Nuclear orientation experiments on melted or implanted *Au*Yb alloys

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Nuclear orientation experiments on implanted and melted samples of *Au* ^{175,169}Yb show clearly that the effects of the defects are important in the implanted sample although Yb is soluble in Au up to 6 at.%. Results on the melted sample of *Au* ^{175}Yb indicate that the Kondo temperature T_K is lower than 10 mK. Results on *Au* ^{169}Yb show reorientation effects on intermediate ^{169}Tm levels.

I. INTRODUCTION

The *Au*Yb system has been a source of controversy since EPR experiments[1] showed a strong negative value of Γ, the exchange coupling between the total moment of impurity J, and the spin S of the conduction electrons in the Hamiltonian

$$\mathcal{H} = -2\Gamma[g_J - 1]\vec{J}\cdot\vec{S},$$

while resistivity measurements did not seem to show the resistance minimum characteristic of dominantly resonant exchange[2] ($\Gamma > 0$). In recent resistance measurements by Murani[3] a minimum was detected, and Gonzales and Imbert[4] have interpreted a deviation from Korringa's rule, which they observed for the relaxation time τ_S in Mössbauer experiments on Yb in Au, as being due to a higher-order Kondo-fluctuation term. In order to estimate the Kondo temperature for the system, we have performed nuclear-orientation (N. O.) measurements on isotopes ^{175}Yb and ^{169}Yb using two types of sample: (i) simply implanted or (ii) melted following implanatation. For the second type, the original aim was to obtain more dilute samples.

We will first discuss the differences between samples considering only results at saturating applied fields, then we will take into account results at lower fields. Finally, from results on the melted samples (which are closest to ideal dilute solutions) we deduce the resonant-exchange strength.

II. EXPERIMENT

First of all, the samples were prepared by the same implanatation technique used by Spanjaard *et al.*[5] and Bernas *et al.*[6] in previous studies of ^{175}Yb and ^{169}Yb. An isotope separator with post acceleration of 80 keV was used to inject separately the ^{175}Yb and ^{169}Yb ions into a gold foil (99.999% Au, Johnson Matthey) at a total energy of 120 keV. This corresponds to a penetration of 150 Å. Allowing for the finite resolving power of the separator, local concentrations were about 100 to 1000 ppm (doses around 10^{13} atoms/cm^2). Lower doses could not be used in the case of ^{175}Yb because of the relative weakness of the γ rays to be observed (283, 396 keV) and in the case of ^{169}Yb because of the long half-life of the isotope (31 days).

To obtain greater dilution, some samples were melted after implantation. Melting was performed in a graphite crucible under 100 Torr of argon. Following melting, the Yb concentration is below 1 ppm; etching with aqua regia showed that the activity was uniformly distributed through the metal.

Samples were spot welded to a heat link leading to a chrome alum salt pill. Cooling by adiabatic demagnetization immediately after implantation gave sample temperatures down to 11 mK as measured by a ^{60}Co in Co monocrystal primary ther-

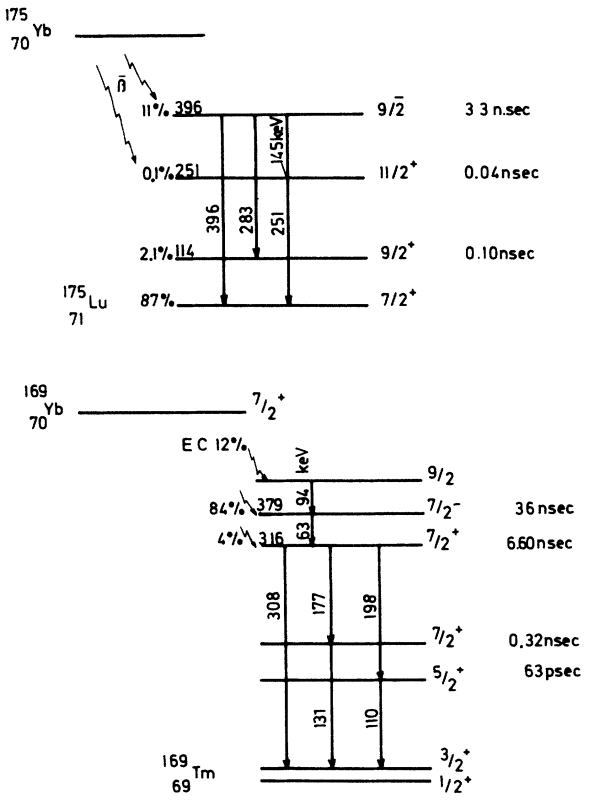

FIG. 1. Decay schemes of ^{169}Yb and ^{175}Yb. Only the γ rays measured in this work are shown.

