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DETERMINATION OF THE ^{57}Co HYPERFINE FIELD IN $\text{Pd}(^{57}\text{Co})$ FROM MÖSSBAUER EMISSION SPECTRA IN THE REGIME OF FAST RELAXATION

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Résumé. — Les spectres d'émission Mössbauer obtenus pour $\text{Pd}(^{57}\text{Co})$ au-dessous de ~ 400 mK dans des champs magnétiques externes montrent une augmentation de la largeur de la raie résonnante de ^{57}Fe et indiquent une polarisation de noyau de ^{57}Co plus faible qu'attendu. Les résultats expérimentaux sont expliqués de façon consistante par une composante perpendiculaire de la relaxation opérant sur les niveaux ($I = 3/2$) et ($I = 5/2$) de noyau de ^{57}Fe .

Abstract. — Mössbauer emission spectra obtained on $\text{Pd}(^{57}\text{Co})$ below ~ 400 mK under an applied external magnetic field show a broadening of the ^{57}Fe resonance lines and indicate an unexpectedly low polarization of the ^{57}Co nucleus. The experimental data are consistently explained by a perpendicular component of relaxation acting on the ^{57}Fe ($I = 3/2$) and ($I = 5/2$) nuclear levels.

Mössbauer spectroscopy on dilute alloys which stay paramagnetic down to lowest temperatures is essentially stimulated by questions concerning the formation of giant moments and the compensation of local moments. In some favourable examples like $\text{Pt}(\text{Fe})$ or $\text{Pd}(\text{Fe})$ it is even possible to observe the slowing down of the impurity spin-conducting electron relaxation using Mössbauer emission spectroscopy on $\text{Pt}(^{57}\text{Co})$ and $\text{Pd}(^{57}\text{Co})$ [1, 2]. From these experiments the ^{57}Fe hyperfine magnetic field B^{Fe} as a function of applied external magnetic field B and temperature T is determined. Deviations from a free-spin Brillouin dependence of $B^{\text{Fe}}(B, T)$ are often found due to a reduction of the local moment by the Kondo-effect. In addition to the information obtainable on the hyperfine field acting on the daughter nucleus ^{57}Fe one may gain information on the hyperfine field present at the parent nuclei ^{57}Co at very low temperatures. In this case the population differences in the polarized long-lived (270.9 d) ^{57}Co nuclear hyperfine levels lead to an unequal population of the hyperfine states of the short-lived ($T_{1/2} = 98.5$ ns) excited $^{57}\text{Fe}(I = 3/2)$ level giving rise to a typical asymmetric Mössbauer resonance pattern. From the relative intensities of the different hyperfine transi-

tions it is possible to determine the ^{57}Co hyperfine field B^{Co} [3]. Of course, this procedure is only allowed if the rates of relaxation of the excited $^{57}\text{Fe}(I = 3/2)$ and ($I = 5/2$) nuclear levels are negligible in comparison to the inverse life times of these levels. The decay diagram of ^{57}Co with the relevant nuclear parameters is shown in figure 1. The influence of relaxation shows up in both a broadening of the resonance lines and a depolarization of the excited ^{57}Fe levels. Therefore a determination of B^{Co} simply from the intensity ratios of the appropriate hyperfine transitions will necessarily lead to an underestimate of B^{Co} if the influence of relaxation is not taken into account.

FIG. 1. — Decay diagram of ^{57}Co with the relevant nuclear parameters (adopted from Ref. [4]).

As experimental examples we use recent data [2] on the giant moment alloy Pd(^{57}Fe) (< 1 ppm ^{57}Co in 5n Pd) which stays paramagnetic down to 18 mK showing no sign of Kondo-compensation at the ^{57}Fe sites or impurity-impurity interactions. In figure 2 we have depicted a typical spectrum taken at 25 mK with an applied magnetic field $B = 0.05$ T oriented parallel to the direction of γ -ray observation. The essential features of the peculiar line broadening of the outer and inner resonance lines as well as their anomalous ratio of intensities which is indicative for an unexpectedly small polarization at these low temperatures can be explained using a fairly simple

FIG. 2. — Mössbauer emission spectrum of Pd(^{57}Co) (< 1 ppm ^{57}Co in 5n Pd) taken at 25 mK under an applied external magnetic field of 0.05 T oriented parallel to the direction of the γ -ray.

theory. A theoretical treatment of the influence of relaxation in an intermediate excited state on Mössbauer emission spectra has been given by Hartmann-Boutron and co-workers [5-8] and was applied to the spectra of Au(^{170}Yb). The observed changes in population due to relaxation were of the order of a few percent. Here we will follow the general concept for the description of relaxation spectra as introduced by Afanas'ev and Gorobchenko [9]. The form of the Mössbauer emission spectrum can be expressed as

$$\varphi(\omega) = -\frac{\Gamma_{3/2}}{\pi} \text{Re Tr} [(\rho_{3/2}^0 \bar{G}_{e_1 e_1}(-i\Gamma_{3/2})) \times (\eta_v \hat{j}^+) \bar{G}_{ge_1}(-\omega - i\Gamma_{3/2})(\hat{j} \eta_v^*)] \quad (1)$$

