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Muon spin relaxation and trapping in crystals with defects

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Abstract. Muon spin relaxation in metals with trapping being taken into account is considered. It is shown that, owing to the motional narrowing, the spin relaxation of free (untrapped) muons in crystals is almost undetectable. The main contribution to the relaxation is from the trapped muons. In the case when the characteristic relaxation time of the muon space distribution is much less than its spin relaxation time, the fraction of trapped muons as well as the temperature dependence of the spin relaxation rate are found on the base of the ergodic assumption. In the opposite case the spin relaxation observed is defined by the characteristic time of the slowest process of space distribution relaxation. The experimental data on Bi, Cu and Al are interpreted within the consideration developed.

1. Introduction

Muon spin resonance (μSR) is the effective tool for investigation of magnetic fields in crystals and their time dependences. The use of the μSR method demands information on the muon conditions: whether the muon is trapped or tunnels from one interstice to another. A number of experimental and theoretical articles relevant to μSR in metals (see, e.g., Cox 1987) have been published but a consistent theoretical description of experimental results has not yet appeared. One of the main questions with respect to such a description is about the value of the muon spin relaxation rate at low temperatures. If a positive muon tunnels coherently from one interstitial site to another, then the suppression of relaxation due to the motion is so strong that the experimental observation of the relaxation seems to be impossible. The situation is different in reality and, to make the theory agree with experiment, one has to assume that the value of the tunnelling matrix element is some powers less than that obtained in the theory (Welter *et al* 1983). At the same time, if one assumes that muons are trapped at low temperature, it becomes unclear whether the concentration is independent of the relaxation rate over a wide temperature interval (Barsov *et al* 1983).

In the present paper this discrepancy is explained and eliminated. We shall show that at low temperatures the muons are trapped by point defects and the concentration independence of the relaxation rate is due to a logarithmic dependence of the muon-trapping characteristic temperature on the concentration of point defects.

We begin by obtaining the relaxation rate of muons in the case of band motion and then trapping is taken into account. In the last part of the paper the theoretical results are compared with the experimental results.

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2. Muon spin relaxation in the case of band motion

In pure crystals at low temperatures the muon is described by a Bloch wavefunction; so the spin relaxation time is the characteristic time of scattering with a spin upset due to the dipole–dipole interaction between magnetic moments of the muon and the host nuclei. A similar description for electrons in semiconductors has been given by Abrahams (1957). For non-correlated nuclei spins the relaxation time of the muon spin is

$$\tau_s^{-1}(\boldsymbol{k}) = \frac{2\pi}{\hbar\Omega}\int |V_{1/2,-1/2}(\boldsymbol{k}-\boldsymbol{k}')|^2\delta[\varepsilon(\boldsymbol{k})-\varepsilon(\boldsymbol{k}')]\frac{\mathrm{d}\boldsymbol{k}'}{(2\pi)^3}. \tag{1}$$

Here $\boldsymbol{k}$ and $\boldsymbol{k}'$ are the initial and final quasi-momenta of the muon, Ω is the elementary-cell volume, $\varepsilon(\boldsymbol{k})$ is the dispersion of muons, and $V_{1/2,-1/2}(\boldsymbol{k}-\boldsymbol{k}')$ is the amplitude of the muon scattering with spin upset.

If the muon's temperature T is higher than their band width ε_0, the magnitude of the characteristic quasi-momentum is of the order of the Brillouin momentum k_B and we obtain the estimation

$$\tau_s^{-1} = \sigma_0^2\hbar/\varepsilon_0 \tag{2}$$

where σ_0 is the relaxation rate in the absence of muon diffusion. Equation (2) does not differ from the estimation obtained from classical considerations, when one assumes the muon to be a classical particle hopping between the interstices with a frequency $\varepsilon_0/\hbar$ (Welter *et al* 1983). The temperature dependence of τ_s in this interval is governed by that of ε_0 connected with infrared renormalisation (Kondo 1984):

