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MOSSBAUER SPECTROSCOPY: A PROBE OF LOCAL SPIN RELAXATION IN METALS

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1. INTRODUCTION

The purpose of this talk is to give a discussion of the theory of Mössbauer effect studies of local spin relaxation in metals. A considerable number of observations of relaxation effects in the Mössbauer spectra of nuclei in various systems have been reported in the literature [1]. However, only a few successful experiments were done on local moments in metals. In fact, as we will see, the observability of relaxation effects in Mössbauer spectra is restricted to a relatively small frequency window of electronic spin relaxation frequencies, depending on the intrinsic width of the Mössbauer line and the magnitude of the hyperfine coupling. In spite of this fact it seems that the Mössbauer effect as a tool for determining local electronic spin relaxation rates has received less attention in the past than it probably deserves.

Why should one want to do Mössbauer experiments in order to learn something about the dynamics of local moments in metals. The answer is that *EPR* experiments frequently do not yield the desired information about the impurity spin dynamics because of the well-known bottleneck phenomenon or other more technical difficulties. In these cases it is advantageous to look at the nuclear spin system instead, which, by virtue of its hyperfine coupling to the local spins, carries part of the information about the local spin dynamics. Unfortunately, *NMR* experiments on the magnetic impurity nuclei are very difficult because of intensity problems [2]. On the other hand, Mössbauer experiments present less intensity problems and in certain cases produce almost the same amount of information about the spin dynamics as *NMR* experiments.

2. GENERAL FORMULAS AND DESCRIPTION OF THE MODEL

The total absorptivity $I_{tot}(\omega)$ of a Mössbauer transition can be written as a superposition of lines corresponding to the various possible nuclear transitions [3]

$$I_{tot}(\omega) = \sum_{m_g m_e l m} \begin{pmatrix} I_e & I_g & l \\ -m_e & m_g & m \end{pmatrix}^2 \left| \vec{\pi} \cdot \vec{T}_{lm}(\vec{B}, \vec{k}) \right|^2 I''_{m_g m_e}(\omega) \tag{1}$$

Here I, m denote the nuclear spin and magnetic quantum numbers and the indices g, e refer to the ground and excited state of the nucleus, respectively. $T_{1m}(\vec{B}, \vec{k})$ is the nuclear l-pole transition element and $(\vec{k}, \vec{\pi})$ are momentum and polarization of the absorbed γ-quantum. $\vec{B}$ denotes a static magnetic field. The quantity of interest to us is the spectral function $I''_{m_g m_e}(\omega)$, which describes the frequency distribution for a definite nuclear transition from the ground state level $| I_g m_g \rangle$ to the excited state level $| I_e m_e \rangle$. From linear response theory we know that $I''_{m_g m_e}(\omega)$ is given by

$$I''_{m_g m_e}(\omega) = \int_{-\infty}^{\infty} dt \langle [D_{m_g m_e}(t), D^+_{m_g m_e}(0)]_- \rangle \, e^{i\omega t} \tag{2}$$

where $D = | m_g \rangle \langle m_e |$ is a nuclear transition operator. $\langle A \rangle$ denotes the thermal average of the operator A at a temperature T.

Structure of the Mössbauer line can be caused by various sources. For the present purpose, we are mainly interested in the magnetic hyperfine splitting, which comes about by the coupling of the nuclear spin to other spin systems in the metal. In the framework of a model, in which we represent the magnetic impurity in a metal by a local spin in the sea of conduction electrons, interacting via the usual exchange interaction $J \vec{S} \cdot \vec{s}\,(0)$, we have two possibilities for the nuclear spin to couple to: the local spin itself and the conduction electron spins at the nuclear site. The corresponding interaction hamiltonians will be denoted by $A \vec{I} \cdot \vec{S}$ and $A' \vec{I} \cdot \vec{s}\,(0)$. Note that A and A', like I, are different for the excited and ground state, respectively. It seems that both interactions are of equal importance for the hyperfine splitting. On the other hand, the nuclear spin relaxation occurs mainly via the coupling to the local electron spin, the usual direct Korringa relaxation being orders of magnitude smaller [2]. In the following we shall discuss the hyperfine coupling to the local spin only.

