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Longitudinal muon spin relaxation in metals and semimetals and the Korringa law

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Abstract

The longitudinal muon spin relaxation in metals and semimetals is suggestive of a form of Korringa relaxation in which the hyperfine interaction between the muons and the conduction electrons plays a dominant rôle. We give an alternative derivation of the Korringa law and show how muons may thus be used to study interactions with conduction electrons at interstitial sites. The alternative derivation links the topic to the use of implanted muons both as probes of magnetic and correlated-electron systems and as proton analogues, modelling the behaviour of hydrogen impurity in metals and semimetals.

1. Introduction

The μSR technique of muon spin relaxation is increasingly used to study a variety of condensed matter systems [1–3]. In these experiments a beam of almost completely spin-polarized muons is stopped in the sample under investigation. Following implantation the muons thermalize by Coulombic processes in 0.1–1 ns, in metals retaining the full initial polarization. The observed quantity is then the subsequent time evolution of the muon spin polarization on a microsecond timescale. This can be recorded by counting emitted decay positrons, e.g. in directions forward and backward with respect to the initial polarization, thanks to the asymmetric nature of the muon decay, which takes place in a mean time of 2.2 μs.

In many systems of current interest the relaxation function provides information concerning magnetic ground states and spin correlations associated with magnetically fluctuating systems [4]. Here we are concerned with longitudinal relaxation due to dynamical interactions. This is T_1-relaxation in NMR parlance and can be measured in magnetic fields applied parallel to the initial muon polarization or indeed in zero field. (The decay asymmetry can equally well be measured in null external field so zero-field measurements are something of a μSR speciality; in this paper we do not consider the T_2-relaxation due to static, e.g. nuclear dipolar, interactions, which can also be measured in zero field or in a transverse-field muon spin-rotation experiment.) In non-magnetic metals, longitudinal or spin–lattice relaxation has generally been thought to be unobservably slow on the μSR timescale, but sufficiently sensitive

measurements have lately revealed significant muon spin–lattice relaxation in a variety of metals and semimetals [5]. Measured in a longitudinal magnetic field, the relaxation rate is independent of field up to several tenths of a tesla and generally increases monotonically with temperature. This is highly suggestive of a form of Korringa relaxation which is associated with the fluctuating hyperfine interaction between the implanted muons and the conduction electrons.

We discuss this effect in section 2 and present a description of muon Korringa relaxation in section 3. Section 4 contains a discussion of the results and an outline of future experiments and analysis.

2. Muon Knight shift

The magnetic properties of metallic systems which show no long-range magnetic ordering are often dominated by the conduction electrons. The magnetic susceptibility is then the sum of the Pauli paramagnetism (associated with the conduction electron spins) and Landau diamagnetism (associated with the conduction electron orbital motion). The conduction electronic spin susceptibility can itself be measured using nuclear magnetic resonance (NMR) via either the Knight shift or longitudinal relaxation. We discuss the first effect in this section and turn to the second in the following section.

The Knight shift [6] is a small shift, $\Delta\omega$, in the NMR frequency, ω, which is due to the contact interaction between the conduction electron spin and the nuclear spin. It can be understood by imagining that individual conduction electrons hop on and off a given nucleus and therefore that the net hyperfine coupling which the nucleus experiences is the result of averaging over all the electron spin orientations. This net hyperfine coupling will be zero without an applied field because the average of the spin orientations will vanish; the net hyperfine coupling will be non-zero in a non-zero static field because this will polarize the electron spins. The Knight shift, $K = \Delta\omega/\omega$, is therefore proportional to the conduction electron density at the nucleus (which expresses the dependence on the coupling strength) and also to the Pauli spin susceptibility (which expresses the dependence on the degree to which an applied field polarizes the electrons).

