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Theoretical Description of Muonium Depolarization in KCl

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Abstract

The spin dynamics of muonium in potassium chloride (KCl) at room temperature is investigated theoretically. The predictions obtained by solving a master equation for the muonium spin system are compared to recent muon spin rotation measurements in transverse and longitudinal field. Information about the mobility of muonium, its coupling to the magnetic moments of the host, and its chemical lifetime is obtained.

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I. Introduction

The positive muon is used extensively as a probe in solid–state physics and chemistry. In insulators, semiconductors, and liquids the muon may bind an electron to form a one–electron atom, called muonium (Mu), which can be studied by measuring the time dependence of the muon spin polarization.[1] Muonium is a light hydrogen–like atom; its small mass ($m_\mu = 1/9\ m_p$) causes a higher zero point motion amplitude and usually leads to a higher diffusion rate. Due to the the similarity between muonium and hydrogen, μSR (muon– spin–rotation) experiments often complement ESR (electron–spin–resonance) data.

In the presence of an external field $\vec{B}$ the magnetic interactions of a muonium atom in its ground state are given by the spin Hamiltonian

$$H_{Mu} = A\vec{S}_\mu \cdot \vec{S}_e + \gamma_e \vec{S}_e \cdot \vec{B} + \gamma_\mu \vec{S}_\mu \cdot \vec{B}. \tag{1.1}$$

This Hamiltonian can be diagonalized analytically.[2] The four eigenvalues are given by

$$\begin{aligned} E_1/h &= \nu_1 = \nu_0/4 + \Gamma B/2 - \gamma_\mu B, \\ E_3/h &= \nu_3 = \nu_0/4 - \Gamma B/2 + \gamma_\mu B, \\ E_{2,4}/h &= \nu_{2,4} = -\nu_0/4 \pm \frac{\left(\nu_0^2 + \Gamma^2 B^2\right)^{1/2}}{2}, \end{aligned} \tag{1.2}$$

where $\nu_0 = A/h$ and $\Gamma = (\gamma_e - \gamma_\mu)/h$.

In a μSR experiment where the μ^+ polarization is initially parallel to the applied field, (longitudinal field–LF case) one then obtains :

$$P_\mu^{\parallel}(t) = (1-\alpha) + \alpha \cos \omega_{24} t, \tag{1.3}$$

where $\omega_{24} = 2\pi(E_2 - E_4)/h$ and $\alpha = \nu_0^2/\left(2\nu_0^2 + 2\Gamma^2 B^2\right)$.
In the transverse field (TF) case the initial polarization is perpendicular to the applied field, and one gets

$$\begin{aligned} P_\mu^{\perp} = \frac{1}{2}\big[&\cos^2\beta\,(\cos\omega_{21}t + \cos\omega_{43}t) \\ &+ \sin^2\beta\,(\cos\omega_{41}t + \cos\omega_{23}t)\big], \end{aligned} \tag{1.4}$$

where $\tan(2\beta) = \nu_0/\Gamma B$ and $\omega_{ij} = 2\pi(E_i - E_j)/h$.

In a typical solid muonium is surrounded by atoms with non–zero magnetic moments, which results in a nuclear hyperfine (nhf) broadening of the observed μSR signals. This broadening has limited the study of Mu in the alkali halides to longitudinal field quenching experiments ,[3] until a new technique was developed, which allows the observation of muonium precession frequencies in high transverse field (TF) where the nhf interaction is quenched. [4]

Recently both the longitudinal quenching method [5] and the new TF technique [6] have been applied to study potassium chloride (KCl) and potassium bromide (KBr) at various temperatures. Since the experiments were carried out independently, no common analysis of all the data has been given until now. From the field dependence of the relaxation rates in high TF it was possible to deduce that muonium is diffusing rapidly. [6] On the other hand the quenching curves in longitudinal field were fitted by assuming that the muonium state seen in TF is preceded by another short lived muonium state with a reduced hf–coupling.[5] In the last case, in order to get a good fit, it was also necessary to introduce electron spin exchange mechanisms à la Ivanter and Smilga[3,7] in both muonium states.

In this paper we will describe these measurements using a recently developed model,[8,9] based on the construction of a *master equation* for the muonium spin system. Since at present the only available TF data are those at room temperature we will restrict ourselves to this particular case. The model used can provide information about the muonium diffusion rate, the average value for the hf coupling of Mu with its neighboring nuclear magnetic moments, and the chemical lifetime of the muonium state. The physical implications of the present description will be discussed and compared to the previous analysis.[5,6]

II. Theoretical Model

In a recent paper we showed how the theory of master equations for open systems can be applied to the description of spin relaxation processes of muonium in solids.[8] Within

this approach an equation of motion for the reduced density matrix of the Mu spin system was derived by taking into account the interaction of the bound electron with the host.

