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Quantum theory of diffusion: temperature dependence of diffusion of light interstitials in Debye solids

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Abstract. The temperature dependence of the motion of light interstitials is calculated using the quantum theory of Flynn and Stoneham. The results are compared with the asymptotic expressions given previously. They show that the high temperature asymptote is accurate over a wider range of temperature than expected, whereas the low temperature form is of very restricted application. Deviations from the asymptote depend both on the temperature and on the ratio of the activation energy to the Debye energy. Results for protons in Ta agree remarkably well with the theory for an activation energy 0·188 eV and for a hopping integral J of 29% of the Debye energy.

1. Introduction

Flynn and Stoneham (1970) recently developed a quantum theory of diffusion which described the motion of light interstitials in metals. The theory successfully predicted the motion energy in a number of cases, and explained the qualitative differences between interstitial motion in bcc and fcc lattices. Although formal expressions for the diffusion rate at all temperatures were derived, results were given only in the limits of very high and very low temperatures. This paper gives results at intermediate temperatures, with particular application to proton motion in bcc tantalum.

The theory makes four major assumptions. These are (i) the Born–Oppenheimer approximation that the electrons follow all nuclei adiabatically, (ii) the adiabatic approximation that the light interstitial follows the motion of the host atoms adiabatically, (iii) the linear approximation that the interstitial energy is linear in the displacements of host atoms and (iv) the Condon approximation that a transition matrix element is independent of host lattice coordinates. These assumptions appear to work well for bcc hosts. Thus the linear approximation (iii) and the Condon approximation (iv) were verified by the relation between the activation energy and volume of solution for various light interstitials in bcc Fe, and by the agreement between predicted and observed activation energies for various systems (Flynn and Stoneham 1970). The Condon approximation breaks down for fcc hosts, where the transition matrix element is sensitive to the motion of the two host atoms which lie close to the jump path. The present work tends to check the adiabatic and Condon approximations (ii and iv) since these assumptions are the most important in determining the general form of the temperature dependence.

2. Summary of the theory

At high temperatures, the hopping time τ is predicted to be given by

$$1/\tau = \left(\frac{\pi}{4\hbar^2 E_a kT}\right)^{1/2} |J|^2 \exp(-E_a/kT) \tag{1}$$

where E_a is an activation energy which may be related to the volume of solution. At low temperatures, a power law dependence is predicted instead, with $1/\tau$ proportional to T^7. We shall examine the range of temperatures for which these asymptotic forms are adequate.

At temperature T, the hopping time is inversely proportional to an integral of the form

$$I(E_a, T) = \exp(-f) \int_{-\infty}^{\infty} dt\, (\exp g - 1). \tag{2}$$

For a Debye solid with maximum phonon energy $\hbar\omega_D$ the functions f and g are

$$f(a) = \gamma \int_0^1 dx\, x^3 \coth(ax) \tag{3}$$

$$g(a, t) = \gamma \int_0^{\infty} dx\, x^3 \operatorname{cosech}(ax) \cos(xt) \tag{4}$$

where $a \equiv \hbar\omega_D/2kT$ and $\gamma \equiv 20E_a/\hbar\omega_D$. The hopping time depends on two independent parameters. The asymptotic expressions for the hopping time correspond to

$$I = \frac{45}{4} \pi \frac{\gamma^2}{a^7} \exp(-\gamma/4) \tag{5}$$

at low temperatures, found by expanding the exponentials, and

$$I = \left(\frac{\pi a}{\gamma/10}\right)^{1/2} \exp(-a\gamma/10) \tag{6}$$

at high temperatures, found by the method of steepest descents.

The integral has been evaluated numerically for intermediate temperatures using two Harwell Library subroutines. The $g(a,t)$ integration used a routine for oscillatory integrands, due to W E Hart whilst the other integrations used a Simpson's method routine with a variable step length; this was written by M J D Powell. The final integral should be accurate to 1 %. In all cases it was verified that the numerical results had the correct asymptotes.

3. Deviations from asymptotic behaviour

In figure 1 we show the ratio of the calculated diffusion rate to its high temperature asymptote for E_a equal to $2\hbar\omega_D$ (roughly correct for Fe:H) and E_a equal to $7{\cdot}5\ \hbar\omega_D$ (roughly correct for Nb:H and Ta:H). It can be seen that the high temperature asymptote is reasonably accurate to temperatures significant below the Debye temperature and it is accurate over a wider range of temperatures for the smaller value of $E_a/\hbar\omega_D$.