$\hat{j}$ is the current operator for the $|I = 3/2\rangle \rightarrow |I = 1/2\rangle$ nuclear transition of ^{57}Fe , η_v is the polarization vector, $\Gamma_{3/2}$ is the natural linewidth of the $|I = 3/2\rangle$ state. The indices $\kappa = g, e_1, e_2$ distinguish the nucleus in the $|I = 1/2\rangle$, $|I = 3/2\rangle$ and $|I = 5/2\rangle$ states. $\rho_{3/2}^0$ is the density matrix for the $|I = 3/2\rangle$ state at $t = 0$, i.e. just after the decay $|I = 5/2\rangle \rightarrow |I = 3/2\rangle$.

$$-i\Gamma_{3/2} \rho_{3/2}^0 \bar{G}_{e_1 e_1}(-i\Gamma_{3/2}) = \bar{\rho}_{3/2}(-1/\Gamma_{3/2}) \quad (2)$$

is simply the density matrix averaged over the nuclear lifetime $\hbar/\Gamma_{3/2}$. $\rho_{3/2}^0$ in turn is determined by the dynamics of the decay from the $|I = 5/2\rangle$ state, i.e. by the lifetime-averaged density matrix

$$\bar{\rho}_{5/2}(-1/\Gamma_{5/2}) = -i\Gamma_{5/2} \rho_{5/2}^0 \bar{G}_{e_2 e_2}(-i\Gamma_{5/2}) \quad (3)$$

and the transition matrix elements to the $|I = 3/2\rangle$ state. Finally $\rho_{5/2}^0$ is determined by the E.C. decay of ^{57}Co (see Eq. (9) below). In eqs. (1, 2, 3) $\bar{G}_{\kappa\kappa'}(-\omega)$ are Green's function superoperators averaged over the states of the thermal bath which are given in the fast relaxation case by

$$\bar{G}_{\kappa\kappa'} = (-\omega + \langle \hat{L}_{\text{hf}}^{\kappa\kappa'} \rangle + \hat{M})^{-1} \quad (4)$$

where

$$\langle \hat{L}_{\text{hf}}^{\kappa\kappa'} \rangle = \langle B_{\text{hf}}(T) \rangle (\hat{A}\hat{I}_z) \quad (5)$$

is the Liouville operator representing the transition of the Mössbauer system under the average hyperfine (hf) interaction. $\hat{M}$ is the relaxation superoperator, the frequency dependence of which can be neglected for $\omega_{\text{hf}} \ll k_B T$ which is fulfilled here. With an applied magnetic field along the z -direction and under the condition $k_B T \tau_{\text{rel}}/\hbar \gg 1$ (τ_{rel} is the time of electron-spin relaxation) which is valid in the present case, one can write $\hat{M}$ in the following form [10]:

$$\hat{M} = i\gamma_{\parallel}(\hat{A}\hat{I}_z)(\hat{A}\hat{I}_z) + i\gamma_{\perp}((\hat{A}\hat{I}_x)(\hat{A}\hat{I}_x) + (\hat{A}\hat{I}_y)(\hat{A}\hat{I}_y)) + \beta(\hat{A}^2\hat{I}_z) \quad (6)$$

$\hat{M}$ represents longitudinal ($\sim \gamma_{\parallel}$) and perpendicular ($\sim \gamma_{\perp}$) fluctuation of the hyperfine magnetic field from the average and a term for the quasi-magnetic hyperfine interaction ($\sim \beta$) (the meaning of these terms is the same as in Ref. [10]). In eq. (6) we neglect terms of the order $(\hbar\omega_{\text{hf}}^e/k_B T)^2$. The simple form of $\hat{M}$ makes calculation of the relaxation line shapes in the Mössbauer spectra straightforward. Such a calculation could be used to obtain a least squares fit to the data

We now want to stress some basic physical consequences of the relaxation process in connection with our experimental example.

