

NON- CLASSICAL DIFFUSION PROCESSES

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This paper surveys quantum effects in diffusion, with special emphasis on isotope effects for hydrogen isotopes in metals. The various possible contributions to the isotope effect are surveyed, and their importance assessed. The bcc metals (V, Nb, Ta) and fcc metals (Cu, Ni, Pd) involve different mechanisms, and there are still doubts in detail about some aspects. A full understanding requires knowledge of the hydrogen–metal interactions. Recent theoretical work supports some of the qualitative ideas discussed, and offers promise for future analyses.

Ce papier passe en revue les effets quantiques en diffusion en mettant particulièrement l'accent sur les effets isotopiques pour les isotopes de l'hydrogène dans les métaux. Les différentes contributions possibles à l'effet isotopique sont passées en revue et leur importance est évaluée. Les métaux cubiques centrés (V, Nb, Ta) et les métaux cubiques à faces centrées (Cu, Ni, Pd) impliquent différents mécanismes, et il existe encore des doutes dans le détail sur quelques aspects. Une compréhension complète requiert une connaissance des interactions métal-hydrogène. Un travail théorique récent supporte quelques-unes des idées quantitatives présentées et offre des promesses pour des analyses futures.

In dieser Arbeit werden Quanteneffekte bei der Diffusion mit besonderer Betonung des Isotopieeffekts für die Wasserstoffisotope in Metallen betrachtet. Die verschiedenen möglichen Beiträge zum Isotopieeffekt werden abgeschätzt und ihre Bedeutung kritisch bewertet. Die krz. Metalle V, Nb und Ta und kfz. Metalle Cu, Ni und Pd betreffen unterschiedliche Mechanismen, über einige Gesichtspunkte bestehen noch Zweifel. Ein volles Verständnis erfordert die Kenntnis der Wasserstoff-Metall-Wechselwirkungen. Neuere theoretische Arbeiten stützen einige der diskutierten qualitativen Ideen und bieten gute Aussichten für zukünftige Analysen.

1. Introduction

Diffusion studies have a long and venerable history. During this time, ideas of behaviour on an atomic scale have changed enormously. Yet neither the discovery of the electron nor the belief that Schrödinger's equation, not Newton's law of motion, determines microscopic phenomena have had a major effect on diffusion. I think it worthwhile to analyse the reasons for the continued dominance of classical descriptions, as well as indicating the areas where quantum theories have been successful and the phenomena which lack a simple classical interpretation.

One major reason for the limited role of quantum theories is that diffusion has been primarily a phenomenological science, based on Fick's laws and the Arrhenius equation rather than on an atomistic description. Since both quantum and classical theories agree that diffusion should be thermally activated at high temperatures, there is little to encourage experimenters to venture into the treacherous areas of quantum physics.

But there have been developments in recent years which do encourage using the quantum approach more actively, going beyond the mere addition of quantum statistics to classical models.

This brief review will be concerned with two main areas: quantum effects in diffusion and related phenomena, and isotope effects. These two topics are not simply related, although they have some common areas. In particular, isotope effects in diffusion constants, activation energies, heats of transport and effective charges can contain indications of quantum behaviour. Isotope effects in many other phenomena have been surveyed recently by Alefeld and Wipf [1], and range from thermal conductivities to effects on superconducting transition temperatures. Quantum effects have been reviewed too both by myself [2,3] by Sussmann [4], and by Flynn [5]. No attempt will be made to duplicate their analysis. This is perhaps the time to stress that *quantum effects are those which become insignificant when Planck's constant becomes zero*. The temperature need not be low, contrary to popular mythology.

The myth comes from the observation that, in quantum statistics, one finds \hbar only in the combination $\hbar\omega/kT$. If statistics alone are important, then high T and low \hbar are equivalent. But diffusion involves dynamics as well as statistics, and indeed the mechanism of diffusion may be altered when \hbar is finite. Quantum effects can occur at all temperatures.