Knight shifts are not merely the preserve of host nuclei, but can be measured with implanted muons. Experimentally one looks for a shift in the muon spin-precession frequency under the application of a known transverse field. Muon Knight shifts are commonly measured in heavy-fermion systems by measuring the precession frequency of implanted muons in a single crystal as a function of the orientation of the crystal axes with respect to the applied field [7]. The angle dependence arises because there is a contribution to the muon Knight shift from the dipolar interaction of the muon with localized f moments [8]. Such measurements are a powerful tool for identifying muon sites in d- and f-electron systems [9, 10]. Nevertheless, for the systems of interest in this paper, there is no such contribution to the muon Knight shift, K_μ. The effect is entirely due to the Pauli susceptibility and is therefore proportional to $g(E_F)$, the density of states at the Fermi level, so

$$K_\mu \propto A\chi(0,0) \propto Ag(E_F) \tag{1}$$

where A is the hyperfine coupling constant and $\chi(q,\omega)$ is the dynamical susceptibility.

3. Muon Korringa relaxation

A second method of probing the electron spin susceptibility is via measurement of the longitudinal relaxation of nuclear spins. It is well known that the two methods are closely

connected, the static average of the hyperfine interactions causing the Knight shift and fluctuations about this average providing the mechanism for relaxation. The dominant T_1-processes are flip–flop transitions of the electron and nuclear (or muon) spins, in which the difference in electron and nuclear Zeeman energies is taken up by a change in kinetic energy of the conduction electron. The exchange in energy between the nucleus and the conduction electrons is very small, so only electrons within $k_B T$ of the Fermi surface are able to participate since only these have empty states nearby into which they can make a transition. Thus for simple metals the spin–lattice relaxation rate T_1^{-1} is proportional to temperature, as enshrined in the Korringa relation

$$\frac{1}{T_1} = \frac{4\pi k_B T K^2}{\hbar}\left(\frac{\gamma_n}{\gamma_e}\right)^2 \tag{2}$$

which also shows that T_1^{-1} is proportional to the square of the Knight shift [11]. The direct proportionality is not expected to extend to very high temperatures or to apply when there is a strong variation in density of states at the Fermi surface, e.g. in the semimetals.

In the original treatment by Korringa, nuclear relaxation was formulated in terms of spin-flip scattering of the conduction electrons. Equation (2) must apply equally to muon Knight shifts and spin relaxation. In making the link to muon spin relaxation in magnetic metals however, it is useful to consider an alternative derivation. In this approach the muon spin-relaxation rate $\lambda = T_1^{-1}$ is written in terms of the response function $S(\boldsymbol{q}, \omega)$ (also known as the dynamic structure factor [12]) as

$$\lambda = \frac{1}{T_1} \propto \sum_{\boldsymbol{q}} A^2(\boldsymbol{q}) S(\boldsymbol{q}, 0) \tag{3}$$

where $A(\boldsymbol{q})$ is the $\boldsymbol{q}$-dependent hyperfine coupling which involves a form factor [13] which depends on the muon site. This connection occurs because the relaxation rate is proportional to the correlation function of the fluctuating fields at the muon site which can be converted into a sum over all q of the zero-frequency response function. We then use the fluctuation-dissipation theorem

$$S(\boldsymbol{q}, 0) = \lim_{\omega \to 0}\left[\frac{n(\omega)+1}{\pi}\chi''(\boldsymbol{q}, \omega)\right] = \lim_{\omega \to 0}\frac{k_B T}{\pi\hbar}\frac{\chi''(\boldsymbol{q}, \omega)}{\omega} \tag{4}$$

where $n(\omega) = (\exp(\hbar\omega/k_B T) - 1)^{-1}$ is the Bose factor, $\chi(\boldsymbol{q}, \omega) = \chi'(\boldsymbol{q}, \omega) + \mathrm{i}\chi''(\boldsymbol{q}, \omega)$ is the dynamical susceptibility and the equality holds at high temperature where $n(\omega) \to k_B T/\hbar\omega \gg 1$. Before proceeding, it is worth examining the form of the dynamical susceptibility. In many magnetic systems this is often modelled as a damped simple harmonic oscillator in the overdamped limit and at low frequencies such that

$$\chi(\boldsymbol{q}, \omega) = \frac{\chi(\boldsymbol{q}, 0)}{1 - \mathrm{i}\omega/\Gamma(\boldsymbol{q})} \tag{5}$$

where $\Gamma(\boldsymbol{q})$ becomes the linewidth of the corresponding Lorentzian lineshape observed in a neutron scattering experiment and hence that

$$\frac{\chi''(\boldsymbol{q}, \omega)}{\omega} = \frac{\chi(\boldsymbol{q}, 0)\Gamma(\boldsymbol{q})}{\omega^2 + \Gamma(\boldsymbol{q})^2}. \tag{6}$$

