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LETTER TO THE EDITOR

Quantum diffusion in FCC metals

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Abstract. The functions governing the temperature dependence of small-polaron diffusion are calculated to high accuracy for octahedral interstitials in Cu, Pd, Ni and Pt hosts. The experimental data on the diffusion of positive muons in copper at $80\ \mathrm{K} < T < 300\ \mathrm{K}$ are analysed on the basis of these results. Excellent agreement with experiment is obtained. The diffusive regime occurring below 80 K, which is of a very different nature, is not analysed because the existing theories do not allow for realistic calculations yet.

The particularly high mobility of hydrogen and its isotopes in certain metals suggests that quantum effects take place in the migration of the defects [1]. In the quantum theory of diffusion the interstitial particle jumps between adjacent preferred sites in the crystal by tunnelling through the potential barrier separating them. The motions of the crystal ions make the potential barriers dynamical objects, and play then an essential role in these microscopic transport processes [1–10]. The thermally averaged probability per unit time $\omega_{\Delta l}(T)$ of a transition between two impurity states localised in contiguous interstitial sites l and $l + \Delta l$ is proportional to the diffusion coefficient $D(T)$, related by a constant factor depending only on the geometry of the lattice. For octahedral occupancy in FCC hosts the diffusion coefficient is related to $\omega_{\Delta l}(T)$ and the mean time $\tau(T)$ for which an impurity remains in a site by

$$D(T) = a^2 \omega_{\Delta l}(T) = (a^2/12)(1/\tau(T)). \tag{1}$$

where a is the lattice parameter.

The temperature dependent rate $\omega_{\Delta l}(T)$ of phonon-assisted tunnelling hopping of a self-trapped interstitial impurity has been calculated in the context of the small-polaron theory, and explicit expressions for the temperature dependent diffusivity $D(T)$ are available in the literature [1–10]. The validity of the small-polaron theory, which in its traditional version resorts to the Condon approximation and Born–Oppenheimer separation of crystal and impurity variables [2], for the diffusion of massive interstitials has been questioned. However, the refinement of the theory in order to make it applicable to the transport of atomic species [10] leads to the conclusion that, as long as the impurity states are well localised and the coupling between the impurity and crystal

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variables is linear in the ionic displacements, the main correction reduces to multiplying the small-polaron diffusivity by a constant factor [11]. On this basis one has [10, 11]

$$D(T) = (D_0/\sqrt{f(T)})\exp(E_a/k_B f(T)) \tag{2}$$

where

$$E_a = F^2 \sum_q \frac{\sin^2(\frac{1}{2}\boldsymbol{q}\cdot\Delta\boldsymbol{l})}{2MN\omega_q^2}\left|\sum_L e^{i\boldsymbol{q}\cdot\boldsymbol{L}}\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{e}}_q\right|^2 \tag{3}$$

and $f(T)$ is an auxiliary function of T whose explicit form depends only on the crystal structure and dynamics. It is given by

$$f(T) = \frac{\hbar F^2}{2k_B E_a}\sum_q \frac{\sin^2(\frac{1}{2}\boldsymbol{q}\cdot\Delta\boldsymbol{l})}{2MN\omega_q}\left|\sum_L e^{i\boldsymbol{q}\cdot\boldsymbol{L}}\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{e}}_q\right|^2 \coth\left(\frac{\hbar\omega_q}{2k_B T}\right) \tag{4}$$

where $q = (\mu, \boldsymbol{q})$ characterises the crystal mode of the branch μ, wave vector $\boldsymbol{q}$, frequency ω_q and polarisation vector $\hat{\boldsymbol{e}}_q$, and $l = (\alpha, \boldsymbol{l})$ labels an impurity state of band index α localised in the interstitial site $\boldsymbol{l}$. Vectors $\boldsymbol{L}$ connect an interstitial position with the neighbouring ionic sites and $\Delta\boldsymbol{l}$ connects two adjacent interstices. The forces exerted by the interstitial impurity on the neighbouring crystal ions are assumed central, and their strength is denoted by F.

The equations for E_a and $f(T)$ written above follow from assuming that the conduction electrons interact adiabatically with the impurity and the crystal ions. They also incorporate a fractional error of [8–11]

$$\eta = (k_B\Theta_D^2/\pi^2 E_a f(0)) \tag{5}$$

which comes from approximations made in the mathematical steps preceding the final result (2). As long as $\eta \ll 1$, equations (2), (3) and (4) remain valid down to $T = 0$.