2. General mechanisms of diffusion

It is useful to classify diffusion mechanisms into three broad groups [3]. These are not the conventional divisions into vacancy and interstitialcy mechanisms, for example, but a much more fundamental split depending on broad features of how the jump occurs.

(1) Cases where jumps occur when some generalized atomic coordinate exceeds a critical value Q_0 . This includes classical diffusion, when Q_0 usually refers to a saddle-point configuration. However, there may be argument in detail about what reaction coordinate Q_0 is appropriate, or indeed whether only one reaction coordinate is needed. Flynn and Stoneham's model of H diffusion in fcc metals [6] is also in this class, since the transition matrix element is only large when the atoms straddling the jump path have moved sufficiently.

(2) Cases where jumps occur when some generalized coordinate lies in some small range δQ close to a critical value Q_0 . This includes the Flynn–Stoneham model for H diffusion in bcc hosts illustrated in fig. 1. Here the hydrogen causes lattice distortion centred on the (initial) interstice it occupies; Q_0 is the distortion necessary for the hydrogen to have the same energy in the initial and final neighbouring interstices.

(3) Cases where jumps proceed by excitation to

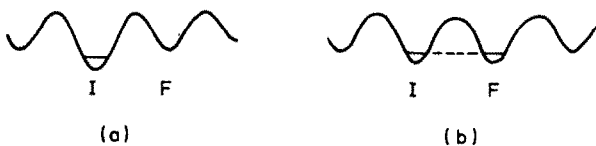


Fig. 1. Illustration of diffusion limited only by the self-trapping distortion. In (a) the interstitial has a lower energy in the central site than in the adjacent ones and cannot tunnel; in (b) a fluctuation makes two sites energetically equivalent. The activation energy is the energy needed to produce the fluctuation.

some well-defined excited state for which rapid motion can occur.

All three groups give thermally-activated behaviour at high temperatures, although the origin of the activation energy E_a differs from case to case:

(1) (i) For classical diffusion E_a is a saddle-point energy, possibly with minor corrections; (ii) for the “lattice-activated” case of Flynn and Stoneham, E_a is the energy needed to strain the host lattice so that the transition matrix element is appreciable (fig. 2).

(2) E_a is a lattice energy, being the energy to distort the lattice so that the diffusing particle would have the same energy in the initial and final positions.

(3) E_a is the excitation energy of the important excited state, again with possible minor corrections.

There may be a slight temperature dependence of the pre-exponential factor τ_{00} , although this is rarely significant. For a single simple harmonic oscillator at high temperatures, for example, the probability that the displacement lies within δQ of Q_0 is proportional to $T^{-1/2} \exp(-E_0/kT) \delta Q$, and the probability that Q exceeds Q_0 varies as $T^{1/2} \exp(-E_0/kT)$; in both cases E_0 is $\frac{1}{2}M\omega^2 Q_0^2$.

Clearly the pre-exponential factor is not enough to be sure of the type of mechanism. The isotope effect gives a number of clues, and certain measurements (notably of heats of transport) are particularly important guides [12]. In particular, for some mechanisms [e.g. (2)] there is a contribution proportional to the activation energy in the reduced heat of transport ($Q^* = \alpha E_a + \beta$), whereas in others [e.g. (2) or (1i) above] there is no such term.

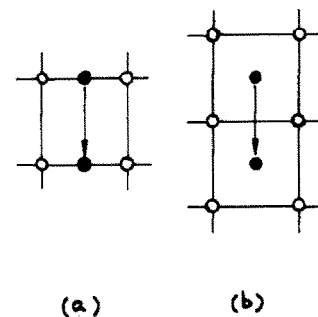


Fig. 2. Contrast between “polaron-limited” diffusion [(a) and also fig. (1)] and “lattice activated” case where the atoms straddling the jump-path have to move by some critical separation before the transition matrix element is appreciable.