3. THEORY OF RELAXATION EFFECTS IN MÖSSBAUER SPECTRA

It is not difficult to predict qualitatively how the local spin relaxation affects the Mössbauer spectra. As with *NMR*, we can distinguish two different regimes, corresponding to slow and fast electron spin relaxation, respectively.

If there is no relaxation at all, the Mössbauer spectrum is composed of lines corresponding to the energy levels of the coupled nuclear spin-electron spin system, the width being given essentially by the natural linewidth of the Mössbauer transition. With increasing relaxation, the Mössbauer linewidth is increased, too. This behavior characterizes the regime of slow relaxation.

On the other hand, for fast electron spin relaxation the electron spin flips many times during a single nuclear spin precession, so that the fluctuations average out.

The faster the spin relaxes, i.e. the more rapid the spin flips, the more complete are the fluctuations averaged out. In the regime of fast relaxation we therefore expect only a single line at a position given by the time averaged value of the local spin, the linewidth *decreasing* with increasing relaxation rate. This is quite similar to the motional narrowing of *NMR* lines in liquids. Let us turn to the discussion of the fast relaxation regime first.

3A. FAST RELAXATION REGIME

In the fast relaxation regime, the theory of the Mössbauer lineshape is particularly simple and the connection of Mössbauer linewidth and local spin relaxation rate is very direct. The intensity profile for any definite Mössbauer transition ($m_g \rightarrow m_e$) is a simple Lorentzian [4, 5]

$$I''_{m_g m_e}(\omega) = \frac{\Gamma}{(\omega - \omega_0 - \Delta)^2 + \Gamma^2} \tag{3}$$

where Δ is the hyperfine shift in a magnetic field B.

$$\begin{aligned} \Delta &= (\Delta_L/B_0)\left[B + B_0 \langle S^2 \rangle / S\right], \\ \Delta_L &= \mu_n B_0 (m_g g_g - m_e g_e) \end{aligned} \tag{4}$$

and $\langle S^Z \rangle$ is the thermal expectation value of the local spin in the external field B. The hyperfine coupling A has been expressed in terms of the saturation field: $A = \mu_n g B_0/S$. The linewidth Γ is given by

$$\Gamma = \Gamma_0 + \gamma_L + \gamma_T \tag{5}$$

where γ_L and γ_T denote contributions to the Mössbauer linewidth from longitudinal and transverse impurity spin fluctuations, respectively,

$$\gamma_L = \Delta_L^2 (T/S^2)(\chi_L''(\omega)/\omega)_{\omega=0} \Rightarrow \Delta_L^2 (T \mathring{\chi}_L/S^2)\, T_1 \tag{6a}$$

and

$$\gamma_T = \Delta_T^2 (T/S^2)(\chi_T''(\omega)/\omega)_{\omega=0} \Rightarrow \Delta_T^2 (T \mathring{\chi}_T/S^2) \frac{T_2}{1 + (hT_2)^2} \tag{6b}$$

with

$$\Delta_T^2 = g_g^2 \left[I_g(I_g + 1) - m_g^2\right] + g_e^2 \left[I_e(I_e + 1) - m_e^2\right].$$

In Eqs. (3) and (5), ω_0 and Γ_0 denote energy and natural linewidth of the considered Mössbauer transition. The quantities $\chi_L''(\omega)$, $\mathring{\chi}_L$ and T_1 are the longitudinal absorptive part of the dynamical susceptibility, static susceptibility and spin relaxation time and similar for the transverse quantities. The susceptibilities in Eqs. (6) are defined in the usual way, however without the factor $(\mu_B g)^2$. $h = g\mu_B B$ is the local spin Zeeman splitting.

Let me stress that Eqs. (6) express the relaxation broadening $\gamma_L + \gamma_T$ in terms of the *exact* local spin susceptibilities, whatever the relaxation mechanism for the local spin may be. In particular, Eqs. (6) are valid for local spin relaxation in the Kondo regime.

