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THE DIFFUSION OF HYDROGEN AND ITS ISOTOPES IN BCC METALS*

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ABSTRACT

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It has been suggested that light interstitials in metals diffuse in much the same manner as do self-trapped electronic carriers (small polarons) in semiconductors and insulators. Namely, the motion is assumed to occur via a succession of phonon-assisted quantum-mechanical tunneling events. Indeed, such interstitial jumps have been modeled formally by adopting Holstein's non-adiabatic approach to small-polaron hopping motion. It is the purpose of the present work to transcend this theory and explicitly calculate the diffusion constant for models of the interatomic interactions associated with an interstitial in a metal. With this procedure the conditions under which quantum-mechanical tunneling is the predominant mode of light interstitial transport in metals are investigated. In addition, in situations characterized by interstitial tunneling motion the validity of simplifying assumptions of the formal theory are examined. It is found that there are meaningful examples of light interstitial diffusion which do not correspond to tunneling through a barrier. Also, in those instances where tunneling motion does prevail, the influence of excited states of the interstitial wells, the breakdown of the Condon approximation, and the predominance of adiabatic hopping qualitatively affect the hopping rate. The occurrence of these situations reflects fundamental physical differences between an electron tunneling between the relatively deep potential wells of an insulator and an atom moving between interstitial positions in a metal. The magnitudes, temperature dependences and isotope dependences of the calculated diffusion constants are consistent with existing diffusion data on bcc metals.

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The diffusion of a light interstitial, such as hydrogen or one of its isotopes, in a solid represents one example of a broad class of situations in which one is concerned with a relatively light particle moving amongst a collection of displaceable particles of greater mass. In these situations one regards the diffusion of the light particle as being controlled by the motions of the heavier atoms. In particular, this view is central to situations in which the diffusing particle is severely localized within the atomic displacement pattern which it induces around itself. In these circumstances one often refers to the unit comprising the particle and the associated atom deformation as a small polaron. Because this composite particle is typically very massive (being associated with an extremely narrow small-polaron bandwidth), at all but some very low temperature situations it is appropriate to view small-polaron motion as proceeding via a succession of phonon-assisted hops between adjacent positions.¹ While the notion of small-polaron hopping motion was originally advanced to describe the motion of electronic carriers in low-mobility semiconductors and insulators,¹ it may also be applied to the problem of light interstitial diffusion in solids.² Nonetheless, the simplifications which are explicitly employed in developing the theory of electronic small-polaron hopping motion are often inappropriate for atomic diffusion. For example, studies of simple models of the diffusion of hydrogen in bcc metals indicate that this is so.³

In this paper we present a generalization of Holstein's occurrence-probability treatment of small-polaron hopping motion which transcends these simplifications. After establishing this semiclassical treatment of small-polaron hopping, we enumerate the simplifications which characterize electronic small-polaron hopping. We then note that these assumptions define a physical situation which generally departs from that of light interstitial diffusion; indeed, the resulting (electronic) theory conflicts with experiments for hydrogen diffusion in bcc metals. However, the results of explicit calculations of the diffusion constant for models of hydrogen and its isotopes in a bcc metal which employ the generalized formalism are in general accord with experiments. The generic features of these studies are then discussed with emphasis being placed on understanding the trends of the physical phenomena which accompany changes of the parameters. In particular, this work provides a framework within which the isotopic dependences observed for hydrogen diffusion in metals can be understood.

Generally, small polaron transport involves the light particle moving between sites in response to the everchanging potential associated with the (zero-point and thermal) motions of the relatively heavy atoms of the lattice. At low temperatures the predominant motion involves the quantum-mechanical tunneling of the heavy atoms of the lattice between positions which are consistent with the light particle occupying initial and final sites, respectively. However, at sufficiently high temperatures (typically above a small fraction, $\leq 1/3$, of the characteristic phonon temperature) the transfer of the light particle is described by the semiclassical occurrence-probability approach in which the vibratory motions of the solid are viewed classically.¹ Namely, as the heavy atoms of the material vibrate through a myriad of configurations they occasionally occupy positions for which the energy of the light particle of the occupied site momentarily coincides with the energy which it would have if it occupied a different site. The temporary degeneracies, termed coincidence events, are each associated with the particle having a finite probability of moving between these sites. The rate characterizing the motion of the particle between the occupied level of one site and a vacant level of a different site is the thermal average (over atomic positions and velocities) of the product of the occurrence rate for a coincidence event between the two levels, $r_{i,j}$, and the probability that the diffusion atom avails itself of the coincidence events by negotiating a hop, $P_{i,j}$:

$$R_{i,j} = \langle r_{i,j} P_{i,j} \rangle. \quad (1)$$

Furthermore, the transfer probability, $P_{i,j}$, depends upon the characteristic transfer time, $\hbar/J_{i,j}$, and the duration of a coincidence $[\hbar/\epsilon_{i,j}]^{1/2}$ through the single quantity $f_{i,j} = (2\pi/\hbar) |J_{i,j}^2/\dot{\epsilon}_{i,j}|$, where $J_{i,j}$ and $\dot{\epsilon}_{i,j}$ are, respectively, the transfer integral and the time derivative of the difference in the local energy levels, both evaluated at the coincidence event. Explicitly,

$$P_{i,j} = [1 - \exp(-f_{i,j})][1 - \frac{1}{2}\exp(-f_{i,j})], \quad (2)$$

where $P_{i,j}$ rises from zero to unity as $f_{i,j}$ passes from zero to infinity. The net hopping rate for hopping between equivalent sites, R , is then the thermal average of the rates associated with hopping between each pair

of levels of the two interstitial wells:

$$R = \frac{\sum_i \exp(-E_i/kT) \sum_j R_{i,j}}{\sum_i \exp(-E_i/kT)} \quad (3)$$

where E_i is the equilibrium energy of the system when the i -th level is occupied, k is the Boltzmann constant, and T is the temperature.

In treating electronic small-polaron motion one is typically concerned with tunneling motion of an electron between rather deep (many eV) potential wells. In these instances, while an occupied well is generally deepened as a result of the polaronic distortions associated with its occupation, the augmentation is usually by only a fractionally small, albeit significant, amount. As a result the local wavefunctions and intersite transfer integrals are often approximated by the values they possess in the absence of atomic distortions; this is the so-called Condon approximation. In addition the fact that interlevel energy separations of an electronic system are typically very large compared with the thermal energy leads to the usual neglect of transport in all but the lowest of the electronic bands. In the occurrence-probability approach these simplifications are incorporated by 1) the neglect of the dependence of the $J_{i,j}$'s on atomic distortions in Eqs. (1) and (2), and 2) the retention of only that $R_{i,j}$ which corresponds to motion between the groundstates of both initial and final wells in Eq. (3).¹ Furthermore, with few exceptions,⁴ studies of hopping have been simply carried out perturbatively to lowest (second) order in the transfer integrals; this corresponds to $J_{i,j}$ adopting the small $-J_{i,j}$ limit of $P_{i,j}$ ($P_{i,j} = 2 f_{i,j}$) - termed the nonadiabatic limit.

The problem of light interstitial diffusion in metals is different from that of electronic small-polaron motion in that one is concerned with motion of a very much heavier particle between wells which are often much shallower than typical electronic wells. Furthermore, in these instances, the polaronic distortions can be a major fraction of the overall depth of an occupied well. As a result, reflecting the heavier mass of the diffusing particle and the relative shallowness of the wells at a coincidence event, the transfer integrals are typically very much more sensitive functions of the atomic displacement pattern at a coincidence than in the electronic situation. In other words, with a relatively small change ($\sim kT$) in strain energy, coincidence configurations associated with transfer integrals

of greatly different magnitudes can be established;³ namely, the Condon approximation is inappropriate. Furthermore, the possibility of generating coincidence events with large transfer integrals precludes restricting the calculations to the nonadiabatic limit.³ Finally, it is obvious that the energy level separations for light interstitials, such as hydrogen, are generally very much smaller than those characteristic of the electronic situation. This leads one to consider multilevel transport. Thus the simplifications which attend the application of the general small-polaron theory to electronic hopping motion are not to be generally adopted in treating light interstitial diffusion in metals. The theory must be utilized in its full generality.

In fact there are major discrepancies between experiment and the predictions obtained by applying the electronic theory to light interstitial diffusion. Namely, the theory predicts that the diffusion coefficient will be thermally activated above a small fraction of the characteristic phonon temperature and depart from an Arrhenius behavior at lower temperatures, with this feature depending little on the diffusing isotope.^{5,6} In addition, the activation energy for diffusion is predicted to decrease with increasing isotope mass.^{2,7} These phenomena are, however, not observed. For example, the diffusion constant for hydrogen in niobium departs from an Arrhenius temperature dependence at about the Debye temperature.⁸ Furthermore, such a break is not evident for deuterium or tritium diffusion in niobium.^{8,10} The most striking disagreement is the increase of the high-temperature activation energy for diffusion with increasing isotope mass.^{8,10}

Transcending the simplifications of the electronic theory and utilizing the generalized occurrence-probability formulation one can obtain results, shown in Figure 1 for light interstitial diffusion which are in general accord with the experimentally observed curves.³ The associated calculations involve simple models and computational simplifications which are adopted in order to render it possible to implement the generalized occurrence probability formalism. The physical phenomena which are manifested by the model calculations are nonetheless quite general. It is to these features which we direct our attention.