Examples of the various mechanisms have been discussed by Flynn [5] and Stoneham [7]. Simple vacancy motion and most impurity diffusion falls into category (1). Category (2) appears to cover H in bcc metals, and the reorientation of H trapped by O or N in Nb [7] is a particularly good example. Other instances include a number of systems which are not discussed in conventional diffusion work. Examples are μ^+ diffusion [9] and the small polaron systems such as the V_k centre in alkali halides [5,7] and the electronic hole in MnO [10]. It is worth stressing that many systems show behaviour closely analogous to diffusion but without involving matter transport over large distances. Perhaps the best example of case (3) is in this group, namely the orientation of O_2^- ions substituting for anions in alkali halides.

3. Sources of isotope effects

This section summarizes the ways in which isotope mass can affect diffusion rates. Since it is usual to describe diffusion data by fits to Arrhenius expressions (even if valid over restricted temperature ranges only), the effects on the activation energy and pre-exponential factor are given separately in table 1. The main point of this section is to indicate just how complicated and varied isotope effects can be, in contrast to naive views often expressed. The question of which mechanisms actually operate in particular systems, notably H in metals, is taken up later. For both future use and simplicity of exposition it is useful to think mainly of the interstitial diffusion of an impurity atom.

3.1. Classical effects

In the classical treatments, the activation energy depends on the potential energy of some saddle-point configuration, and is independent of isotopic mass. The pre-exponential factor does depend on mass, basically through the mean square amplitude of thermal vibration in the reaction coordinate [5]. The simplest theories give a rate proportional to $M^{-1/2}$. However, the isotope effect is reduced because of the participation of atoms other than the diffusing particle in the motion leading to the jump.

Classical theory is usually developed for harmonic systems, and assumes a jump will occur whenever a

Table 1

Contributions to the isotope effect.

Here a *positive* effect is one which increases the rate for lighter masses, i.e. the lighter the mass, the smaller the activation energy or the larger the pre-exponential factor

Effect	Pre-exponential factor	Activation energy
1. Classical:	$(m_{\text{eff}}^{-1/2})$	
conventional	+	nil
probability of successful jump	-	nil
2. Quantal:		
(a) zero-point motion polaron effect		-
(b) tunnelling matrix elements purely overlap effect:	+	nil
dependence on geometry:		+
(c) excited states delocalized:		+
harmonic oscillator:		-
(d) local tunnelling states	(reduce isotope dependence)	

saddle point is crossed in the right direction. Molecular dynamics calculations (which usually include anharmonicity) stress how hard it is to justify this view, for there are often "jumps" in which the diffusing particle moves straight back to the site it has vacated. Bennett [13] has suggested another criterion, as follows. Suppose one considers the motion from A to B via a saddle-point S shown in fig. 3. Then a successful jump is one

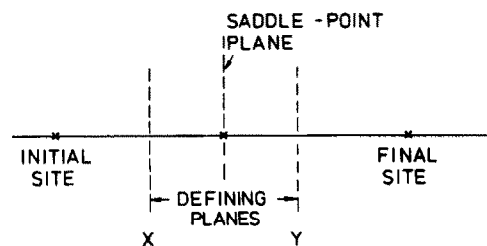


Fig. 3. Geometry used by Bennett [13] to define jumps, avoiding problems met in the classical definition in terms of the saddle point alone.

in which the system passes from A through X (between A and S) and then through Y (between S and B) without making any subsequent intermediate crossings of X.

The classical definition is achieved if X and Y coincide with S. The importance of the molecular dynamics work is that the probability that a jump will be successful after X is reached is isotope dependent. Bennett has given promising results which may remove some of the anomalies in the literature. In particular, he suggests heavy isotopes have a larger chance of a "successful" transit from X to Y. Obviously this depends on the precise choices of X and Y. Bennett's choice is a sensible one, albeit isotope-independent; since X and Y presumably correspond roughly to the limits of vibrational (rather than diffusive) excursions from the initial and final sites one could argue for an isotope-dependent choice, which would reduce the effect.

