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THEORY OF DELOCALIZATION AND QUANTUM DIFFUSION OF MUONIUM IN INSULATORS

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Abstract

It is shown that in insulators, muonium should delocalize into Bloch waves up to quite high temperatures, of order $70^{o}K$. The dissipative coupling to Debye phonons will give a long-time stochastic behavior, and a microscopic theory quantitatively explains the puzzling T^{-3} behavior observed for the quantum diffusion coefficient at intermediate temperatures, in recent experiments in KCl. The theory is generally applicable to particle motion in the presence of a phonon heat bath.

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A particle coupled to some background "thermal bath" will make a transition at low temperature from classical to quantum behavior, provided the coupling is weak enough. The details of this transition, particularly where the quantum motion involves tunneling, have interested theorists for decades, beginning with studies of polarons[1] and continuing with the much heavier muon. Most attention, however, has been devoted to the case where the particle is "*ohmically*" coupled to background electrons – this coupling has a strong inhibitory effect on tunneling, and can even suppress it altogether.[2–4] Experiments on muonium diffusion in Cu and Al are in good agreement with these theories.[5]

Clearly, to enhance the quantum behavior it is necessary to remove the electrons, and this has been done very recently in experiments[6] on muonium (μ^+e^-) in KCl insulator. This leaves only the coupling to phonons, and previous theory for this case has indicated either a T^{-9} dependence of the muon diffusion coefficient D (coming from 2-phonon processes[7]) or an $\exp(-\hbar W/kT)$ dependence (coming from one-phonon processes [8]); here $W(T)$ is imagined to be a muonium bandwidth. However the experiments give a completely different result;[9] at intermediate temperatures, ($10^oK \leq T \leq 70^oK$), $D \sim T^{-3}$, apparently beginning to flatten off for $T \leq 10^oK$.

Thus theory and experiment seem in complete disagreement. In this letter we resolve this disagreement, and give a quantitative theory of the diffusion, with no adjustable parameters, which agrees very well with the experiments. We also show that the observed diffusion rates must be interpreted rather differently from what is usually thought.

A crucial insight into the question is obtained by studying the related a problem of particle tunneling between two wells whilst coupled to a phonon bath, for which the Hamiltonian is

$$H = \frac{1}{2}M\dot{\underline{R}}^2 + V(\underline{R}) + \sum_{\underline{q}} \hbar\omega_{\underline{q}}\left(\alpha_{\underline{q}}^\dagger \alpha_{\underline{q}} + \frac{1}{2}\right) + \frac{1}{2}\sum_{\underline{q}} \frac{M_q}{\omega_q} e^{i\underline{q}\cdot\underline{R}}(\alpha_{\underline{q}} - \alpha_{\underline{q}}^\dagger) \tag{1}$$

coupling the muonium coordinate $\underline{R}(t)$ to Debye phonons via the matrix M_q. In (1) we assume the high frequency effects of optical phonons have already been incorporated into the renormalization of M, $V(\underline{R})$ and $M_{\underline{q}}$ (and counter terms are not written explicitly). Now this problem can be mapped by standard methods[2] on to a two-level system coupled to phonons, *provided* the level splitting $\tilde{\Delta}$, and temperature T, are both $\ll \hbar\Theta_D$, the Debye energy, and also $\ll \tilde{E}_a$, the activation energy over the barrier (for KCl, $\Theta_D \sim 231^oK$ and $\tilde{E}_a \sim 390^oK$). These conditions obtain for $T \leq 70^oK$, where the puzzling T^{-3} behavior occurs.

The time-dependence $\underline{R}(t)$ may be calculated in this two-well problem using the "*dilute-blip*" approximation[2], and one finds for the "*return probability*" $P(t)$ to the initial starting well after t to be

$$P(t) = e^{-\Gamma(T)t}\cos(\tilde{\Delta}(T)t) \tag{2}$$

$$\Gamma(T) = \frac{\pi}{2}\gamma\Theta_D\left(\frac{\tilde{\Delta}(T)}{\Theta_D}\right)^3 \coth\left[\frac{\hbar\tilde{\Delta}(T)}{2kT}\right] \tag{3}$$

$$\tilde{\Delta}(T) = \tilde{\Delta}_o \exp\left\{-4\gamma\left(\frac{kT}{\hbar\Theta_D}\right)^2 \int_0^{\hbar\Theta_D/kT} \frac{x\,dx}{e^x - 1}\right\} \tag{4}$$