At the highest temperatures the diffusion curves for the positive muon and the three isotopes of hydrogen appear simply activated with a nearly common prefactor. In these situations the hopping motion is mainly adiabatic. This is manifested by the prefactor achieving its

adiabatic value, $v_D d^2 \approx 10^{-3} \text{ cm}^2/\text{sec}$, where v_D is the Debye frequency and d is the jump distance.⁴ Furthermore, the lightest "isotope", the positive muon, has the simple Arrhenius behavior characteristic of the electronic approximation to the semiclassical adiabatic hopping motion of a small polaron. In this case, the activation energy is just the energy required to form the lowest energy coincidence. The heavier-massed isotopes, however, show clear departures from this simple activated behavior. In these instances the high-temperature adiabatic motion is not associated with the lowest energy coincidence but rather with excited coincidence. Thus with a reduction of the temperature, lower energy coincidence, associated with smaller $P_{i,j}$'s (and hence smaller prefactors), make an increasingly large contribution to the net diffusion rate. That is, the higher energy adiabatic coincidences are frozen out producing smaller prefactors and activation energies as the temperature is reduced. At sufficiently low temperatures, the lowest energy coincidence will predominate. Since the hopping activation energy associated with the lowest energy coincidence tends to decrease with increasing mass, in this situation, the heavier isotopes will diffuse faster than the light ones. This is manifested by the crossing of the hydrogen and muon curves in Figure 1.

The essential aspects of these curves rely on 1) transcending the Condon approximation, 2) permitting diffusion involving excited coincidences and excited states, and 3) allowing the $P_{i,j}$'s to range fully from nonadiabatic ($P_{i,j} \ll 1$) to adiabatic ($P_{i,j} = 1$) limits. The effects of these generalizations for a given system depend upon the distributions of transfer integrals and associated coincidence energies as functions of the deformation parameters. It is these distributions which determine the magnitude and temperature dependence of the diffusion constant.

Trends in the behavior of the diffusion coefficient are coupled with systematic alterations of the physical parameters. For example, increasing the depth of the local potential wells and increasing the barrier between initial and final wells involved in a coincidence increases the activation energy associated with adiabatic hopping. Furthermore, studies of tunneling through simple barriers indicate that the transfer integrals (proportional to the two-site tunnel splittings) become less sensitive to isotope and deformation changes as the depth of the coincident wells is increased. As a result the isotope effect will tend

to be less pronounced as one proceeds from systems with shallow wells (small adiabatic activation energies) to those with deep wells. Furthermore, as the sensitivity of the transfer integrals decreases the sharpness of the break between high- and low-temperature behavior increases. These trends are consistent with experiment for the transport of hydrogen and its isotopes in bcc metals.⁹

In thinking about the isotope effect it is useful to realize that the apparent activation energy may be written as the sum of three separate contributions: $E_A = \epsilon_2 - |J| + \Delta\epsilon_2$. The first, ϵ_2 , is the minimum energy required to form a coincidence. This is the activation energy of Holstein's nonadiabatic theory of electronic small-polaron hopping motion.¹ This contribution tends to decrease as the mass of the diffusing particle increases.^{2,7} The second term: $-|J|$, accounts for the reduction of E_A associated with the spreading of the wavefunction of the particle between the sites involved in the coincidence;⁴ $|J|$ tends to decrease with an increase in particle mass. Finally, $\Delta\epsilon_2$ is the characteristic energy of the coincidences which dominate the diffusion relative to that of the lowest energy coincidence, ϵ_2 .³ This term tends to increase as the mass of the particle increases. In the case of the bcc metals, the second and third terms appear to dominate the isotope effect, yielding a net activation energy which increases as the mass of the isotope increases. In the case of fcc metals the converse situation appears to prevail. Most generally, however, it is important to realize that the isotope dependence of E_A involves the competition of terms with opposite mass dependences. Furthermore, the relative importance of the three contributions changes as the temperature is altered. As the temperature is lowered, the final term (and in some instances the second term) tend to decrease.

In summary, we find that the breakdown of the "Condon" approximation, the predominance of adiabatic hopping, and the influence of excited coincidences all qualitatively affect the small-polaron hopping rate in instances of light interstitial diffusion. Furthermore, explicit model calculations can account for the observed magnitudes, temperature dependences and "anomalous" isotope dependences of the hydrogen diffusion in bcc metals (niobium being the most-studied example). Indeed, the general features and trends for the diffusion of hydrogen and its isotopes in metals appear consistent with the theory outlined above. Detailed accounts of this work are in preparation.

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Figure 1: The diffusion constant (cm^2/sec) is plotted versus reciprocal temperature for the positive muon and the three isotopes of hydrogen diffusion in a crude model of a bcc metal with parameters chosen to correspond to niobium.