1. We first discuss the broadening of the resonance lines by relaxation which has its origin in the presence of $\bar{G}_{ge_1}$ in eq. (1). As seen from the data the broadening of the resonance lines represents only a small perturbation of the overall hyperfine splitting. Then the individual resonance lines preserve Lorentzian shape and may simply be described by an effective linewidth $\Gamma_{\text{eff}} = \Gamma_{3/2} + \Delta\Gamma$. The broadening $\Delta\Gamma$ can be easily related to the relaxation constants

$$\Delta\Gamma(|I = 3/2, I_z = 3/2, -3/2\rangle \rightarrow |I = 1/2, I_z = 1/2, -1/2\rangle) = \gamma_{\parallel}(3/2 A_{e_1} - 1/2 A_g)^2 + \gamma_{\perp}(3/2 A_{e_1}^2 + 1/2 A_g^2) \quad (7)$$

$$\Delta\Gamma(|I = 3/2, I_z = 1/2, -1/2\rangle \rightarrow |I = 1/2, I_z = -1/2, 1/2\rangle) = \gamma_{\parallel}(1/2 A_{e_1} + 1/2 A_g)^2 + \gamma_{\perp}(7/2 A_{e_1}^2 + 1/2 A_g^2) \quad (8)$$

(where $|I = 3/2, I_z = 3/2, -3/2\rangle$ is a Liouville ket, see [10]).

2. A further effect of relaxation is the change of population of the ^{57}Fe excited nuclear levels which is governed by $\bar{G}_{e_2e_2}(i\Gamma_{5/2})$ and $\bar{G}_{e_1e_1}(i\Gamma_{3/2})$. Despite the about eight times shorter lifetime of the $|I = 5/2\rangle$ state in comparison to the $|I = 3/2\rangle$ state the influence of relaxation on the population of the $|I = 5/2\rangle$ state must be taken into account since its hyperfine constant is about three times larger than that of the $|I = 3/2\rangle$ state. We have the general form for the initial density matrix of the $|I = 5/2\rangle$ state in eq. (3) :

$$\rho_{5/2}^0 = \frac{1}{4} + a_1 I_z + a_2 \left(I_z^2 - \frac{1}{3} I(I+1) \right) + a_3 \left(I_z^3 - \frac{41}{20} I_z \right) + \dots \quad (9)$$

The constants a_1 , a_2 and a_3 are determined by the population in the ^{57}Co levels and the transition probabilities to the different $^{57}\text{Fe}(I = 5/2)$ levels. Inserting (9) in (3) and (3) in (2) we finally find that in the presence of relaxation the average density matrix of the $|I = 3/2\rangle$ state is :

$$\begin{aligned} \bar{\rho}_{3/2}(-1/\Gamma_{3/2}) = & \frac{1}{4} + \frac{a_1 I_z}{\left(\frac{2\gamma_{\perp} A_{3/2}^2}{\Gamma_{3/2}} + 1 \right) \left(\frac{2\gamma_{\perp} A_{5/2}^2}{\Gamma_{5/2}} + 1 \right)} + \\ & + \frac{a_2 \left(I_z^2 - \frac{1}{3} I(I+1) \right)}{\left(\frac{6\gamma_{\perp} A_{3/2}^2}{\Gamma_{3/2}} + 1 \right) \left(\frac{6\gamma_{\perp} A_{5/2}^2}{\Gamma_{5/2}} + 1 \right)} + \frac{a_3 \left(I_z^3 - \frac{41}{20} I_z \right)}{\left(\frac{12\gamma_{\perp} A_{3/2}^2}{\Gamma_{3/2}} + 1 \right) \left(\frac{12\gamma_{\perp} A_{5/2}^2}{\Gamma_{5/2}} + 1 \right)}. \end{aligned} \quad (10)$$

Using eqs. (7), (8), (10) we now can derive the analytical form of the resonance spectrum (Eq. 1)

$$\varphi(\omega) = -\frac{\Gamma_{3/2}}{\pi} \sum_{m_{e_1} m_g} \frac{\bar{\rho}_{3/2}(-1/\Gamma_{3/2})_{m_{e_1} m_{e_1}} |(\eta_v \hat{j}^+)_{m_{e_1} m_g}|^2}{(\omega - \omega_{m_{e_1} m_g})^2 + (\Gamma_{\text{eff } m_{e_1} m_g})^2} \quad (11)$$

which is no more than a sum of broadened Lorentzian lines in the positions $\omega_{m_{e_1} m_g}$ of the nuclear transitions ($|I = 3/2, I_z = m_{e_1}\rangle \rightarrow |I = 1/2, I_z = m_g\rangle$) with intensities which are governed by $\bar{\rho}_{3/2}(-1/\Gamma_{3/2})$, i.e. by $\gamma_{\perp}$. We stress that the approximation involved is $\gamma_{\parallel}, \gamma_{\perp} \ll A^{-1}$. In (10) and (11) we keep all terms in the expansion with $\hbar\omega_{\text{hf}}^{\text{Co}}/k_B T$, whereas we neglect terms higher than first order in $\hbar\omega_{\text{hf}}^{\text{Fe}}/k_B T$ since $\omega_{\text{hf}}^{\text{Co}} \gg \omega_{\text{hf}}^{\text{Fe}}$ ($\mu_{3/2}^{\text{Fe}} \cdot B_{\text{sat}}^{\text{Fe}}/\hbar \sim 2.4 \times 10^8 \text{ s}^{-1}$ [2],

$$\mu_{7/2}^{\text{Co}} \cdot B_{\text{sat}}^{\text{Co}}/\hbar \sim 10^{10} \text{ s}^{-1}$$

[this work]).