where the $T = 0$ values are given by $\Gamma_0 = (\pi/2)\gamma\Theta_D(\tilde{\Delta}_0/\Theta_D)^3$, and $\tilde{\Delta}_0 = \Delta_0 e^{-\gamma}$, where

$$\gamma = \frac{1}{4}\sum_{\underline{q}} \frac{|M_q|^2}{\omega_q^2}(1 - \cos \underline{q} \cdot \underline{a}_o) \tag{5}$$

is the usual Debye-Waller factor, (with a_o the lattice spacing) and $\omega_q = cq$. For KCl, $\gamma \sim 0.85$; and we shall find that for muonium, $\hbar\tilde{\Delta}_o \sim 9.85^oK$, so that $\hbar\Gamma_o \sim 0.0239^oK$. Note that also for KCl, $|M_q|^2 \approx (10/3)\tilde{E}_a\omega_q$ in Debye approximation.

A complete analysis of (2)-(4) is lengthy, but the important features are rather simple. For $0 < T < 70^oK$, $\tilde{\Delta}(T)$ hardly varies, its leading temperature dependence being $\tilde{\Delta}(T) \sim \Delta_o[1 - (2\gamma/15)(kT/\hbar\Theta_D)^2]$. For $kT \leq \hbar\tilde{\Delta}_o$, the damping $\Gamma(T)$ is roughly constant, varying as $\Gamma(T) \sim \Gamma_o[1 + 2\exp(-\hbar\tilde{\Delta}_o/kT)]$. In Fig.1 we show the behavior of $\Gamma(T)$ and $\tilde{\Delta}(T)$ for $T \leq 70^oK$, alongside the experimental data. It must be emphasized that $\tilde{\Delta}_o$ in these plots is not obtained by fitting to the low-T data, but is extracted from the quite separate high-T data (see below). It is thus encouraging to see the apparent low-T convergence of the measured ν, extracted from the data, to our $\tilde{\Delta}_o$.

Now from Fig.1 we see that at low and intermediate $T \leq 70^oK$, $\Gamma(T)/\tilde{\Delta}(T) \ll 1$. Thus we are in the regime of ***very weak damping***, and so the muonium motion in this region is Bloch coherent hopping, with only occasional absorption and emission of phonons. Moreover, since $\tilde{\Delta}_o$ is not small, we expect single phonon absorption/emission processes to be of overriding importance. These two conclusions are quite different from previous work.[7,8]

However these results also pose a paradox – why should the rate ν extracted from experiments fall off so steeply for $T > 10^oK$, when[10] $\tilde{\Delta}(T)$ varies so slowly? The crucial point is that the experiments are apparently not measuring the inter-site hopping rate at all (except for $kT \ll \hbar\tilde{\Delta}_o$, or else for high temperatures when we have incoherent thermal-activated hopping between sites). The low and intermediate-T coherent hopping proceeds at a frequency $\sim v/a_o$, with the muonium velocity $v \sim O(a_o\tilde{\Delta}(T))$; however $v(t)$ *changes* after each muonium-phonon interaction, so that these high-frequency ($\sim \tilde{\Delta}_o$) parts of ν will be washed out[11] in the experiment except for $T \ll \tilde{\Delta}_o$. Here the observed $\nu(T)$ will arise from the much less frequent muonium-phonon interactions, which are responsible for the long-time "*quantum diffusive*" evolution of the muonium coordinate (more strictly, of its density matrix).

We now show, by putting this picture on a quantitative basis, that is agrees remarkably well with experiment. We start with a *band* picture for the muonium (justified by the above calculations), with tight-binding spectrum (at $T = 0$) of[10]

$$\epsilon_{\underline{k}} = 2\tilde{\Delta}_o(\cos k_x a_o + \cos k_y a_o + \cos k_z a_o) \tag{6}$$