mometer and a carbon-resistance secondary thermometer for greater sensitivity.[7] The anisotropy of the γ rays from the ^{175}Yb or ^{169}Yb and from the ^{60}Co was observed as a function of applied field ($H \leq 150$ kOe) with a planar Ge detector of 19-cm^3 volume and 2.5-keV resolution. The spectra were analyzed by computer. Because of absorption in the cryostat and the high relative intensity of the Compton background at lower energies, only γ rays above 150 keV were analyzed: 308, 198, and 177 keV for ^{169}Yb and 283 and 396 keV for ^{175}Yb (Fig. 1). We will, in fact, discuss only the results on the γ rays giving the highest anisotropy, 198 keV for ^{169}Yb and 283 keV for ^{175}Yb. For the other γ rays, the measured relative anisotropies are

$$^{175}\text{Yb:}\quad \frac{E_{396}}{E_{283}} = -0.285 \pm 0.020;$$

$$^{169}\text{Yb:}\quad \frac{E_{177}}{E_{198}} = -0.1 \pm 0.5, \qquad \frac{E_{308}}{E_{198}} = -0.61 \pm 0.02\ .$$

These ratios confirm results reported by Krane *et al.*[8] on a sample of Au ^{169,175}Yb, which was prepared by neutron irradiating a *Au*–1-at.%-Yb alloy. As the ^{169}Yb interpretation is complicated by the possibility of reorientation in the $\frac{7}{2}^-$ 379-keV and $\frac{7}{2}^+$ 316-keV levels of ^{169}Tm (whose half-lives are 36 and 660 nsec, we will first of all discuss the ^{175}Yb, showing later that the ^{169}Yb results are consistent with this analysis.

III. γ ANISOTROPY—USE OF EFFECTIVE HYPERFINE FIELD

The angular distribution of γ rays, $W(\theta)$, from oriented nuclei is related to the orientation parameters B_k by[9]

$$W(\theta) = \sum_k Q_k U_k F_k B_k P_k(\cos\theta), \qquad (1)$$

where $U_k F_k$ are purely nuclear parameters, related to spins and multipolarities, $P_k(\cos\theta)$ are Legendre polynomials, and Q_k are solid-angle corrections. We define the anisotropy by the relation

$$E(\theta) = W(\theta) - 1\ .$$

To simplify the presentation we will also represent anisotropy in terms of an effective field H_{eff}, which is the field that would produce the observed anisotropy if the Hamiltonian were

$$\mathcal{H} = g_n \mu_n H_{\text{eff}} I_z\ ,$$

where $g_n \mu_N I$ is the nuclear moment. If the interaction is purely magnetic, this description has an immediate physical sense in a strong applied field where the electronic magnetization is saturated along $\vec{H}$ and the coupling $A\vec{I}\cdot\vec{J}$ simply becomes $\Delta I_z J_z$ with $J_z = J$ so that