Various kinds of interactions can affect the electron spin :(1) the nhf interaction between the muonium electron and the magnetic moments of neighboring nuclei; (2) the exchange interaction of the electron with paramagnetic dopant atoms; (3) at higher temperatures collisions with charge carriers; (4) all mechanisms which lead to spin –lattice relaxation. Instead of investigating one particular microscopic interaction, we assumed that the electron spin $\vec{S}_e$ is coupled to a *random fluctuating field* $\vec{T}(t)$ which approximates the relaxation mechanisms described above. Thus, in addition to the free spin Hamiltonian (1.1), we have an interaction

$$V = \delta_{ex}\vec{S}_e \cdot \vec{T}(t). \tag{2.1}$$

This particular choice of the interaction possesses many of the features of a dipolar coupling, yet it is relatively simple to treat. The Cartesian components of the fluctuating field $T_i(t)$ $(i = x, y, z)$ are assumed to jump randomply between the two values $\pm T_i$ with a probability per unit time equal to $(2\tau_c)^{-1}$. Such a change in the field may have its origin in the diffusion of the muonium atom, in collision with charge carriers, or in the flipping of localized spins due to exchange or spin–lattice relaxation. The correlation functions between the components of $\vec{T}(t)$ are easily found to be[10]

$$\begin{aligned} c_{\kappa\lambda} &= < T_\kappa(t+\tau)T_\lambda(t) > \\ &= \delta_{\kappa\lambda} < T_\kappa^2 > e^{-|\tau|/\tau_c}, \qquad \kappa, \lambda = x, y, z. \end{aligned} \tag{2.2}$$

Assuming that the fluctuating field is isotropic

$$< T_x^2 > = < T_y^2 > = < T_z^2 > = 1, \tag{2.3}$$

the equation of motion for the density matrix of muonium, ρ_{Mu}, can be obtained[8]

$$\dot{\rho}_{Mu}(t) = \left(-iL_{Mu} + \int_0^\infty d\tau K(\tau)\right)\rho_{Mu}(t), \tag{2.4}$$

with

$$K(\tau) = \delta_{ex}^2 \sum_{\kappa,\alpha,\beta} \left(\frac{1}{\tau_c} \| + i L_{mu} \right)^{-1} F^{o\kappa} F^{\alpha\beta}, \tag{2.5}$$

and where L_{Mu} and $F^{\alpha\beta}$ are the Liouville operators corresponding to H_{Mu} and $S_\mu^\alpha S_e^\beta$ respectively.[11] Defining the muon–, electron–, and mixed polarization by

$$P_{\mu e}^{ij}(t) = Tr\left(\rho_{Mu} \sigma_\mu^i \tau_e^j\right), (i,j = 0,1,2,3), \tag{2.6}$$

one can show that the derived master equation for ρ_{Mu} is equivalent to a system of 15 coupled linear differential equations for the polarization components. The solution of this system is usually obtained by a Laplace transformation and leads to the explicit time dependence of the polarization components of interest. In general the muon polarization is given by $\vec{P}_\mu(t) = \sum_{j=1}^{15} A_j exp(\lambda_j t)$, where the A_j's are the observed amplitudes and the λ_j's are complex frequencies. In the case of free muonium ($V \equiv 0$) the λ_j's are pure imaginary and are given by the differences $i\left(E_\alpha - E_\beta\right)/h$ between the energy eigenvalues of the Hamiltonian (1.1). The introduction of irreversible relaxation processeses, as given by (2.1), leads to damping effects, i.e. to a non–vanishing real (negative) part in the λ_j's. In a typical longitudinal (transverse) μSR experiment one would then measure

$$\begin{aligned} P_\mu^{\|}(t) &= (1-\alpha) e^{-\Lambda_\| t} + \alpha e^{-\Lambda_{24}} \cos\omega_{24} \\ P_\mu^{\perp}(t) &= \frac{1}{2}\Big[\cos^2\beta \left(e^{-\Lambda_{21} t} \cos\omega_{21} t + e^{-\Lambda_{34} t} \cos\omega_{34} t \right) \\ &\qquad + \sin^2\beta \left(e^{-\Lambda_{23} t} \cos\omega_{23} t + e^{-\Lambda_{41} t} \cos\omega_{41} t \right) \Big], \end{aligned} \tag{2.7}$$

where $\Lambda_\|$,Λ_{24} ($\Lambda_{21}, \Lambda_{34}, \Lambda_{23}and\Lambda_{41}$) are the so–called parallel (transverse) relaxation rates. If the muonium atom has a finite lifetime τ_R, after which it undergoes some process, e.g. a reaction into a diamagnetic μ^+ state, all the expressions for the polarizion components have to be multiplied by a factor $\exp(-t/\tau_R)$.