In most cases of interest $\eta < 0.01$ and, provided that the electrons behave adiabatically, equations (2)–(4) are expected to describe well the quantum contribution to the diffusion of light interstitials. The point is whether this contribution actually predominates over the one produced by classical over-barrier jumps in specific systems and whether the adiabatic response of the electrons does prevail. For $T > \Theta_D/2$, where Θ_D is the Debye temperature of the host crystal, $f(T)$ becomes proportional to T and (2) takes the form of an activated Arrhenius law with effective activation energy E_a. Most experiments are in this range of temperatures and the quantum or classical nature of the underlying microscopic processes does not emerge directly from the data. However, the effective activation energy E_a is expected to be smaller than the barrier heights between interstices, and the observation of small slopes in the Arrhenius diagram of the diffusivity data has been taken as indicative that the quantum mechanism dominates the diffusion [12].

It is widely accepted that at $T < 250$ K the transport of hydrogen and its isotopes in the BCC metals Ta, Nb and V, for which $E_a < 70$ meV, proceeds by phonon-assisted tunnelling [12]. The situation for the FCC metals is quite different. Diffusion of hydrogen in Pd, Cu and Ni has effective activation energies of about 230, 403 and 408 meV, respectively, and seems to be classical [1]. However, experiments show that the migration of positive muons in Cu differs substantially from that of hydrogen and its isotopes. Gurevich *et al* [13] report $E_a = 46$ meV for the diffusion of positive muons in copper at 77 K $< T <$ 300 K, i.e. ten times smaller than the effective activation energy for protons. The quantum nature of the diffusion of the muons, which in this context are

light hydrogen isotopes, in Cu up to room temperature seems apparent. The same conclusion may be expected to apply to other FCC metals.

However, experimental [14] and theoretical [15–19] evidence for μ^+ in Cu show that below 90–100 K the electrons cease to respond adiabatically, which determines the breakdown of the equations written above. The onset of this low-temperature regime seems connected with the tendency of the impurity states localised in different sites to develop coherence when the thermal disorder of the lattice is reduced. The electronic drag frustrates the free propagation of the muons and the system goes through a new diffusive regime. Though this explanation has proven to fit the experimental data fairly well [14, 16] the theory is not developed enough to allow realistic calculations for specific systems.

In this letter we focus on the small-polaron regime and report accurate calculations of the functions $f(T)$ governing the temperature dependence of the diffusion coefficient together with the ratios E_a/F^2 for Cu, Pd, Ni and Pt. Knowledge of the ratio E_a/F^2 may be of practical interest because it allows one to obtain the force that the impurity exerts on the neighbouring ions from the value of E_a which fits the diffusion data. The force F can be obtained independently from diffraction experiments measuring the local distortions caused by the defects. Though these studies are generally less precise they are useful to test the theory by comparing results. We use our results to fit the experimental data on the mean time $\tau(T)$ spent by a positive muon in an octahedral interstice of Cu [20].

Tables 1 and 2 show our results for $f(T)$ and E_a/F^2. They were obtained by introducing the normal modes of Cu, Pd, Ni and Pt in (3) and (4) and integrating over the Brillouin zone. The vibrational modes were obtained from a general force model for the lattice dynamics, considering up to eighth-nearest neighbours, and with the force constants obtained by Nilsson and Rolandson [21], Miiller and Brockhouse [22], Birgenau *et al* [23] and Dutton *et al* [24] from neutron scattering experiments.

The integration over the Brillouin zone is in general the main source of numerical errors, and the most computer-time-consuming stage of the calculation. The computations of the frequency and polarisation vectors of the crystal modes are performed with negligible numerical error. The integrals over the Brillouin zone were accomplished with the method of Chadi and Cohen [25]. The results shown in tables 1 and 2 were obtained from the fifth set of special points of Chadi and Cohen [25], which assigns 2992 points to each 1/48 of the Brillouin zone. Practically no difference was found between the results of integrating with the fourth and fifth sets of special points, which ensures that no significant error was introduced by the numerical integrations. The static lattice Green functions for Cu, Pd, Ni and Pt were also calculated in order to compare with the corresponding results published previously by MacGillivray and Sholl [26] using the fifth set. Very good agreement was obtained. The calculation of $f(T)$ for 200 values of T took about three hours in an APOLLO 3500 work station.

Figure 1 shows the $1/\tau(T)$ data [20] for positive muons in Cu together with the fit given by the equation

$$1/\tau(T) = (A/\sqrt{f(T)}) \exp(-E_a/k_B f(T)). \tag{6}$$

with $f(T)$ taken from table 1. The parameters A and E_a were varied in order to adjust to the experimental values. Their values are listed in table 3. The fit to the three curves, which correspond to orientations of the external magnetic field along three crystallographic symmetry directions, is remarkable.