$$H_{\text{eff}} = H_n(\text{sat}) = AJ/g_n\mu_N\ .$$

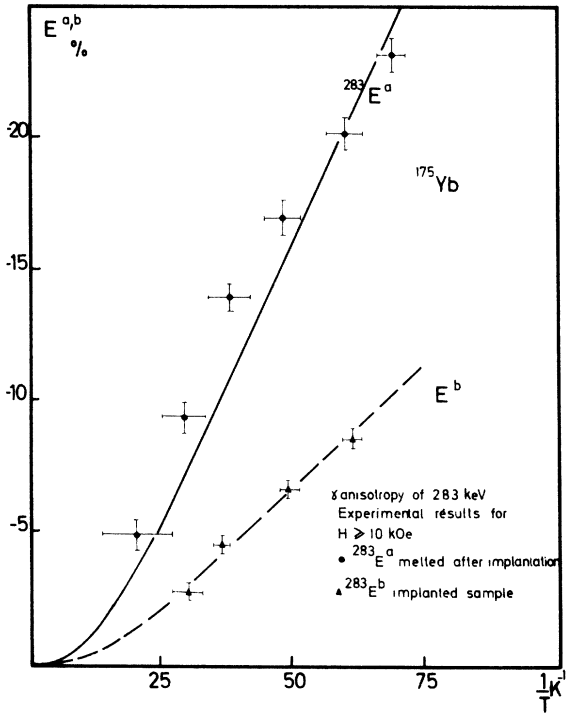

FIG. 2. 283-keV γ-ray anisotropy of ^{175}Yb in the implanted-melted sample (a) and implanted sample (b) as a function of $1/T$ for $H \gtrsim 10$ kOe. The solid line corresponds to a pure magnetic coupling with $H_n(\text{sat}) = 1.8$ MOe $^{175}\mu = 0.58\mu_N$.

In low fields, H_{eff} is usually only phenomenological but has the convenient advantage of eliminating practically all the explicit temperature dependence of the anisotropy. For instance, if the true Hamiltonian of the system (paramagnetic ion plus nucleus) is

$$\mathcal{H} = A\vec{I}\cdot\vec{J} + g\mu_B\vec{H}\cdot\vec{J}\ ,$$

H_{eff} is not proportional to the magnetization of the ion but is nevertheless a single-valued function which can be thought of as the nuclear-orientation analog of the Brillouin function.[10]

IV. RESULTS

A. High field, ^{175}Yb

Figure 2, which shows the anisotropy as a function of $1/T$ for the melted and the implanted samples for $H_{\text{app}} \geq 10$ kOe, shows that the implanted sample has a much lower anisotropy than the melted sample. This behavior is not specific to ^{175}Yb; an analogous effect is observed with ^{169}Yb (Fig. 3).

This increase in anisotropy cannot be attributed to an oxidation of the Yb during melting. The oxide Yb_2O_3 has an antiferromagnetic-ordering temperature of 2.3 K (and from Mössbauer measurements

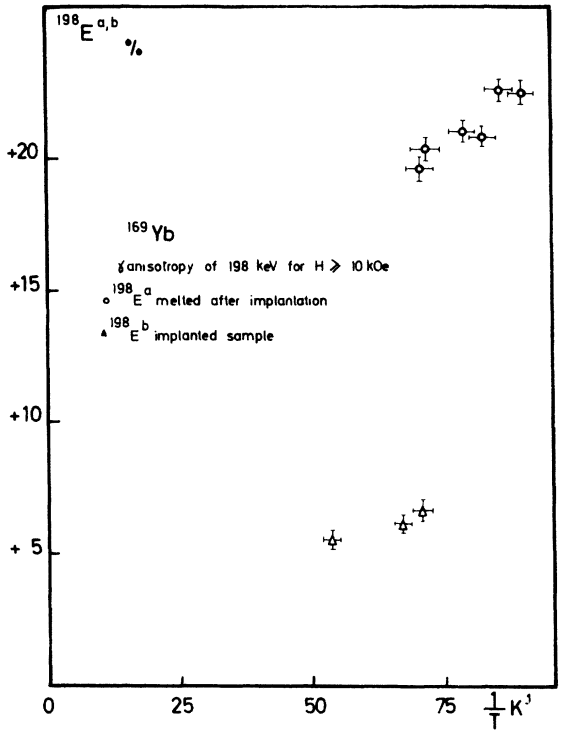

FIG. 3. 198-keV γ-ray anisotropy of ^{169}Yb in the implanted-melted sample (a) and implanted sample (b) as a function of $1/T$ for $H \gtrsim 10$ kOe.

a strong quadrupole effect[11]). This would lead to practically zero alignment for $g\mu_B H_{app} < kT_N$, i.e., for $H_{app} < 10$ kOe, which is not the case (Fig. 4). (In fact, one sample which was certainly oxidized due to bad-gas conditions during annealing showed zero anisotropy at all applied fields.)