Finally let us summarize what are the measured quantities that we will study in this paper. In the TF case we will be interested in the field dependence of the measured transverse relaxation rates Λ_{21} and Λ_{34} (in high field $\sin^2\beta \approx 0$ and the transitions $2 \rightarrow 3$

and $4 \rightarrow 1$ are not seen). In the longitudinal quenching experiment we will focus our attention on the residual polarization, which is given by

$$\bar{P} = \tau_R \int_0^\infty dt e^{-t/\tau_R} P_\mu^{\parallel}(t), \tag{2.6}$$

and is also measured as a function of applied field.

III. Application to KCl

In this Section the model described in Sec.II is applied to the specific case of potassium chloride (KCl) at room temperature. Assuming that the muonium hyperfine coupling ν_0 is known, the model contains only three free parameters: the interaction strength δ_{ex} between the bond electron and the stochastic field $\vec{H}(t)$, the correlation time τ_c of the fluctuating field, and the lifetime of the muonium state. The value of ν_0 in KCl at room temperature is given in Ref.(6), ($\nu_0 = 4280$ MHz). With this information we solved Eq.(2.4) explicitly and performed a *simultaneous* fit of both available measurents in KCl at room temperature: i.e. the field dependence of the transverse relaxation rates in high TF and the residual polarization $\bar{P}$ in the quenching experiment. The best fit was obtained with $\tau_c = 0.19(1)$ns, $\delta_{ex} = 60(2)$MHz, and $\tau_R = 0.50(3)\mu$s. The results are shown as solid lines in Figs.1 and 2 together with the experimental data. In Fig.2 the measured asymmetry rather than polarization is plotted versus field.[12]

The correlation time of the fluctuating field ($\tau_c = 0.19$ ns) is found to be quite small, and this indicates that muonium is rapidly diffusing in KCl at room temperature. In fact such fast fluctuations can not be explained in terms of flipping of localized spin due to exchange or spin–lattice relaxation. Qualitatively this was predicted by Baumeler et al.[6] who obtained $\tau_c = 1.1$ ns. The fact that our value is about six times smaller is not surprising if one considers that in Ref. 6 the field dependence of the measured TF relaxation rates was fitted to a simple power law ($\Lambda = k/B^n$) and the hopping time was then deduced from the value of k in the motional narrowing limit. Our model predicts a more complicated dependence of Λ on the applied field (the solid curve in Fig.1 is not a power law), and this accounts for the discrepancy in the values found for τ_c.

Physically the fact that muonium is diffusing rapidly is hardly surprising. Considering the isotope effect between Mu and hydrogen one can easily see that the ground state vibrational energy in an harmonic potential is about three times larger for muonium than it is for hydrogen. Thus the classical barrier to diffusion is smaller and the probability for tunneling larger.

The second quantity obtained from the fit is the coupling between the electron spin and the fluctuating field representing the neighboring magnetic moments. We obtain $\delta_{ex} = 60$ MHz, a value which can be compared to that for interstitial hydrogen in KCl ($\approx$ 30 MHz). [13] The couplings differ by about a factor 2, but this is due to our modelling the interaction of the elctron spin with a classical field of magnitude 1 (Eq.(2.3)). In reality the bond electron is coupled to nuclear magnetic moments, in the case of KCl mainly to nearest ^{35}Cl nuclei which have spin 3/2. Another source of difference may arise from the nhf isotope shift, which can be taken into account following the model calculation of Spaeth.[13] However this effect amounts to just a few percent. Finally the fact that the nhf interaction is usually anisotropic should not represent a major problem since during the fast diffusion process the anisotropic part of the interaction is averaged out.

The last parameter in our model is the reaction time τ_R after which muonium undergoes a chemical reaction. We obtain $\tau_R = 0.5\mu$s, which is very close to the value extracted from a recent measurement by Morozumi et al.,[14] who saw a transition from Mu to a diamagnetic product state with the same reaction time.

IV. Discussion and Conclusions

The aim of this work was to show that, at least at room temperature, all present μSR results in KCl can be explained using a single model. One problem of the master equation approach is the relative complexity in the formulation of the equation of motion for the density matrix of muonium, and the necessity of solving this equation numerically by diagonalizing a (15×15) matrix. Obviously this requires more computing time compared to a more usual fitting procedure using a simple analytical expression. In doing this,

however, one reduces the introduction of phenomenological parameters to a minimum and therefore it is possible to decribe the essential mechanisms on a more microscopic basis.