$$\varepsilon_0 = \varepsilon_{00}[\max(T, \varepsilon_{00})/D]^K \tag{3}$$

where ε_{00} = constant, D is the conduction electron band width, and the index $K \sim N^2(0)U_1^2$, $N(0)$ being the conduction electron density of states at the Fermi surface, and U_1 is the electron–muon scattering amplitude. Thus, we can write

$$\tau_s^{-1} = (\sigma_0^2\hbar/\varepsilon_{00})(T/D)^{-K}. \tag{4}$$

For the case $T \ll \varepsilon_0$ the characteristic muon thermal momentum k equals $k_B(T/\varepsilon_0)^{1/2}$ and one obtains from equation (1)

$$\tau_s^{-1} = (\sigma_0^2\hbar/\varepsilon_0)(T/\varepsilon_0)^{1/2}. \tag{5}$$

Assuming a definite time dependence of the dipole field correlation function, Kondo (1986) predicted exactly the same temperature dependence. Such a result differs from the classical dependence even qualitatively.

For the characteristic values $\sigma_0 \simeq 10^5$–$10^6\ \mathrm{s}^{-1}$ and $\varepsilon_0 \simeq 10^{-1}$–1 meV the quantity τ_s is several orders greater than the observation time; so muon spin relaxation at low temperatures must be unobservable.

Of course, band motion takes place only when the muon free path length considerably exceeds the inter-atomic distance a. For the opposite limiting case a correct calculation of the rate of muon hopping between neighbouring interstices has not been carried out up to now (Morosov and Sigov 1989). It is very likely, however, that the time τ_s in this range is also much longer than the observation time. At high temperatures the main contribution to diffusion is from the classical over-barrier hopping.

3. Muon spin relaxation in the case of trapping

The foregoing considerations demonstrate that muon trapping is the cause of the muon spin relaxation observed in experiments. We have shown (Morosov and Sigor 1989) that any point defect is a trap for a muon in metals. In fact, a point defect interacts indirectly with muons through acoustic phonons (elastic interaction) and through conductivity electrons. The long-range part of the latter interaction is caused by the defect-induced Friedel oscillations in the electron density. The resulting long-range part of the muon–defect interaction at a distance $\boldsymbol{R}$ has the form

$$W(\boldsymbol{R}) = \Omega\{W(\boldsymbol{n}) + [N(0)U_1(2k_F)U_2(2k_F)/2\pi\bar{\varepsilon}^2(2k_F)]\cos(2k_F R)\}/R^3 \tag{6}$$

where $\boldsymbol{n} = \boldsymbol{R}/R$, U_2 is the amplitude of the electron scattering from a defect, k_F is the Fermi momentum of electrons and $\bar{\varepsilon}\,(2k_F)$ is the dielectric constant.

The first term in equation (6), which allows for the elastic interaction, may be either positive or negative, depending on the orientation of the vector $\boldsymbol{n}$ with respect to the crystallographic axes. One can easily see that owing to the changing sign of $W(\boldsymbol{n})$ and $\cos(2k_F R)$ there exist a number of interstices with $W(\boldsymbol{R}) < 0$, the interstice with the lowest energy W_0 at $k_F a \simeq 1$ corresponding to $R \simeq a$. So, many bonded states with significantly different $W(\boldsymbol{R})$ are created for a muon in the metal by any point defect.

Let us accept a standard assumption that as a result of thermalisation a muon in a metal occupies any interstice with equal probability. That is why its distribution function is essentially non-equilibrium (in the opposite case the probability of occupation of the interstice with $W(\boldsymbol{R}) < 0$ should be greater).

By analogy to pions (Fabritius *et al* 1986) the characteristic relaxation time of the muon space distribution t_0 can be found from the equation

$$\mathrm{d}\kappa/\mathrm{d}t = (1/\tau_1)(1-\kappa) - (1/\tau_2)\kappa \tag{7a}$$

where κ denotes the fraction of trapped muons, and τ_1 and τ_2 are the characteristic trapping and escape times, respectively. The solution of equation (7*a*) is

$$\kappa(t) = \tau_2/(\tau_1+\tau_2) + [\kappa(0) - \tau_2/(\tau_1+\tau_2)]\exp(-t/t_0) \tag{7b}$$

where

$$t_0 = \tau_1\tau_2/(\tau_1 + \tau_2). \tag{8}$$

For simplicity we assume the presence of traps of one type only.