One observes that for not too high fields both the longitudinal and the transverse contribution to the linewidth are proportional to the respective local spin relaxation times rather than relaxation rates, as expected from the qualitative discussion above. It is evident that a measurement of the relaxation broadening of the Mössbauer line is equivalent to a measurement of the local spin relaxation times T_1 and T_2. Unfortunately, the presence of the natural line broadening Γ_0 makes it difficult to determine the relaxation broadening, if the local spin relaxation is too fast.

Let me now briefly sketch how the theoretical result, Eqs. (3)-(6), is obtained. We define a complex response function by

$$I(z) = \int \frac{d\omega}{\pi} \frac{I''(\omega)}{\omega - z} = -\langle\langle D; D^+ \rangle\rangle, \tag{7}$$

the imaginary part of which is proportional to the Mössbauer intensity profile of a transition ($m_g \rightarrow m_e$). Introducing a self energy $\Sigma(z)$ for the Mössbauer transition we write

$$I(z) = -\frac{1}{z - \omega_0 - \Delta + \Sigma(z)} \tag{8}$$

where Δ as defined by Eq. (4) is the hyperfine shift by the effective field at the nucleus. Since we expect $I''(\omega)$ to be a Lorentzian, Σ will be independent of z in the vicinity of the resonance.

On the other hand, the exact equations of motion for $I(z)$ yield

$$(z - \omega_0 - \Delta) I(z) = -1 + \phi(z) / (z - \omega_0 - \Delta) \tag{9}$$

where $\phi(z) = \langle\langle [D, H_{int}]_- ; [D^*, H_{int}]_- \rangle\rangle$. Here H_{int} is the hamiltonian describing the interaction of the nucleus with its surroundings, with, however, a term $A \langle S^z \rangle I^z$ subtracted from the hyperfine hamiltonian. Comparing Eqs. (8) and (9) for $|z - \omega_0 \Delta| > |\Sigma(z)|$ we find

$$\Sigma(z) = -\phi(z) \tag{10}$$

Evaluating the correlation function $\phi(z)$ in lowest order of the hyperfine coupling one obtains Eqs. (5)-(6) for the Mössbauer linewidth Γ. The assumption implicit in the above derivation that the nuclear spin resonance has to be sharp compared to the electron spin resonance leads to the condition

$$\Delta_L \langle\langle 1 / T_1 ,$$

characterizing the fast relaxation regime.

3*B*. GENERAL CASE AND SLOW RELAXATION REGIME

In the slow relaxation regime and in the transition regime the theory of the Mössbauer line shapes is more involved. In general, one has to first diagonalize the coupled nuclear spin-local spin Hamiltonian and then subject this system to the perturbation caused by the coupling of the local spin to the matrix. Such a calculation, in which the coupling local spin-matrix was included in lowest order has first been performed by Afanasiev and Kagan for insulators [6]. The first calculation of this type for metals was done by Hirst [7], who evaluated the Mössbauer line-broadening in the lowest order of the exchange coupling of local spin and conducting electrons. It is nontrivial to extend such a calculation beyond perturbation theory as is necessary in cases where perturbation theory is invalid, e.g. in the Kondo regime. There exists a general formulation of the microscopic theory of Mössbauer line-shapes based on the Liouville projection operator method [8], which however has not been evaluated beyond lowest order perturbation theory. In order to circumvent the mentioned difficulty a number of authors [9] employed a stochastic model description, which does not suffer from the limitations of a perturbation theoretic treatment, but on the other hand contains one or several phenomenological parameters whose relation to the microscopic local spin dynamics remains obscure.

The problem of diagonalizing the coupled nuclear spin-local spin system is considerably simplified if an external magnetic field of sufficient strength (usually a few hundred *G*) is present. The transverse hyperfine coupling is then suppressed, since the local spin is almost exactly quantized in the direction of the external field (Paschen-Back-Effect). A necessary condition for this is $h \gg A_T, \frac{1}{T_2}$, where h, A_T and T_2 are the local spin Zeeman splitting, the transverse hyperfine coupling constant and the transverse local spin relaxation time.