By contrast, the low temperature asymptote is not reached until kT is only a few per cent of $\hbar\omega_D$. Moreover, the predicted rate may become either higher or lower than the low temperature asymptote as the temperature is raised from absolute zero. These features may be understood as follows. At low temperatures the transitions are dominated

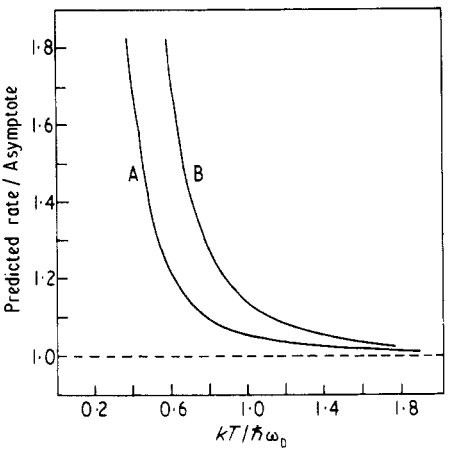

Figure 1. Ratio of the predicted diffusion rate D to its high temperature asymptote for A, $E_a = 2\hbar\omega_D$, and B. $E_a = 7{\cdot}5\hbar\omega_D$. Note the scales are linear, not logarithmic, and note also the zero of the ordinate.

by two-phonon processes (see the appendix of Flynn and Stoneham 1970). As the temperature is increased two effects occur: the two-phonon rate decreases from the value predicted from its low temperature asymptote, while three-phonon processes also become significant. These effects work in opposite directions, so that the sign of the deviation depends on the actual values of the parameters.

4. Comparison of experiment and theory for Ta:H

In figure 2 we compare the theory with results on Ta:H compiled by Wert (1970) from data of Merisov *et al* (1966) and Cannelli and Verdini (1966). The system Ta:H is particularly suitable for two reasons. First, the experimental data are mutually consistent.

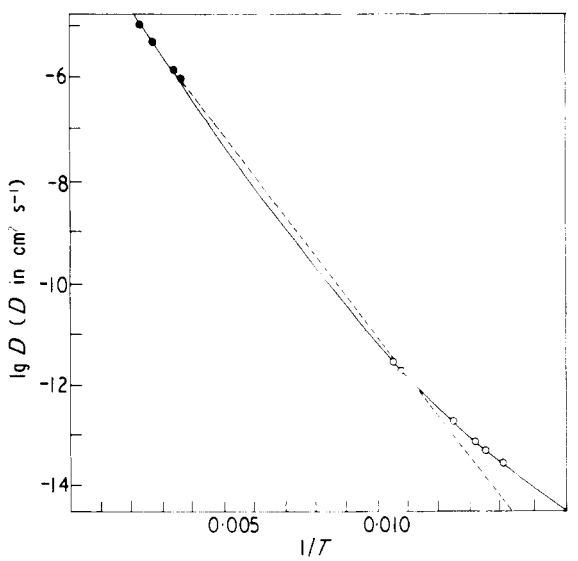

Figure 2. Predictions for H in tantalum compared with experiment. ● Merisov *et al* (1966); ○ Cannelli and Verdini (1966); Full line, present work; broken line, Went (1970).

This suggests there are no major complications, like hydride precipitation, in the system under consideration. Secondly, the Debye model seems to be 'rather better for tantalum than for most other materials' (Woods 1964). This feature, shown by neutron scattering data, is probably associated with the lack of dispersion in the transverse branches of the phonon spectrum.

The fit of theory to experiment was achieved by allowing small changes only in $E_a/\hbar\omega_D$, and by fitting $|J|^2$ from the results at the highest temperatures. *There are no extra parameters to describe the deviations of the curve from linear.* The fit proves to be remarkably good and includes the pronounced curvature in the low temperature data.

The relevant parameters obtained from the fit are an activation energy E_a of 0·188 eV and a matrix element $|J|$ of 0·292 $\hbar\omega_D$. The activation energy should be compared with the value 0·18 eV predicted from the volume of solution by Flynn and Stoneham (1970). The very precise agreement is fortuitous, but gratifying. Wert's fit of a simple Arrhenius expression gives a related (but not equivalent) parameter $Q \simeq 0{\cdot}155$ eV. It is much harder to predict $|J|$ but the result obtained is in the general range expected theoretically.

Acknowledgments

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