Table 1. Values of $f(T)$ for Pd, Cu, Ni and Pt.

	$f(T)$ (K)			
T (K)	Pd	Cu	Ni	Pt
0	134.94	149.02	179.35	111.14
10	134.94	149.02	179.35	111.14
20	134.95	149.03	179.35	111.17
30	135.05	149.07	179.36	111.46
40	135.50	149.34	179.45	112.47
50	136.63	150.09	179.77	114.51
60	138.65	151.58	180.53	117.67
70	141.60	153.90	181.90	121.86
80	145.44	157.09	183.96	126.94
90	150.08	161.07	186.75	132.77
100	155.41	165.78	190.24	139.21
110	161.34	171.11	194.38	146.15
120	167.77	176.99	199.11	153.51
130	174.63	183.34	204.38	161.20
140	181.85	190.09	210.11	169.18
150	189.37	197.18	216.26	177.39
160	197.15	204.58	222.77	185.81
170	205.16	212.23	229.60	194.38
180	213.37	220.10	236.71	203.11
190	221.74	228.17	244.07	211.96
200	230.26	236.41	251.66	220.91
210	238.90	244.80	259.44	229.96
220	247.66	253.32	267.39	239.08
230	256.52	261.95	275.50	248.28
240	265.46	270.69	283.75	257.55
250	274.49	279.53	292.12	266.87
260	283.58	288.45	300.61	276.24
270	292.74	297.44	309.19	285.65
280	301.96	306.50	317.87	295.11

Table 2. Ratio between the effective activation energy E_a for small-polaron diffusion of octahedral impurities and the square of the force F exerted by the defects on the nearest ions.

Crystal	E_a/F^2 (erg dyn^{-2})
Pd	6.599×10^{-6}
Cu	9.129×10^{-6}
Ni	6.855×10^{-6}
Pt	5.258×10^{-6}

The average of E_a for the three orientations of the field turns out to be $\bar{E}_a = 133$ meV. Making use of table 2 one obtains that the force exerted by an interstitial muon on the neighbouring Cu ions is $F = 1.53 \times 10^{-4}$ dyn. From the static lattice Green functions tabulated by MacGillivray and Sholl [26] one has $\delta = 9.98 \times 10^{-5} F$ (cgs units), where δ is the shift of the Cu ion closest to the octahedral interstitial position. In our case it

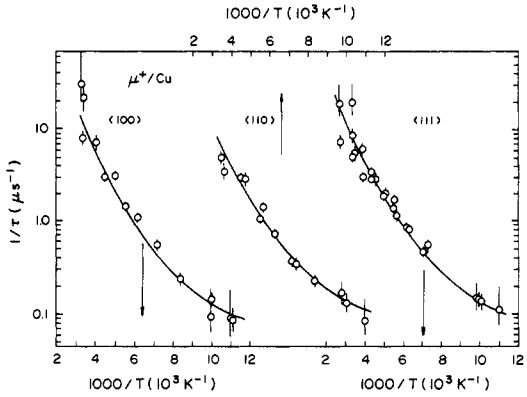

Figure 1. Inverse of the mean time τ spent by a positive muon in an octahedral site of Cu for external magnetic fields along the crystallographic directions ⟨100⟩, ⟨110⟩ and ⟨111⟩. The open circles represent the experimental data of [20]. The full curve is the fit given by (6) with $f(T)$ taken from table 1 and the parameters of table 3.

Table 3. Parameters for (6) giving the fit shown in figure 1 to the data of [20].

Direction	E_a (meV)	A ($\mu s^{-1} K^{1/2}$)
⟨100⟩	143	3.85×10^{-4}
⟨110⟩	125	1.23×10^{-4}
⟨111⟩	132	1.89×10^{-4}

turns out to be $\delta = 0.15$ Å. This corresponds to a displacement of 8% from the muon, which compares reasonably well with the experimental value of Camani *et al* [27].

Replacing $\bar{E}_a$ and $f(0) = 149$ K in (5) one obtains $\eta = 0.003$, i.e. negligible error down to $T = 0$. This marks an important difference from a previous analysis of the data of Schilling *et al* [20] on the basis of an older treatment of the small-polaron diffusion [5] which rapidly loses accuracy for $T < \Theta_D/2$ [8, 9]. Equations (2)–(4) constitute a much more reliable tool for the interpretation of the data.

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