More specifically we showed that the field dependence of the TF relaxation rates does not follow a simple power law, but rather $\log \Lambda / \log B$ increases with decreasing applied magnetic field. This should be taken into account in a quantitave analysis of the data. The LF quenching data were fitted without introducing any precursor state and we did not make use of any Ivanter and Smilga relaxation mechanism.

At present we can not prove whether our description applies at lower temperatures. From the temperature dependence of the quenching data[5] one can see that some additional process is going on at about 100 K, where anomalous quenching curves $\bar{P}(B)$ were measured. At 100 K the picture may be more complicated due to a $\mu^+ \rightarrow$ Mu transition, which should be included in the model we have being using here. Finally we suggest that the quenching curves should be complemented by additional information describing the explicit time dependence of the longitudinal muon polarization function $P_\mu^{\parallel}(t)$. This would not only put more constraints on the fitting results but may also be helpful in the identification of the relaxation mechanisms involved.

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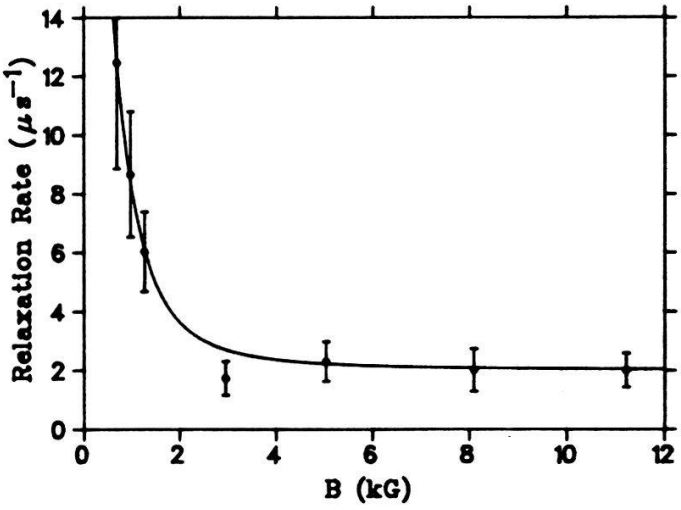

Fig. 1 Transverse relaxation rate vs field for muonium iin KCl at room temperature. The circles refer to a recent measurement by Baumeler et al..[6] The solid line was obtained solving our model on Mu depolarization with $\tau_c = 1.9 \times 10^{-10} s, \delta_{ex} = 60$ MHz, and $\tau_R = 0.5 \times 10^{-6} s$.

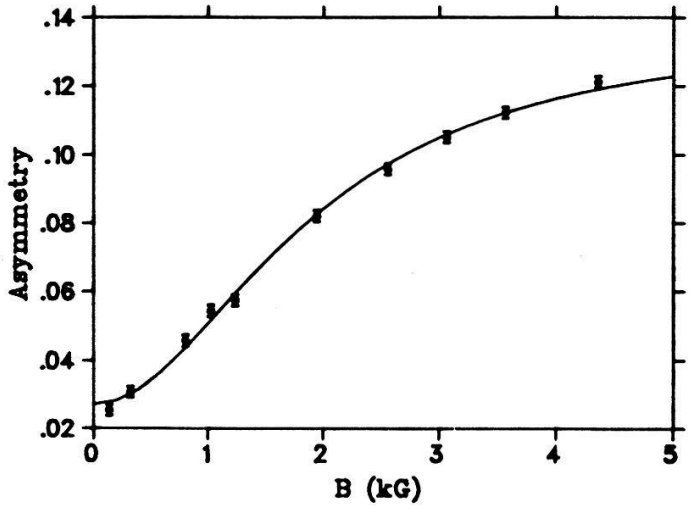

Fig. 2 Asymmetry vs longitudinal field strength for muonium in KCl. The circles refer to a recent measurement by Gygax et al.[5] performed at room temperature. The solid line represents the fit to these data using our model on muonium relaxation. The parameter values are the same as those of Fig. 1 : $\tau_c = 1.9 \times 10^{-10} s, \delta_{ex} = 60$ MHz, and $\tau_R = 0.5 \times 10^{-6} s$.

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11. Here $S^o_{(\mu,e)} = ||\ /2$ and $S^\alpha_{(\mu,e)} (\alpha = x, y, z)$ are the spin operators for the muon (electron). It is easy to show that the elements $S^\alpha_\mu S^\beta_e (\alpha, \beta = o, x, y, z)$ build a basis in the

16–dimensional space $\mathcal{L}_{Mu}$ of the muonium spin system. In this space every Liouville operator, such as L_{Mu} or $K(\tau)$, is then given by a linear transformation represented by a 16 × 16 matrix.

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