3.2. Quantum effects

The qualitative differences between classical and quantal approaches have been reviewed recently [2–4] and will not be repeated here. But there are three main ways in which isotope effects arise.

(a) There is zero-point motion which causes a distortion of the surrounding lattice. This "polaron" effect alters the activation energy, increasing it for lighter isotopes. Other effects of zero-point motion will be mentioned later.

(b) The jump frequency is proportional to the square modulus of a matrix element. Normally this element, J , will be bigger for lighter masses. Thus J may depend on the overlap of initial and final state wavefunctions, and this is usually bigger for the larger zero-point motions of lighter atoms. However, in some cases the matrix element is very small unless atoms straddling the jump path move by more than some critical amount. The critical movement leads to a term in the activation energy corresponding to the strain energy needed to make the movement. Since the critical amount is isotope-dependent, the activation energy will change with isotope. Probably the contribution to E_a will be less for lighter isotopes, simply because the larger zero-point motion makes smaller critical displacements possible.

(c) The vibrational levels of the diffusing particle may be discrete, rather than a continuum. In certain cases diffusion may occur by excitation to a well-defined excited state. Two obvious effects on the activa-

tion energy can be seen. (i) If the excited state is delocalized, so that its energy depends little on the isotope mass, then the activation energy (the difference between ground and excited state energies here) will be less for lighter masses because the zero-point energy $\frac{1}{2}\hbar\omega$ raises the ground state energy of the light mass relative to the heavy mass. (ii) If the levels are like those of a harmonic oscillator, the larger frequency ω for the light mass raises the excited state energies and increases the activation energy.

(d) Local tunnelling states. One effect which proves especially important for H in bcc metals like V, Nb and Ta comes from the possibility that light atoms can tunnel between interstitial sites within one interstice, as well as jumping between interstices [14]. This phenomenon has as its main effect the increase of the transition matrix element and a diminution of the isotope effects in (b). However, the situation is complicated because the precise form of the potential energy surface is affected by the local lattice distortions mentioned in (a).

Another case, which is quantal with a vengeance, concerns the reorientation of O_2^- in alkali halides. Here a pair of like isotopes [e.g. $(O^{17})_2^-$] and a pair of unlike isotopes [e.g. $(O^{16}-O^{18})^-$] behave differently just because of the exclusion principle and its effect on allowed rotational states. However, this is not a case which need cause concern in diffusion. Still further examples of isotope effects should exist, for example in self-interstitial motion in metals. I shall not discuss these, despite their interest, because no measurements exist or seem likely in the near future.

4. Models for quantum behaviour

General features of quantum approaches have been surveyed recently with varied emphasis [2–5]. This section summarizes some of the recent work and relates it to the earlier discussions. I shall usually talk about light interstitials, like H in metals. However, it should be realized that much of the theory has been developed for "small polarons". The two cases are equivalent (apart from a change in vocabulary) in so far as both involve a diffusive motion whose rate is limited by the inertia caused by local lattice distortion. Many of the basic principles were unravelled in the paper of Holstein [17] and in the extension of this work and its

application to diffusion by Flynn and Stoneham [6]. Recent papers often reproduce the same results by different means; in the present outline rather little will be mentioned of these aspects, despite their value.

In the “small” polaron description of light interstitial diffusion, there are three regimes of behaviour. In order of increasing temperature these are as follows.

(1) A propagating regime, where the interstitial propagates through the lattice rather like an electron. Flynn and Stoneham argued that this regime occurs only at temperatures below those of practical importance, although this has been disputed [18].

(2) A hopping regime, where the activation energy is related to the energy associated with lattice distortion (the “self-trapping distortion”) and is *not* a potential energy barrier. This regime appears dominant for hydrogen in metals.