The hyperfine field at Yb in Au is known to be $H_n(\text{sat}) = 1.8$ MOe, measured directly by EPR.[1] This value has been used in analyzing previous nuclear-orientation experiments[12,8] to estimate the nuclear moment of ^{175}Yb. The present results on melted samples show higher anisotropies than samples prepared in other ways, suggesting that these were all incompletely aligned due to effects which we will discuss in Sec. V. Assuming a complete alignment and a purely magnetic hyperfine coupling for the present melted samples, we have the estimate

$$^{175}\mu = (0.58 \pm 0.08)\mu_N .$$

This value is close to that of the neighboring $\frac{7}{2}^-$ nucleus ^{177}Hf ($^{179}\mu = 0.61\mu_N$), which should have the same single-particle moment.

B. Kondo temperature

Figure 5 shows that the effective hyperfine field as a function of applied field for the melted ^{175}Yb sample follows the calculated curve for an Yb ion in a Γ_7 ground state and with a hyperfine coupling of $H_n(\text{sat}) = 1.8$ MOe, $g = 3.34$, so the coupling to the conduction electrons produces no modification of the static properties of the impurity. This means that the Kondo temperature T_K is much lower than the lowest temperature obtained experimentally, $T_K \ll 10$ mK [10]

C. Reorientation effects in ^{169}Tm

In the experiments on an ^{169}Yb sample, prepared also by implantation followed by melting, the anisotropies of the 198-, 308-, and 177-keV γ rays were measured. It was not possible to fit these results simply using the value of the ^{169}Yb nuclear moment ($^{169}\mu = 0.63\mu_N$ [13,8]) and the known U_2F_2 values,[8] so attenuation factors g_2 related to disorientation in the 379- or 316-keV nuclear states had to be introduced. For $H_{app} > 5$ kOe, we find $g_2 = 0.42$ and for $H = 300$ Oe, $g_2 = 0.27$.

V. DISCUSSION

A. Comparison of sample preparations

There are three types of AuYb samples which have been studied: (a) implanted and melted; (b) implanted unannealled; and (c) 1-at.% alloy.[8] From these three types of samples, three different values of 175μ have been deduced (Table I).

In all cases it is assumed that the sample contained ideally isolated Yb impurities interacting only with the conduction electrons and the cubic crystal field produced by the gold ions. Before comparing the results on samples (a) and (b), we will discuss possible reasons why the sample (c) showed lower anisotropy than sample (a).

Since the local concentration in Yb is fairly high for sample (c), the magnetic interactions between impurities are certainly important at N. O. temperatures. Then the hypothesis of isolated Yb ions is certainly incorrect; the first effect of the

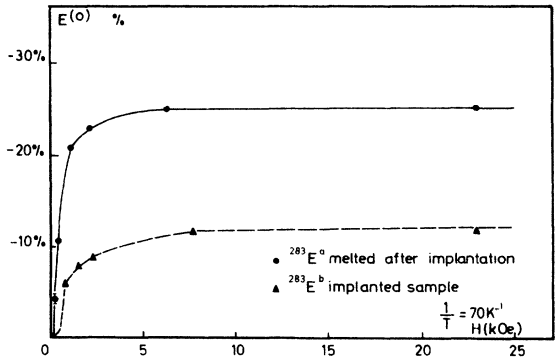

FIG. 4. 283-keV γ-ray anisotropy of ^{175}Yb in samples (a) and (b) as a function of the applied field H for $1/T = 70$ K^{-1}.

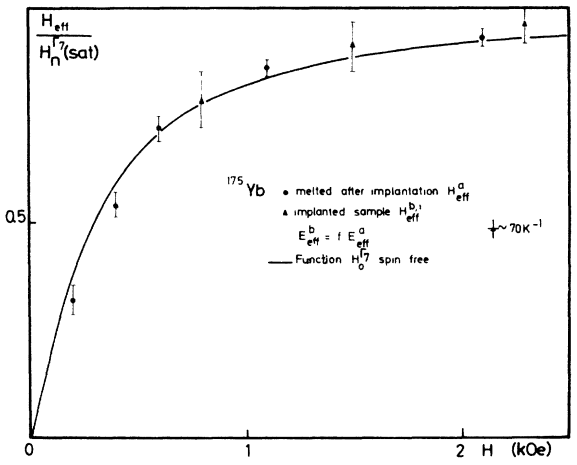

FIG. 5. Variation of the effective hyperfine field of ^{175}Yb in sample (a) as a function of the applied field H for $1/T \sim 70$ K^{-1} compared to the "free-spin" function $H_0^{\Gamma_7}$. We have indicated also the hyperfine field H^b_{eff} deduced from the hypothesis $E^b = fE^a$, with $f = 0.35$.