In the case of metals the escape process is caused by the muon–electron interaction and, following Kagan and Prokof'ev (1986), one can write

$$\tau_2^{-1} \equiv \tau_0^{-1}\exp(-|W_0|/T) = N^2(0)U_1^2(\varepsilon_0^2/\hbar|W_0|)\exp(-|W_0|/T). \tag{9}$$

The correlation between t_0 and τ_s plays the main part in the muon spin relaxation processes. If $t_0 \ll \tau_s$ the relaxation may be investigated using the equilibrium space distribution of muons. Obviously, at equilibrium of the muon ensemble, because of ergodicity the fraction of trapped muons is given by $\kappa = \tau_2/(\tau_1 + \tau_2)$ and equals the fraction of time spent by a muon in the trapped state.

Because of the presence of bonded states there exists a characteristic temperature T_0 of trapping. Within the framework of the elementary statistical theory (Morosov and Sigov 1989) one finds that

$$T_0 = W_0/\ln x \tag{10}$$

where x is the concentration of traps. At $T \gg T_0$ the fraction of trapped muons (muons in bonded states with the energy $W(\boldsymbol{R}) < -T$) is small and almost all muons are free. At $T \ll T_0$, almost all muons are trapped ($\kappa \simeq 1$). The value of κ changes in the temperature

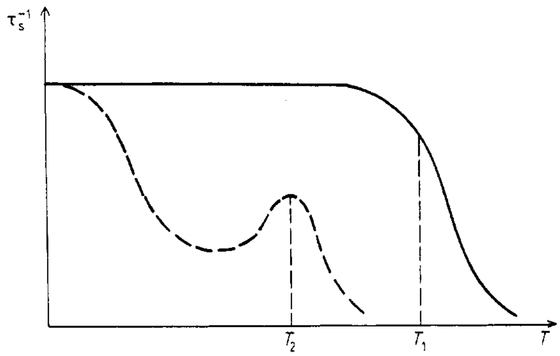

Figure 1. Theoretical temperature dependence of τ_s^{-1}.

interval $T_0/|\ln x|$ near T_0:

$$\kappa = 1 - [1 + \gamma x(T/W_0)^2 \exp(|W_0|/T)]^{-1} \qquad \gamma \simeq 1 \tag{11}$$

(Morosov and Sigov 1989). In the case of trapping, one can introduce the relaxation rate in the form

$$\tau_s^{-1} = \kappa\tau_{s,t}^{-1} + (1-\kappa)\tau_{s,f}^{-1} \tag{12}$$

where $\tau_{s,t}$ and $\tau_{s,f}$ are the muon spin relaxation times for trapped and free states, respectively. It should be noted that the result (12) can be obtained from the system described by Borghini *et al* (1978) by the use of some additional conditions between τ_1 and τ_2. As became clear in § 2, the second term in equation (12) is negligible. It is widely known that

$$\tau_{s,t}^{-1} = \begin{cases} \sigma_t & \sigma_t\tau_2 > 1 \\ 2\sigma_t^2\tau_2 & \sigma_t\tau_2 < 1 \end{cases} \tag{13}$$

where σ_t is the muon spin relaxation rate in the trap.

For the characteristic values of σ_t and τ_0, one has $\sigma_t\tau_0 \ll 1$. So, even for the trapped muons at high temperatures, we cannot observe any relaxation. The temperature T_1 corresponding to the increase in the relaxation rate can be estimated from the condition $\sigma_t\tau_2 \simeq 1$:

$$T_1 = W_0/\ln(\sigma_t\tau_0). \tag{14}$$

In the case $T_0 > T_1$ ($x > \sigma_t\tau_0$), all muons are trapped at T_1 and one should observe the temperature dependence of τ_s^{-1} (figure 1, full curve) which does not depend on x. We assume here the trap microstructure to be independent of temperature but possible violation of such an assumption will be shown further.

We should like to stress that the exponential drop of τ_s^{-1} at T_1 with increasing temperature is caused by the exponential dependence of the escape time and not by the incoherent tunnelling in an ideal crystal assumed by many workers.