(3) A “classical” regime in which diffusion is dominated by either excitation to states above the energy barriers (i.e. as in the classical description) or to states below the barrier for which tunnelling is sufficiently rapid.

Most real systems will show one, or at most two, of these regimes. Propagation is seen only in the reorientation of anisotropic defects, and need not concern us here. The relative roles of regimes (2) and (3) is much harder to decide. However, one sensitive check of a transition between regimes is the heat of transport [12] and it should be stressed that experiment gives no indication of a transition in hydrogen–metal systems. It should also be stressed that regime (3) may only be relevant at temperatures so large as to be irrelevant, for example above a melting temperature.

Of the papers discussing regimes (2) and (3) (refs. [18–23]), several also concern the question of self-trapping, i.e. whether regime (2) can exist at all [18–23]. There seems general agreement that, if a system moves from regime (2) to (3) with increasing temperature, then the activation energy changes from the polaron value to the classical barrier height. However, there is no agreement about the smaller corrections, and some features are ignored (notably the configuration-dependence of the transition matrix element which is important for H in fcc metals [6,2]). Furthermore, at high temperatures, any transition to a classical regime could be hidden by the effects of correlations between successive jumps. In this effect, discussed for polarons by Emin [22], the host lattice distortion recovers only in a time compa-

rable with the rapid jump frequency, and the probability of subsequent jumps is affected.

The role of the excited states of an interstitial in an interstice has been discussed several times. Formulae were given by Flynn and Stoneham, but were not applied because they involved unknown parameters and because they seemed unnecessary. Explicit calculations can be made (e.g. [20]) but these make assumptions about the excited states which are chosen to be algebraically simple, rather than realistic physically. Another aspect which needs detailed discussion is the adiabatic or non-adiabatic nature of the transition. The non-adiabatic case is usually assumed (here the transition matrix element is sufficiently small to be taken to lowest-order perturbation only) although there may be cases where this is inadequate and where estimates of the limits of the regimes may need revision [18,19].

5. Experiment and the isotope effect

Isotope effects have been discerned in a wide range of phenomena, recently reviewed in [1]. This section concentrates on a few examples to illustrate the arguments of the last section.

5.1. Hydrogen in bcc metals

Experiment shows three main features for diffusion in V, Nb and Ta. First, hydrogen always diffuses faster ($D_H > D_D$) than deuterium. Secondly, the pre-exponential factors are insensitive to the isotope. Thirdly, the activation energy for hydrogen is less than that for deuterium ($Q_H < Q_D$). Fig. 4 shows schematically the temperature dependence of D_H/D_D and of the diffusion rates.

It would be unrealistic to discuss these data without mentioning that hydrogen in V, Nb and Ta shows anomalies of several sorts, notably in:

- (i) the magnitude, temperature dependence and scattering-vector dependence of the Debye–Waller factor [24];
- (ii) the widths of quasi-elastic neutron spectra [25];
- (iii) the lack of anisotropy in the elastic dipole tensors [15];
- (iv) specific heat data [16]; and
- (v) the unexpected absolute rates and isotope effects in diffusion data which are discussed now.

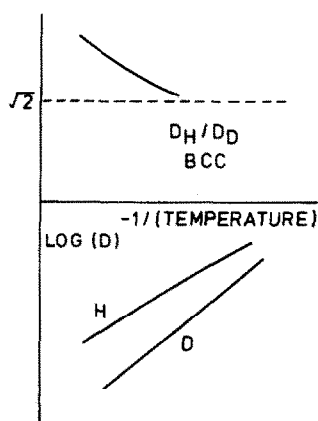


Fig. 4. Schematic illustration of isotope effects in bcc metals like V, Nb and Ta.