This expression is shown in figure 1(a). Hence using equation (4), the zero-frequency response function can be written as $S(\boldsymbol{q}, 0) = \chi(\boldsymbol{q}, 0) k_B T/\hbar\pi\Gamma(\boldsymbol{q})$ and so the relaxation is then given by

$$\lambda \propto k_B T \sum_{\boldsymbol{q}} \frac{A^2(\boldsymbol{q})\chi(\boldsymbol{q}, 0)}{\Gamma(\boldsymbol{q})}. \tag{7}$$

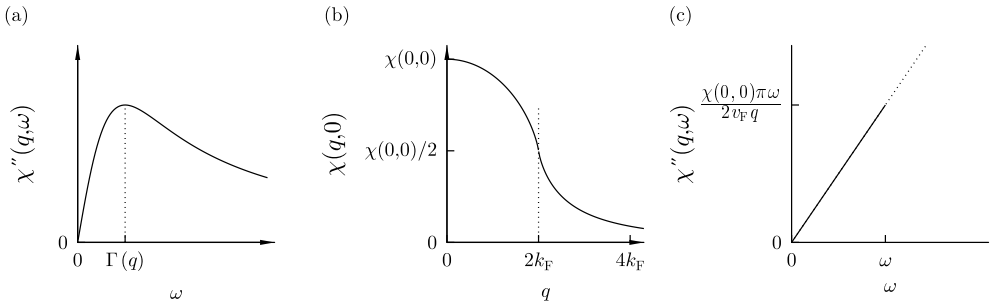

Figure 1. (a) The frequency-dependent imaginary part of the susceptibility of an overdamped mode. (b) The zero-frequency wave-vector-dependent susceptibility for a free-electron gas. (c) The frequency-dependent imaginary part of the susceptibility of an electron gas in the limit of small frequency.

This model works well for a large class of magnetic fluctuations, but is not appropriate for the electron gas since this does not behave like an overdamped oscillator. We need to examine instead the dynamical susceptibility of the electron gas, and for simplicity we consider the isotropic free-electron gas. The zero-frequency wave-vector-dependent susceptibility $\chi(q,0)$ for a free-electron gas is given by the Lindhard expression

$$\chi(q,0) = \frac{\chi(0,0)}{2}\left(1 + \frac{4k_F^2 - q^2}{4qk_F}\log\left|\frac{q+2k_F}{q-2k_F}\right|\right) \tag{8}$$

where $\chi(0,0) = \mu_0\mu_B g(E_F)$ is the Pauli susceptibility and $g(E_F)$ is the density of states at the Fermi energy. This expression is plotted in figure 1(b). The kink in the curve which appears at $q = 2k_F$ is due to the existence of the Fermi surface (the diameter of the Fermi sphere is $2k_F$). This kink becomes progressively more severe as the dimensionality is reduced down from three dimensions [14]. This function is entirely real, but we are interested only in the imaginary part of the susceptibility, which is therefore zero at zero frequency. For small frequency ω, the imaginary part of the dynamical susceptibility is given by

$$\lim_{\omega\to 0}\frac{\chi''(q,\omega)}{\omega} = \frac{\chi(0,0)\pi}{2v_F q} \propto [\chi(0,0)]^2\frac{\hbar}{k_F^2 q} \tag{9}$$

where v_F and k_F are the Fermi velocity and Fermi wave vector respectively [15]. The imaginary part of the dynamical susceptibility is plotted in figure 1(c). We then use the expression derived earlier for the muon relaxation rate which is

$$\lambda \propto k_B T\sum_{\boldsymbol{q}} A^2(\boldsymbol{q})\lim_{\omega\to 0}\frac{\chi''(\boldsymbol{q},\omega)}{\omega}. \tag{10}$$

If the $\boldsymbol{q}$-dependence of $A(\boldsymbol{q})$ can be ignored, then this becomes

$$\lambda \propto k_B T[A\chi(0,0)]^2 \propto K_\mu^2 T \tag{11}$$

which is the Korringa result.