We can envisage the system then as containing $(2S+1)$ different kinds of impurities, corresponding to the possible different orientations of the local spin in the external field. A Mössbauer transition $(m_g \rightarrow m_e)$ is split into $(2S+1)$ lines, reflecting the possible different values of the effective field at the nucleus. It is then natural to introduce projection operators on the $(2S+1)$ local spin states. We define a matrix of Mössbauer response functions

$$I_{\mu\mu'}(z) = -\langle\langle P_\mu D_{m_g m_e}; P_{\mu'} D^+{}_{m_g m_e} \rangle\rangle, \tag{11}$$

where the P_μ are projection operators

$$P_\mu = |\mu\rangle\langle\mu| \qquad \text{and} \qquad S^z|\mu\rangle = \mu|\mu\rangle$$

The intensity profile of a Mössbauer transition $(m_g \rightarrow m_e)$ is then given as the total sum of the absorptive parts of these functions:

$$I''_{m_g m_e}(\omega) = \sum_{\mu,\mu'} I''_{\mu\mu'}(\omega) \tag{12}$$

Completely analogous to the fast relaxation case, we define a self energy matrix, which then is determined in lowest order of the matrix-local spin coupling by comparison with the exact equations of motion for I''. The result for spin $S = 1/2$ is:

$$I_{m_g m_e}(z) = -\frac{\hat{z} + \hat{\Delta} + i\gamma_L}{\hat{z}^2 - \Delta_L^2 + i\gamma_L(\hat{z} - \hat{\Delta})} \tag{13}$$

where

$$\hat{z} = z - \omega_0 - \Delta_L(B/B_0) + i\Gamma_0 \tag{14a}$$

$$\hat{\Delta} = \Delta_L \tanh(h/2T) \tag{14b}$$

and γ_L is the longitudinal local spin relaxation rate (in lowest order in J)

$$\gamma_L = \frac{1}{T_1} = \frac{\pi}{2}(\rho_F J)^2 h \coth(h/2T). \tag{14c}$$

Under the assumed conditions, the transverse spin fluctuation contribution is suppressed (c.f. Eq. (6b) for $hT_2 \gg 1$).

Expressions for $I(z)$ applying to two level local spin systems ($S = 1/2$) have been given by Kubo [10] on the basis of a stochastic model calculation and by Wickman and coworkers [1, 11] on the basis of phenomenological rate equations. In both calculations γ_L is regarded as an adjustable phenomenological parameter.

In the fast relaxation limit, $\gamma_L \gg \Delta$, Eq. (13) reduces to

$$I(z) = -\frac{1}{\hat{z} - \hat{\Delta} + i\Delta_L^2 4T\, \mathring{\chi}_L / \gamma_L} \tag{15}$$

with $\mathring{\chi}_L = \frac{1}{4T}\cos h^{-2}\frac{h}{2T}$, the free spin longitudinal static susceptibility. Eq. (15) coincides with Eq. (3) in the appropriate limit.

In the slow relaxation limit we obtain

$$I(z) = \frac{n_\downarrow}{\hat{z} - \Delta_L + i n_\uparrow \gamma_L} + \frac{n_\uparrow}{\hat{z} + \Delta_L + i n_\downarrow \gamma_L} \tag{16}$$

where $n_{\downarrow,\uparrow}$ are the relative populations of the local spin levels. In this limit the relaxation broadening is proportional to the longitudinal local spin relaxation rate.

It is instructive to derive the equivalent of Eq. (16) for general spin S. The result is

$$I(z) = \sum_{\alpha=-S}^{S} \frac{n_\alpha}{\hat{z} + \alpha \Delta_L + i\gamma_\alpha} \tag{17}$$

where $\gamma_\alpha = (\pi/2)(\rho_F J)^2 h \{[S(S+1) - \alpha^2]\coth(h/2T) + \alpha\}$,

again in the lowest order in J, and

$$n_\alpha = e^{-\alpha h/2T} / \sum_{\alpha = S}^{S} e^{-\alpha h/2T}$$

The Mössbauer relaxation broadening parameters γ_α are related to the longitudinal local spin relaxation $\gamma_L = \dfrac{1}{T_1}$ by the sum rule

$$\sum_{\alpha = S}^{S} \alpha^2 \gamma_\alpha n_\alpha = T \overset{\circ}{\chi}_L \gamma_L \tag{18}$$

One can give arguments that Eq. (18) should be valid in all orders of perturbation theory and in particular in the Kondo regime.