The most probable interpretation of the mechanism of H diffusion in bcc hosts is that of Flynn and Stoneham [6], who argued that the diffusion rate is determined by the inertia associated with lattice distortion by the interstitial hydrogen. This mechanism is illustrated in fig. 1. The evidence is summarized by Stoneham [2]; further support comes from the detailed studies of hydrogen trapped by O or N in Nb [8]. However, in its simplest form, the theory predicts two results at variance with experiment: it suggests a larger activation energy for hydrogen than deuterium, and it suggests a strong mass dependence for the pre-exponential factor.

One way out of the anomalies is to assume [14] that the interstitial is not located at a single interstitial site but, because of its zero-point motion, tunnels rapidly between a group of (possibly inequivalent) sites, making diffusive jumps between groups. An example for a two-dimensional lattice is shown in fig. 5; note that certain sites may be shared between groups. This model solves most of the problems, at least qualitatively. It has some direct backing for Nb from specific heat data [16] and also from neutron data [26], in that the hydrogen seems to be confined mainly but not solely to the tetrahedral sites. Recent calculations for V : H [27] also suggest a multiwell structure of much the sort required.

Since many details remain to be sorted out, it is probably most useful to show how the right qualitative isotope effect could arise without disturbing the agreement already achieved. First, consider the pre-exponent-

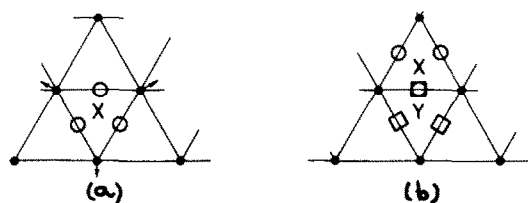


Fig. 5. (a) Example of an interstitial centred at X but spending most of its time at the inequivalent sites \circ . The local lattice distortion is indicated roughly. (b) Example of a diffusive jump between two adjacent sites X and Y for a system like that in (a). Lattice distortions are not shown. Note that one subsidiary minimum is common to both sites X (involving \circ) and Y (involving \square).

ial factor. This depends on the overlap of the hydrogen vibrational wavefunctions on the initial and final sites. If these were simple harmonic wavefunctions associated with a single interstitial site, the absolute rates would be far too small and there would be a large isotope effect. Suppose instead that, even at absolute zero, hydrogen divides its time between N sites tunnelling between the members of one group of N sites, and making occasional jumps to another group. One possibility giving an isotope-independent pre-exponential factor is this. If one of the N sites is shared between adjacent groups [as in fig. 5(b)] then the pre-exponential factor will be dominated by that site and depend on N and not significantly on the isotope. Secondly, consider the activation energy. This depends on the lattice distortion produced by the interstitial. Again, the isotope effect [28,31] is different from what one would expect from the simplest arguments. The accuracy of the measurements is limited, but the distortion and activation energy results may well be consistent. Thus, the problem is why these effects are apposite from what one expects (see [6,29]) from arguing that the distortion is larger when the zero-point motion is larger. The answer is not clear, at least partly because the tunnelling motions assumed are so complex that no simple isotope dependence can be anticipated with confidence. Anomalous isotope effects are indeed seen in analogous but better characterized systems like KCl : Li [30]. One could argue that the isotope effect comes instead from diffusion by excitation to excited states, as suggested especially by Sussmann [4], although this does not work very well in detail and does not seem consistent with heat of transport data [12]. Or one could argue that, whilst the Flynn–Stoneham picture is basi-

cally correct, there are simplifications in detail which are important in a feature as complex as the isotope dependence. In particular, the assumption that the transition matrix element does not depend on the lattice geometry (Condon approximation) may break down, or the excited states may be involved in a variety of subtle ways.

5.2. Hydrogen in fcc metals

The diffusion behaviour in fcc metals is quite different from the bcc case. This (e.g. refs. [2,4,6]) is mainly a fairly natural consequence of the lattice structures. The isotope effect differs in having these three characteristics (fig. 6). First, deuterium diffuses faster than hydrogen below a certain temperature. Secondly, the pre-exponential factors show roughly the classical $M^{-1/2}$ dependence, notably for Ni and Cu; Pd may be anomalous, in that tritium does not seem to follow the trends for H or D. Thirdly, the activation energy for hydrogen is larger than that for deuterium; again, tritium in Pd may be anomalous.