For the non-interacting electron gas the response stretches over a range of frequencies on a scale measured by E_F. As interactions are switched on, the response becomes enhanced, particularly at low spatial and temporal frequencies [16]. This then enhances both the Knight shift and the muon spin-relaxation rate, but by differing amounts because the former is proportional to $\chi(0,0)$ and the latter is proportional to $\sum_{\boldsymbol{q}} A^2(\boldsymbol{q})\chi''(\boldsymbol{q},\omega)/\omega$ and therefore samples a range of $\boldsymbol{q}$. Disorder also plays a significant rôle in enhancing the Korringa relaxation at the expense of the Knight shift [17].

4. Discussion

We now discuss the extensions that must be made to this treatment for the specific case of muons in metals and semimetals. Following implantation, muons thermalize at specific sites before data taking begins. These are invariably intrinsic interstitial sites. Depending on temperature, the muons may subsequently diffuse between adjacent equivalent sites during data taking. Excluding the case of impure or defective material (where the muons may also trap at defect sites), this diffusion is unimportant for the measurement of longitudinal relaxation, be it by the Korringa mechanism or by magnetic fluctuations: usually the hyperfine fluctuations are fast compared with the muon hop rate and dominate the relaxation. It is necessary to consider the local electronic structure, however. This will be essentially identical to the screened-proton state of interstitial hydrogen. The local conduction electron density is enhanced, responding to the interstitial positive charge. In the above derivation we tacitly assume that the screening charge is a superposition of conduction band states, the local build-up affecting only the strength of the coupling.

In the semimetals, the conduction electron density can be insufficient to screen the muon charge effectively. In this case, a hydrogen-like bound state of individual electrons can exist. Transitions in and out of such a localized paramagnetic state can considerably enhance both the Knight shift and the relaxation rate. The μSR data for the semimetal Sb show signs of this incipient muonium formation [18, 19]. In graphite, it may be possible to describe the muon response in terms of the Korringa law, using the particular form of $g(E_F)$ for this material [20], although in view of the low electron density we favour the involvement of a localized paramagnetic state [5]. Atomic muonium itself would be unstable against chemical reaction with the graphitic layers, leading in this case to a molecular radical state which is described in an accompanying paper [21]. In semiconductors, régimes of long-lived and short-lived muonium states can readily be distinguished. A second accompanying paper identifies a resultant paramagnetic shift from the muon Larmor frequency in Si at high temperature and discusses the relation with the particularly strong muon spin relaxation in this case [22]. A consequence of the small density of states at the Fermi level found in semimetals is that states away from E_F play a rôle in relaxing the muon spin at high temperature. This effect can result in the breakdown of the proportionality between the muon spin-relaxation rate and temperature.

In summary, we have shown that muon spin relaxation in metals and semimetals is suggestive of a form of Korringa relaxation. The size of the effect is controlled by a form factor, which depends on the muon site, and the imaginary part of the dynamical susceptibility, which can be enhanced by interactions and disorder. Spin and charge exchange effects on localized defect states can cause additional relaxation in semimetals and semiconductors. In magnetic metals, muon or nuclear spin relaxation is typically dominated by moment fluctuations, correlations or critical phenomena. Our derivation shows that the same formalism can be used to describe Korringa relaxation in non-magnetic metals, thereby linking these topics. For interstitial probes such as the positive muon, studies of Knight shift and spin relaxation promise to link the static aspects of defect charge screening to aspects of dynamics and temperature dependence.

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