magnetic coupling in this random dilute alloy is to produce local molecular fields which are generally not parallel to the applied field and which thus lead to an incomplete alignment of impurities with respect to the external field. This apparent reduction of the γ anisotropy is, for instance, well known in the case of *Cu*Mn alloys,[14] where nuclear-orientation results on concentrated alloys ($c \gtrsim 100$ ppm) can be interpreted by supposing that the local magnetization lies along the resultant of the applied field H and an effective molecular field H_m due to the Ruderman-Kittel-Kasuga-Yosida (RKKY) interactions with other Mn sites. When the ratio H/H_m is small, the macroscopic disorientation strongly attenuates the measured γ anisotropy; in an extreme case such as *Cu*Mn with 1-at.% Mn, no observable anisotropy is obtained even in an applied field of 30 kOe.[14,10] Although the situation for *Au*Yb is certainly less dramatic since the interactions are weaker[15] than for Mn, it is not obvious that the 3-kOe field used by Krane *et al.*[8] was sufficient to saturate their sample. The resultant incomplete saturation would lead to an underestimation of the nuclear moment. In this connection, we note that even for our melted sample (a), a 3-kOe field produced an anisotropy 10% less than saturation. Finally, two further possible causes of error in sample (c) are (i) the assumption that the 145-keV γ ray preceding the 251-keV γ ray [which was used for the (c) measurement] is pure $E1$, and (ii) the possibility that the Yb atoms may occupy sites of less than cubic symmetry due to impurity charge effects, giving rise to an electric quadrupole interaction or nonaxial magnetic hyperfine coupling. For example, Gonzales and Imbert[16] in their *Au*Yb Mössbauer studies found that the hyperfine coupling constant A has a mean anisotropy distribution near 10% for a concentration of 2000 ppm.

Turning to samples (a) and (b), Fig. 3 shows the variation with fields of the Yb anisotropy at constant temperature. It is important to note that both samples saturate around 5 kOe but at different levels, which is not what would be observed if Yb impurities in sample (b) were subject to stronger interaction fields than those of sample (c). [This would give a slower saturation but the same saturation level for sample (b) as for sample (a).]

The simplest way to explain the difference (a) – (b) is to assume that, for sample (b), some Yb atoms (i) are in "good" sites identical to those in sample (a), while other Yb atoms (ii) are in "bad" sites, related to the defects introduced during implantation,[17] and that, in these sites, the nuclei do not align in the applied field. From Fig. 4, we can estimate that the fraction f of the good sites lies between 0.42 (value in strong applied fields) and 0.35 (value for weak applied fields). Therefore, the low value of $^{175}\mu$ estimated by Spanjaard *et al.*[12] was due to the fact that they did not consider this attenuation. (The agreement these authors obtained with a reanalysis of old results by Trace *et al.*[18] appears to have been fortuitous, and their estimate of 0.2 b for the quadrupole moment of ^{175}Yb is certainly too low.)

Thus using our picture, nearly 65% of the Yb sites in the implanted sample do not show alignment. This is perhaps because some Yb atoms have precipitated into intermetallic compounds; or, which is much more probable, that, in the neighborhood of defects, the Yb atoms are subject to strong electrostatic effects which may modify the crystal field or produce a sufficient important quadrupole interaction to prevent the (ii) nuclei

TABLE I. Nuclear moment for ^{175}Yb from three different samples.

Alloy	Yb concentration	$^{175}\mu$ (in μ_N)	Ref.
(a) Melted	~1	0.58 ± 0.06	This work
(b) Implanted	~100	0.29 ± 0.06	Spanjaard *et al.* (Ref. 12) This work
(c) Irradiated	~10 000	0.40 ± 0.05	Krane *et al.* (Ref. 8)

from lining up in the magnetic field. Concerning the second point, it must be noted that the results obtained by Spanjaard *et al.*[5] on samples of Yb implanted into Fe could only be explained by invoking the existence of strong quadrupole effects and unaligned sites, again because of the method of sample preparation.