In the case $T_0 < T_1$ (for small trap concentrations) and for $T < T_1$, one arrives at the condition $\sigma_t\tau_2 \gg 1$. If $t_0 \ll \tau_s$, then equation (12) for the relaxation rate can be used:

$$\tau_s^{-1} = \sigma_t\tau_2/(\tau_1 + \tau_2). \tag{15}$$

Within the temperature interval where $\tau_2 \ll \tau_1$, it yields $\tau_s^{-1} \propto x$, because σ_t and τ_2 are independent of the concentration x, and $\tau_1^{-1} \propto x$. The value of τ_s decreases with decreasing temperature and approaches t_0; therefore the space distribution of muons becomes of a non-equilibrium nature. The regime changes at the characteristic temperature T_2, when

$$\kappa^{-2}(T_2) = \sigma_t\tau_1(T_2). \tag{16}$$

At $T < T_2$ the space relaxation is much slower than the spin relaxation and the observable value of τ_s is defined by the characteristic time of the slowest process. Consequently, one has

$$\tau_s^{-1} = t_0^{-1} = \tau_1^{-1} + \tau_2^{-1} \tag{17}$$

and τ_s is independent of the dipole field.

One can see that in this interval the μSR lineshape is of the Lorentz form.

At $T = T_2$ the increase in τ_s^{-1} with decreasing temperature is changed for a decrease due to a fast exponential increase in τ_2. At $T = T_2$ the value of τ_s^{-1} reaches its maximum with the height

$$(\tau_s^{-1})_{\max} = \kappa^{-1}\tau_1^{-1} = (\sigma_t/\tau_1)^{1/2} \propto x^{1/2} \tag{18}$$

and $T_2 \propto (\ln x)^{-1}$ with logarithmic accuracy. At lower temperatures we have $\tau_2 \gg \tau_1$ and $\tau_s = \tau_1$. The consequent increase in τ_s^{-1} is caused by the decrease in τ_1 with decreasing temperature. If the product $\sigma_t\tau_1$ appears to be less than unity, we can again evaluate τ_s^{-1} from equation (12); $\tau_s^{-1} = \sigma_t$ is constant. The characteristic temperature dependence of τ_s^{-1} at $T_1 > T_0$ is reflected by the broken curve in figure 1.

Now let us consider the case when there are several kinds of trap; this is more close to the real situation in crystals. In this case we have side by side with t_0 a number of characteristic times t_i describing the establishment of an equilibrium distribution of muons between traps of different types. For an example of the traps of two types ($j = 1, 2$) we can write by analogy to equation (7):

$$\mathrm{d}\kappa_j/\mathrm{d}t = \tau_{1j}^{-1}(1 - \kappa_1 - \kappa_2) - \tau_{2j}^{-1}\kappa_j \tag{19}$$

where κ_j is the fraction of muons trapped by traps of the jth type. For the limit $\tau_{2j} \gg \tau_{1j}$ the time t_1 is

$$t_1 = \sum_{j=1}^{2} \tau_{1j} \Big/ \sum_{j=1}^{2} \frac{\tau_{1j}}{\tau_{2j}}. \tag{20}$$

It can easily be seen that the value of t_1 increases exponentially with decreasing temperatures as $\min(\tau_{2j})$. So at low temperatures the distribution of muons between traps is of a non-equilibrium nature. At high temperatures a muon during the observation has time to be trapped by centres of all types and spends most time at the deepest level. However, at low temperatures a muon being trapped stays in the given state during the whole observation time (the probability of escape is negligibly small). The depth of a trap is of no importance and the product $\kappa_j\tau_{1j}$ does not depend on j. The values of σ_{tj} for different traps are not equal; therefore the value of τ_s^{-1} must alter at a temperature $T < T_1$.