Then the reduced density matrix $\rho^{(\mu)}_{\underline{k},\underline{k}+\underline{q}}(t)$ for the muonium (after integrating out the phonons) obeys the equation

$$i\frac{\partial \rho^{(\mu)}_{\underline{k},\underline{k}+\underline{q}}}{\partial t} = [H_0, \rho^{(\mu)}]_{\underline{k},\underline{k}+\underline{q}} + I_{\underline{k},\underline{k}+\underline{q}}, \tag{7}$$

where H_O excludes nondiagonal phonon processes (diagonal ones are already absorbed into $\tilde{\Delta}_o$), and $I_{\underline{k},\underline{k}+\underline{q}}$ is the muonium-phonon collision integral. The general form of $I_{\underline{k},\underline{k}+\underline{q}}$ for single muonium-phonon processes is[12]

$$I_{\underline{k},\underline{k}'} = \pi \sum_{\alpha,\beta} \sum_{\underline{k}_1,\underline{k}_2} \rho^{\alpha}_{ph} \delta(\epsilon_{\underline{k}_1} + \Omega_\alpha - \epsilon_{\underline{k}_2} - \Omega_\beta) \left\{ V^{\alpha\beta}_{\underline{k}_1,\underline{k}_2} V^{\beta\alpha}_{\underline{k}_2,\underline{k}'} \rho^{(\mu)}_{\underline{k},\underline{k}_1} + V^{\alpha\beta}_{\underline{k},\underline{k}_2} V^{\beta\alpha}_{\underline{k}_2,\underline{k}_1} \rho^{(\mu)}_{\underline{k}_1,\underline{k}'} \right\} \tag{8}$$

in the Born approximation, where the total density matrix $\rho(t) \sim \rho^{(\mu)}(t)\rho_{ph}$, and ρ_{ph} is the phonon density matrix in thermal equilibrium. The term in (8) is much larger than that coming from two-phonon processes[7] because $\tilde{\Delta}_o$ is not small. Using $V^{\alpha\beta}_{\underline{k},\underline{k}'} = M_q \delta(\underline{k} - \underline{k}' - \underline{q})$ and $\Omega_\alpha - \Omega_\beta = \hbar\omega_q$, we then find

$$I_{\underline{k},\underline{k}+\underline{q}} = \pi \left(\tau^{-1}_{\underline{k}+\underline{q}} + \tau^{-1}_{\underline{k}} \right) \rho^{(\mu)}_{\underline{k},\underline{k}+\underline{q}} \tag{9}$$

$$\tau^{-1}_{\underline{k}} = \pi \sum_{\underline{q}} |M_q|^2 \rho_{ph} \delta(\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} - \hbar\omega_q) \tag{10}$$

Now in the high temperature limit (Arrhenius) limit, the incoherent thermal over-barrier-hopping motion is described by a stochastic thermal diffusion coefficient $D_T(T) = a_o^2 \nu_T(T)$. The evaluation of $\nu_T(T)$ is standard and gives

$$\nu_T(T) = \left(\frac{\pi}{4\hbar^2 \tilde{E}_a T} \right)^{1/2} \tilde{\Delta}_o^2 \exp\left\{ -\frac{\tilde{E}_a}{T} \right\}. \tag{11}$$

As mentioned above, this equation, when fitted to the high-temperature data of Ref.6, gives a best fit for $\tilde{\Delta}_o \approx 9.85^o K$.

At low and intermediate T the muonium tunnels over long distances as a Bloch wave, in between phonon interactions. Nevertheless, as described above, this behavior will appear as (quantum) diffusion over long times, and can then be described by a quantum diffusion coefficient $D_Q(T) = a_o^2 \nu_Q(T)$. The *rate* $\nu_Q(T)$ is then given as in the usual low-T fermion-phonon interaction by

$$\nu_Q(T) = \frac{1}{3} \tilde{\Delta}_o^2 \gamma^{-1}(T) \tag{12}$$

$$\gamma(T) = 12\pi^2 A \frac{\tilde{E}_a}{\hbar} \left(\frac{kT}{\hbar\Theta} \right)^3 \int_0^{12\hbar\tilde{\Delta}_0/kT} \frac{x^2 dx}{e^x - 1} \tag{13}$$

where $\gamma = 2\sum_{\underline{q}} \tau^{-1}_{\underline{q}}$, and we assume $qa_o \ll 1$ for the temperature of interest (i.e., again, the $kT \ll \hbar\Theta_D$). Evaluation of the coefficient A is tedious but straightforward, giving

$$A = \frac{10}{3} \int_0^\infty dy e^{iy} \int_o^\pi \sin\theta d\theta \int_0^{2\pi} d\phi J_0(8wy \sin\theta \cos\phi) J_0(8wy \sin\theta \sin\phi) J_0(8wy \cos\theta) \tag{14}$$

where $J_0(x)$ is the Bessel function and $w = \tilde{\Delta}_o / \Theta \sim 4.3 \times 10^{-2}$.