As nuclear orientation is not a spectroscopic method, this analysis is necessarily oversimplified. Although the local environment of (ii) ions cannot be specified directly, the recent experiments reported by Behar *et al.*[19] on implanted Cd in Ag (nuclear reactions) suggest that the (ii) impurities do not correspond to a well-defined site coupled for example with one vacancy but rather to ions in the vicinity of groups of vacancies. This picture is furthermore in agreement with what is known about the mobility of the vacancies in noble metals near room temperature (for more details see Ref. 20).

Finally, it is interesting to note that the observed fraction f of impurities in good sites agrees well with the electron-microscope work of Bernas *et al.*,[21] who showed that about 33% of the ions implanted come to rest in a region where there are essentially no defects.

But the most important conclusion which can be drawn from this comparison is that the frequently accepted idea that implantation gives practically ideal alloys for systems which are within the conventional solubility limits[22] is incorrect, at least for Yb; Yb is soluble in Au up to 6-at.%,[23] yet the implanted samples are far from ideal. Whatever the solubility, the defect dynamics (mobility and interaction with the impurity) play an essential role.

The present case is particularly sensitive to all causes of disorientation: ^{169}Yb and ^{175}Yb have presumably significant quadrupole moments ($^{169}Q \sim 3.8$ b from Ref. 13). Also for a rare-earth ion in a nonmagnetic host, small changes in the local symmetry can be very important since nuclear-orientation experiments are particularly sensitive to the lowest crystal-field levels. In addition, it may well be that Yb atoms near defects change valence and enter the nonmagnetic 2^+ state as do Yb atoms in Ag.[2,24]

With Ce implanted into Au and Ag, we have not observed this type of effect and old results[25] on implanted samples agree with recent direct magnetization measurements[26]; but this seems to be due principally to the lower sensitivity of Ce than Yb to defects in cubic lattices (for instance because of the lower quadrupole moment). Recent experiments on *Mg*Ce monocrystal samples (where the results can be expected to be very sensitive to local symmetry) cannot be interpreted in terms of cerium ions in ideal hexagonal sites but rather the defects change the situation radically.[27] Thus in some situations, whatever the solubility, cerium is also sensitive to defects; the influence of defects in any given hyperfine experiment depends in a complex way on the relative sensitivity of the isotope observed to perturbations, and not simply on the solubility of the element. In the present state of the art, nuclear or solid-state results obtained with implanted samples must be regarded with caution.

B. Kondo temperature (melted sample)

The anisotropy as a function of applied field can be completely fitted by the Hamiltonian

$$\mathcal{H} = g\mu_B \vec{H}\cdot\vec{J} + A\vec{I}\cdot\vec{J},$$

giving pure Gorter orientation.[28] This is the same situation as has been found in *Au*Mn[29,14] and means that T_K is much lower than the range of temperature covered experimentally, i.e., $T_K \ll 10$ mK.[10] Spin-flip interactions with the electrons show up, however, well above T_K in other types of experiments, such as the electronic relaxation detected using the Mössbauer effect by Gonzales and Imbert.[4] The low value of T_K is in agreement with the weak-resistance-minimum behavior observed,[3] the low degeneracy of the fundamental state, and the fact that the hyperfine coupling parameter found by the Mössbauer measurements[4] is the same as that found by EPR.[1] If T/T_K and H/H_K are less than one, the apparent coupling constant should change, because the spin J interacts primarily with the conduction electrons rather than with the nuclear spin I.[10] Unfortunately, there is so far no simple system with $T_K \sim 1$ K, where both Mössbauer and nuclear-orientation experiments can be carried out in order to observe simultaneously the effects of Kondo fluctuation on the relaxation time and on the local-moment magnetization of the impurity.

