common Met. 129 (1987) 229–235.
[3] D.G. Westlake, J. Alloys Compounds 90 (1983) 251.
[4] A.V. Skripov, J.C. Cook, D.S. Sibirtsev, C. Karmonik, R. Hemplemann, Phys. Condensed Matter 10 (1998) 1787–1801.
[5] C.T. Chudley, R.J. Elliott, Proc. Phys. Soc. 77 (1960) 353.
[6] D.K. Ross, D.L.T. Wilson, in: Proceedings of the IAEA Symposium on Neutron Inelastic Scattering, Vienna, IAEA, Vienna, 1977.
[7] S.I. Campbell, Ph.D. Thesis, University of Salford, 1998.