Returning to Fig.1, we fit the data using $\nu_T(T)$ for the high-T regime, and $\nu_Q(T)$ for low and intermediate-T and interpolating between the two by summing them.

We see that for intermediate T ($10°K \leq T \leq 70°K$) the expression (12) fits the data rather well, not only giving the observed T^{-3} behavior but also the correct magnitude, using ***no adjustable parameters***. This is a strong confirmation of the theory. For $T \ll 10°K$ we expect it should be possible to distinguish the high-frequency ($\nu \sim \tilde{\Delta}_o$) motion from the low-frequency phonon scattering, and the apparent flattening off of the data for the lowest experimental temperatures may indicate this is so. It would thus be extremely interesting if the experiments of Ref.6 could be continued to $kT \ll \hbar\tilde{\Delta}_o$.

Summarizing, we have shown that a theory of muonium dynamics in KCl insulators need only involve one-phonon interactions with the muonium, and that at temperature $kT \ll \hbar\Theta_D$ the muonium motion is essentially Bloch-like, with diffusion over long times arising from phonon interactions. A quantitative theory agrees very well with the data, provided one realizes that the quantum diffusion rate ν_Q extracted from this data is not an intersite hopping rate, but a measure of the stochastic diffusion induced by the muon-phonon interaction.

Finally, a brief word on the generality of these results is in order. In principle, they should be applicable to the motion of any object moving through a phonon heat-bath on a lattice. This of course makes them relevant to a large variety of systems. But we should add one cautionary note – we have assumed that the particle is in thermal equilibrium with the heat bath. Whilst this is almost certainly true for the KCl case we have studied, it may not be at much lower temperatures. Work on this question is in progress.

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9. In Ref.8, a T^{-3} term is derived for very low temperatures ($kT \ll \hbar\tilde{\Delta}_o$); this also disagrees with our result. Experiments have yet to probe this regime.

10. One should not assume the bandwidth $W(T)$ is equivalent to the $\tilde{\Delta}(T)$ of the two-level problem. or that the muonium-phonon scattering rate is given by $\Gamma(T)$, for band muonium. Although these quantities are similar for low damping, they are not the same. The correct calculation of the band properties is given below. Note, however, that in Eq.(6), we have written the $T = 0$ bandwidth $W_0 \equiv \tilde{\Delta}_0$; the damping is so small here that this a good approximation.

11. A detailed verification of this picture will require the highly non-trivial calculation of the tunneling of a particle in a 3-d lattice of potential wells, in the presence of phonons. This calculation is under way.

12. A cross-term in (8) is ignored – it is negligible in this problem.

Figure Caption

Fig.1. Plots, as a function of temperature, of (i) the temperature dependent "*level-splitting*" $\tilde{\Delta}(T)$, (ii) the temperature dependent damping $\Gamma(T)$, for the two-level problem, and (iii) the data from Ref.6, with a fit from our theory (solid line). All quantities are shown as frequencies – see text for details.

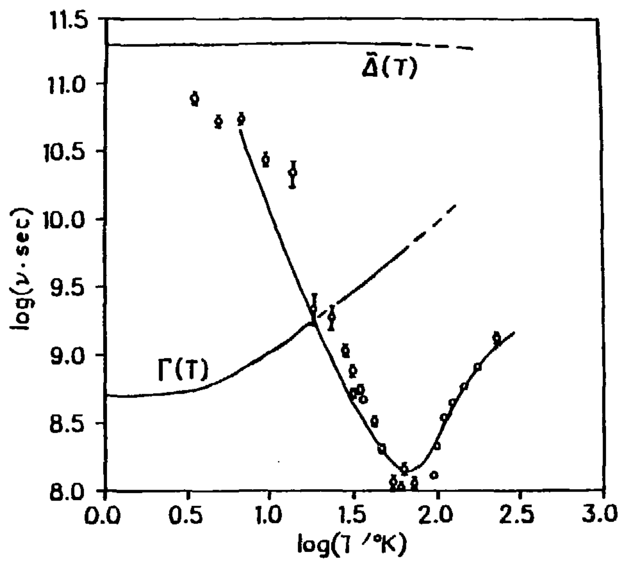

Fig. 1