This completes the theoretical discussion. It appears that relaxation effects in the Mössbauer spectra of magnetic impurities in simple metals are reasonably well understood theoretically. Any measurement of relaxation broadening can be readily interpreted in terms of local spin relaxation rates.

4. DISCUSSION

The question is now: can the Mössbauer effect be used to measure the local spin relaxation rates of a great number of dilute magnetic alloys. Unfortunately the answer is: "no". This is due to the inevitable limitations in the resolution of Mössbauer spectra. It is impossible at present to detect relaxation contributions to the Mössbauer linewidth which are much smaller than the natural linewidth. However, in a few favorable cases, the relaxation broadening can be measured and in these cases it is possible to determine the local spin relaxation with greater precision than in an usual *EPR* experiment. The conditions for observability of relaxation effects are in the fast relaxation limit

$$\Delta_L^2 (\overset{\circ}{\chi}_L T/S^2)\, T_1 \gtrsim \Gamma_0 \tag{19a}$$

and in the slow relaxation limit

$$\frac{1}{T_1} \gtrsim \Gamma_0 \tag{19b}$$

For $\dfrac{1}{T_1} \gtrsim \Gamma_0$ the nonequilibrium population of the nuclear hyperfine levels is important [12]. The resulting modification of the spectra again allows the determination of the local spin relaxation rate.

Among the Mössbauer candidates of the iron group, ^{57}Fe is the most favorable one, having a very narrow natural linewidth. Unfortunately the hyperfine coupling in ^{57}Fe ions is small, too. Inserting numbers we find that the local spin relaxation time T_1 has to be of the order 10^{-10} sec or longer in order that relaxation effects be observable. It has been shown that the local spin relaxation rate, while following the Korringa law $\frac{1}{T_1} = \pi (\rho_F J)^2 T$ well above the Kondo temperature T_K (ρ_F is the density of states, $T_K \simeq \rho_F^{-1} \exp[-1/\rho_F J]$ is the Kondo temperature) approaches the value [13] $\frac{1}{T_1} \approx T_K$ at $T \approx T_K$ and stays constant down to absolute zero [14]. The condition (19a) is therefore not met for Kondo alloys with high Kondo temperature, such as *CuFe* ($T_K \approx 30\,K$), where relaxation times of the order of $T_1 \approx 10^{-12}$ sec are expected for temperatures about and below T_K. However, in alloys with Kondo temperatures of about 100 mK or lower, such as *AuFe*, the relaxation effects are observable in all likelihood [15]. There is only one experiment on this group of alloys known to us, done by Maletta, Rao and Nowik [16] on *MoFe*. Although these authors observed a line broadening, they did not go through the transition to the slow relaxation regime. A theoretical interpretation of this experiment is difficult because of the limited experimental resolution, which led to internal inconsistencies in the theoretical analysis.

There exist a number of rare earth isotopes, which are suitable for the observation of relaxation effects. Although the natural linewidth is typically two orders of magnitude larger than that of ^{57}Fe, the hyperfine coupling is usually stronger by one order of magnitude, too, which compensates for the linewidth.

The first experiment on dilute magnetic alloys in which Mössbauer relaxation effects were observed, was done by Hirst [7] in 1969 on the system *ZrEr*. The local spin relaxation rate was found to obey a Korringa type law from which the exchange coupling constant could be determined.

Recently, Gonzales Jimenez and Imbert [17] investigated the system *AuYb*. By utilizing Hirst's theory for evaluating their spectra, they found a Korringa-type local spin relaxation rate. In later measurements [12], extending to lower temperatures, these authors were able to detect for the first time a Kondo type correction to the spin relaxation rate, which had been predicted theoretically [13, 18].

In conclusion, we may say that although only a limited selection of impurity atoms is suitable for Mössbauer effect experiments and furthermore only a fraction of the multitude of dilute magnetic alloys, which may be composed using these elements as impurities, will permit the observation of relaxation effects, chances are promising that the spin relaxation rates of a few local moment systems can be determined by this method and this even in the Kondo regime.

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