As usual, a unique explanation is lacking. Simple classical descriptions with quantum statistics only are adequate for solubility and diffusion data for hydrogen in Cu, but less so for Ni and still less for Pd. Such semi-classical descriptions seem inadequate for the isotope dependence of effective charges and heats of transport [12,31]. In the alternative Flynn–Stoneham theory, the transition probability depends on certain transition

matrix elements. These matrix elements are of the order of a vibrational energy (which depends on the isotope and is larger for lighter isotopes) and a factor which represents the influence of the atoms straddling the jump path. The activation energy is dominated by the lattice energy required to move these atoms apart by a critical distance for the matrix element to become large. Without detailed interatomic potentials, it is hard to say what isotope effect to expect, although one might expect it to give a lower activation energy for the lighter isotope, contrary to observation. To explain the observed effect one is forced to assume either (i) that it is the stronger isotope effect of the modest polaron contribution [section 3.2(a)] to the activation energy which dominates, or (ii) that the self-trapping lattice distortion caused by the zero-point motion (which is more for lighter isotopes) affects the critical distances by which the atoms straddling the jump path must move so as to give the effect observed.

6. Final comments

The explanation of isotope effects in hydrogen diffusion has certainly not been settled in the last few years. Indeed, there are now even more results needing explanation, ranging over phenomena from effective charges and heats of transport to phase diagrams. As observed in [2], the root of the difficulty in finding an explanation lies partly in the complex mixture of possible effects and partly in our lack of detailed knowledge of the hydrogen–metal interactions. Recent theory ([27] and [32]) shows promise for this second aspect, and one can be a little more optimistic that theory with continued experiment will clarify the basic mechanisms.

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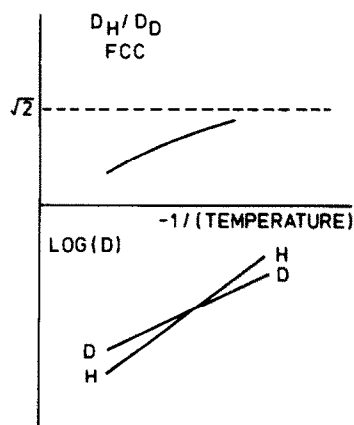


Fig. 6. Schematic illustration of isotope effects in fcc metals like Cu, Ni and Pd.

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Discussion

R.A. Johnson: The classical picture of a migration jump is that of a local vibrational mode by which the saddle-point configuration is attained. The transition probability is related to a barrier height by being proportional to a Boltzmann factor $e^{-E/kT}$. (1) Can we somewhat similarly think of the quantum picture for both the direct and the lattice activated mechanisms as a local vibrational mode by which the appropriate conditions for a tunneling transition are attained? (2) Is the quantum transition probability proportional to the integrated probability of a Boltzmann factor $e^{-E_i/kT}$ times the probability of tunneling at energy E_i ?

A.M. Stoneham: (1) There is an analogy of the sort you mention. One can think of a mode of distortion of the host lattice atoms (and not of the local mode of vibration of the light interstitial) by which appropriate conditions for tunneling are obtained. (2) The quantum transition probability is indeed proportional to an appropriately weighted product of a Boltzmann factor and a tunneling probability for the corresponding energy E_i . Here, the energy is the host lattice strain energy required to produce appropriate conditions for tunneling.

The main difference between the coordinates in the present quantal case and the usual classical case is this: in the classical case the local coordinate is roughly the coordinate of the diffusing particle; in the quantal case the only positions of the host atoms are involved in the local coordinate.

M. Doyama: I just want to point out the similarity between a hydrogen atom and a positron or a positive muon. Your calculation is probably quite applicable to those particles.

A.M. Stoneham: I agree.