4. Comparison with experimental data

4.1. Muons in bismuth

The diffusion of positive muons in bismuth has been investigated by Barsov *et al* (1983) and Gygax *et al* (1988). The temperature dependence of τ_s^{-1} (Barsov *et al* 1983) is shown in figure 2. The absence of concentration dependence of τ_s^{-1} shows that $T_1 < T_0$. In fact, using the experimental data $\sigma_t = 2 \times 10^5\ \mathrm{s}^{-1}$ and $\tau_0 = 7 \times 10^{-12}$ s (Gygax *et al* 1988), we obtain $\sigma_t\tau_0 = 1.4 \times 10^{-6}$, i.e. much less than the impurity concentration in the sample. The presence of the plateau in the range 130 K $< T <$ 175 K (Gygax *et al* 1988) may be explained by the influence of traps of another type with a much larger concentration and a larger value of τ_0 but a smaller value of $|W_0|$.

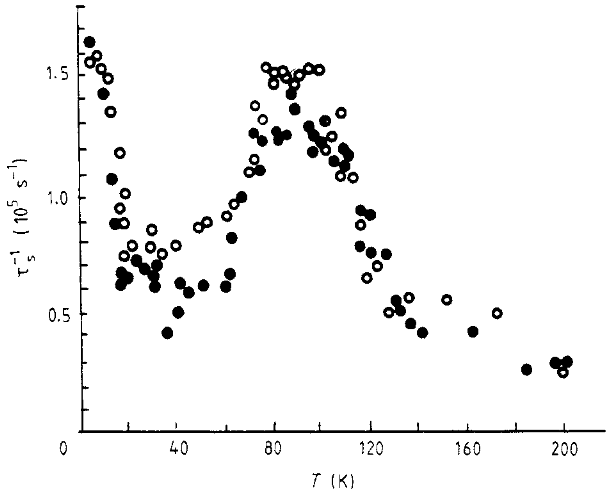

Figure 2. Experimental temperature dependence of τ_s^{-1} in Bi: ○, $x = 10^{-4}$; ●, superpure sample.

The temperature dependence of τ_s^{-1} at $T < 100$ K is caused by a change in the trap structure and in the bonded muon state. It was shown in § 2 that each defect gives rise to a number of interstices with $W(\boldsymbol{R}) < 0$. However, at low temperatures the probability of occupation of the interstice with minimum energy is overwhelming and σ_t is determined by the dipole field at the interstice.

Within the ranges $T < 10$ K and $80\text{ K} < T < 130$ K, muons occupy the interstices with different symmetries (Gygax *et al* 1988). Thus we can deduce that at $T < 10$ K the muon in the interstice of type 1 near the point defect has a minimum energy. Then, during heating, because of the difference in the temperature corrections to the muon energy for interstices of different types, the energy of the muon in the interstice of type 2 at first decreases to that of type 1 and subsequently becomes even less. Now the probability of muon occupation of interstices of type 2 near the defect is dominant.

If the energy difference ΔE between the interstices of types 1 and 2 is less than T, one deals with a two-level system with a comparable probability that these interstices are occupied. In such a case the relaxation rate decreases because of averaging of the dipole field (Gygax *et al* 1988). For a real system the number of equivalent sites may be greater than two and one has to find it by examining a specific trapping centre. The nature of traps in bismuth is unknown, however. In our opinion the decrease in the relaxation rate and the formation of the plateau at $20\text{ K} < T < 60$ K occur because of such extended states.

4.2. *Muons in copper*

The temperature dependence of the relaxation rate in the case of copper (Gurevich *et al* 1972) is fairly well described by the full curve in figure 1. We did not succeed in finding any data on the concentration dependence of τ_s^{-1} for copper.

Assuming that $T_1 < T_0$ and using experimental values $T_1 = 100$ K, $\sigma_t = 2.2 \times 10^5\ s^{-1}$, $W_0 = -540$ K (Gurevich *et al* 1972), we find that $\tau_0 = 2 \times 10^{-8}$ s. Such a result demonstrates that $T_0 < T_1$ for $x < 4 \times 10^{-3}$. Substituting the value of τ_0 in equation (9), we can estimate ε_0 to be 1–3 K at $T = 100$ K. (It should be noted that in semi-metals such as bismuth the main contribution to τ_2^{-1} may be from multi-phonon processes; that is why the value of ε_0 in bismuth was not estimated.)