The influence of the quasi-magnetic term proportional to β is omitted, since it will only lead to a shift of the resonance lines.

It is now possible to determine both $\gamma_{\parallel}$ and $\gamma_{\perp}$ independently from the experimental data : the broadening of the outer resonance lines caused by $\gamma_{\parallel}$ is about 40 times as large as that of the inner ones. The broadening of the outer resonance lines caused by $\gamma_{\perp}$, however, is $\sim 3/5$ that of the inner lines.

Therefore, if $\gamma_{\parallel}$ is not too large, the broadening of the inner lines will give $\gamma_{\perp}$.

Clearly, a determination of $\gamma_{\perp}$ from line broadenings is only possible, if $\Delta\Gamma$ is comparable in magnitude with $\Gamma_{3/2}$. A small $\Delta\Gamma$ which can hardly be detected, however, does not mean that $\gamma_{\perp}$ will not change the population of the excited ^{57}Fe levels. Its influence on population may in some cases be an order of magnitude larger. For an independent estimate of $\gamma_{\perp}$ the intensity ratios of the inner and outer pair of resonance lines may be used in addition. Usually, however, the ratio of the intensities of the inner resonance lines are less accurately known for statistical reasons. The choice of a perpendicular arrangement of B and γ -ray direction seems to be advantageous since it allows also the observation of the strong $\Delta I_z = 0$ transitions.

From the experimental data of figure 2 it is seen that the broadening of inner and outer resonance lines does not obey the ratio expected for parallel relaxation ($\sim 1/40$) only. The parameters $\gamma_{\parallel}$ and $\gamma_{\perp}$ derived from this broadening are listed in table I. From this quite pronounced influence of perpendi-

TABLE I

^{57}Co hyperfine fields B^{Co} derived under the assumptions a) of vanishing and b) of finite relaxation parameter $\gamma_{\perp} A_{e1}^2$. $\gamma_{\perp} A_{e1}^2$ is derived from the measured line broadening. B is the applied field in teslas.

T (mK)	B (T)	$\frac{\gamma_{\perp} A_{e1}^2}{\Gamma_{3/2}}$	$\frac{\gamma_{\parallel} A_{e1}^2}{\Gamma_{3/2}}$	$B^{\text{Co}} (a)$ (T)	$B^{\text{Co}} (b)$ (T)
18	0.01	0.46	0.70	5	17
18	0.2	0.06	0.27	15	19
25	0.05	0.14	0.62	11	18
28	0.01	0.16	0.99	7	12
28	1.0	0.00	0.11	19	19
67	0.018 3	0.16	1.35	7	13
67	0.085 1	0.04	0.04	17	19
388	0.248	0.06	0.20	15	18
		± 0.04	± 0.2	± 1	± 2

cular fluctuation we must expect also that the relative intensities of the resonance lines are severely altered. For comparison we have plotted in table I the values B^{Co} derived from the ratio of intensities of the outer resonance lines in the two alternative ways :

- a) under the assumption $\gamma_{\perp} = 0$, and
- b) taking into account the values $\gamma_{\perp}$ as derived from the line broadening.

Values a) are far from those expected for a free Co moment $\mu = g.J.\mu_B = 10 \mu_B$ and $B_{\text{sat}} = (21 \pm 1) \text{ T}$,

as deduced from magnetization [12] and NO-NMR [13]. Values b) are consistent with $\mu = (9 \pm 2) \mu_B$ and $B_{\text{sat}}^{\text{Co}} = (20 \pm 1) \text{ T}$. These data support our analysis b). Previous NO experiments on the γ -cascade following the β^- -decay of ^{60}Co in Pd [14] between 5 and 10 mK have been interpreted with a strong compensation of the Co atomic moment due to Kondo-effect. Our data indicate that down to 18 mK there is at least no strong reduction of the Co moment.

We have shown that perpendicular fluctuation plays an important role for conduction electron relaxation in 3d impurity doped alloys under applied magnetic field. The population differences of the ^{57}Fe excited levels at lowest temperatures due to the polarization of the ^{57}Co mother nucleus can be drastically reduced by this process. Care must therefore be taken in deriving B^{Co} from the relative intensities of the resonance lines alone, essentially when it is evident from an anomalous broadening of the resonance lines that relaxation processes are present.

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