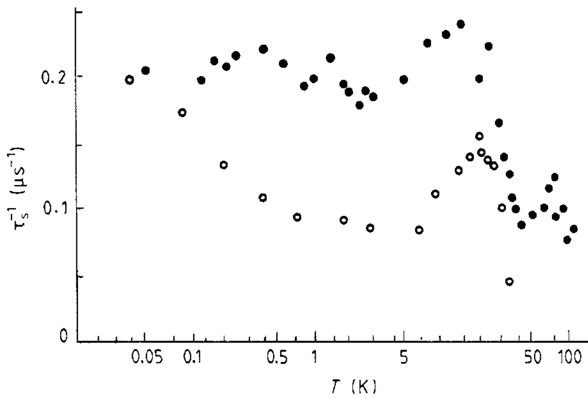

Figure 3. Dependence of τ^{-1} on the concentration of manganese impurities in aluminium; ○, $x = 57$ ppm; ●, $x = 1300$ ppm.

The deviation of τ_s^{-1} from the constant value at $T < 5$ K (Welter *et al* 1983) may be connected with the non-equilibrium distribution of muons between traps of different types in this temperature range. This idea is confirmed by the absence of such a deviation in copper with a large concentration of iron.

4.3. Muons in aluminium

The muon spin relaxation in aluminium has been examined by Kehr *et al* (1982) who observed the dependence of τ_s^{-1} on the concentration of manganese impurities (figure 3). This provided evidence for the inequality $T_0 < T_1$ in the range of small x-values.

The theory developed in the present paper allows us to explain the nature of the impurity peak in τ_s^{-1} at $T = 20$ K and its evolution with increasing manganese concentration. One has $T_0 > T_1$ for $x = 1300$ ppm, but $T_0 < T_1$ for $x = 57$ ppm. Comparing the values of $(\tau_s^{-1})_{max}$ for $x = 57$ ppm and τ_s^{-1} for $x = 1300$ ppm at low temperatures, we find the values $\kappa = 0.7$, $\tau_1 = 10\ \mu s$ and $\tau_2 = 15\ \mu s$ at $T = T_2$. Using the known values of x and $T_2 = 20$ K, we obtain from equation (11) that $W_0 = -240\ K$.

For single-crystal samples the value of τ_s^{-1} at $T \to 0$ tends to unity and remains the same limit when the concentration of manganese differs by as much as 23 times; so we deduce that $\sigma_t \tau_1 < 1$ at $T \to 0$.

The situation changes for polycrystalline samples, and the reason for this may be either the strong muon scattering from the grain boundaries or the muon trapping at the boundaries, i.e. the competition between two types of trap (grain boundaries and manganese atoms), the value of σ_t for the grain boundaries being smaller.

5. Conclusions

(i) The spin relaxation of free muons in crystals is unobservable owing to the effect of motional narrowing.

(ii) The muon spin relaxation may be detected only if muons are trapped.

(iii) In the case $\tau_s \gg t_0$, one can find the temperature dependence of τ_s on the basis of the ergodicity assumption.

(iv) The exponential drop in τ_s^{-1} at T_1 with increasing temperature is caused by the exponential dependence of the escape time and not by the incoherent tunnelling in an ideal crystal.

(v) If the relaxation of the space distribution of muons is much slower than their spin relaxation, then the observed value of τ_s equals t_0.

(vi) The presence of traps of different types may lead to a temperature dependence of τ_s in the range $T < T_1$.

It is meaningful to investigate the temperature dependence of the relaxation rate in single-crystal samples with impurities of a known type whose concentration may be varied in a wide range. Increasing the concentration, we observe a crossover from the regime $T_0 < T_1$ (when a concentration dependence of τ_s^{-1} does exist) to the regime $T_0 > T_1$ (when the value of τ_s^{-1} does not depend on the concentration). This type of investigation may allow us to verify experimentally the result given by equation (10) and to estimate the muon band width ε_0 (the magnitude of the tunnelling matrix elements) in the metal using the obtained value of τ_0.

Thus it can be seen that we have managed to propose an approach which allows us to describe the main features of muon spin relaxation at low temperatures.

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