C. Reorientation effects in ^{169}Tm

Equation (1) used to relate the γ anisotropy to the nuclear hyperfine coupling assumes (a) that the parent nuclei are in thermal equilibrium, (b) that if the excited daughter states are not pure I_z states, their half-lives are short enough for no reorientation to occur, and (c) that the half-lives of the intermediate daughter states are too short for relaxation to occur. Generally, for intermediate state half-lives less than 10^{-10} sec, these conditions are fulfilled. However, in ^{169}Yb[16] there are intermediate levels with half-lives of 36 and 660 nsec. The first state can lead to interference attenuation, of the type discussed by Steenberg,[30] who pointed out that half-lives of the order of 10^{-8} sec were optimum for such attenuation. In addition the longer-lived state can allow thermal repopulation; as it has been shown[31,32] nuclear relaxation for paramagnetic impurities can be very short

The attenuation g_2 that we measured is the prod-

uct of these two effects, which we are unable to separate because of the selection of γ rays measured. The fact that g_2 varies slowly with $H > 2$ kOe shows that the Tm is rather insensitive to the applied field. This is consistent with the susceptibility measurements of Williams *et al.*,[33] which show that Tm in Au has a singlet ground state and a first excited state at 7 K, so that at 0 K the Tm magnetization is that induced by the mixing effect of the field.

Krane *et al.*[8] have measured the successive g_2 attenuations due to the 36 and 660-nsec levels by measuring the 94, 63, and 198-keV γ rays. They obtain

$$g_2(36 \text{ nsec}) = 0.22,$$

$$g_2(660 \text{ nsec}) = 0.51,$$

which leads to a total attenuation of the 198-keV γ ray of 0.11, four times stronger than in our sample (a). This differences corresponds probably to the high concentration of samples (c) (see Sec. V A).

In simpler cases, reorientation could be a useful tool to measure the nuclear relaxation time. For instance, low-temperature Mössbauer studies when the half-life of the Mössbauer state is comparable to the nuclear relaxation time are perhaps a good method to measure the relaxation. Fe in Cu and Au, where the parent (Co) is nonmagnetic, seem particularly interesting.

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[1]L. J. Tao, D. Davidov, R. Orbach, E. P. Chock, Phys. Ref. B 4, 5 (1971).

[2]J. Boes, A. J. Van Dam, A. Bijvoet, Phys. Lett. A 28, 101 (1968); J. Bijvoet, thesis (Amsterdam, 1969) (unpublished).

[3]A. P. Murani, Solid State Commun. 12, 295 (1973).

[4]F. Gonzales-Jimenez, P. Imbert, Solid State Commun. 13, 85 (1973).

[5]D. Spanjaard, thesis (Orsay, 1971) (unpublished); D. Spanjaard, R. A. Fox, J. D. Marsh, N. J. Stone, *Hyperfine Interactions and Excited Nuclei*, edited by G. Goldring and R. Kalish (Gordon and Breach, New York, 1971), p. 113.

[6]H. Bernas, thesis (Orsay, 1972) (unpublished). H. Bernas and H. Gabriel, Phys. Rev. B 7, 468 (1973).

[7]J. Sanchez, A. Benoit, and J. Flouquet (unpublished).

[8]K. S. Krane, C. E. Olsen, and W. A. Steyert, Nucl. Phys. A 197, 352 (1972).

[9]R. J. Blin-Stoyle and M. A. Grace, *Handbuch der Physik* (Springer, Berlin, 1957), Vol. 42, p. 555; D. A. Shirley, Ann. Rev. Nucl. Sci. 16, 89 (1966).

[10]J. Flouquet, Ann. Phys. (Paris) (to be published).

[11]G. M. Kalvius, G. K. Shenoy, and B. D. Dunlap, *Les Éléments de Terre Rare* (C. N. R. S., Paris, 1970), Vol. II, p. 477.

[12]D. Spanjaard, J. D. Marsh, and N. J. Stone, J. Phys. F 3, 1243 (1973).

[13]R. J. Chanpeau, J. J. Michel, and H. Walther (unpublished).

[14]I. R. Williams, thesis (Oxford, 1968) (unpublished).

[15]B. Caroli, J. Phys. Chem. Solids 28, 1427 (1967).

[16]F. Gonzales-Jimenez and P. Imbert (unpublished).

[17]D. Dautreppe, *Hyperfine Interactions and Excited Nuclei*, edited by G. Goldring and R. Kalish (Gordon and Breach, New York, 1971), p. 3.

[18]M. A. Grace, G. E. Johnson, R. G. Scurlock, and R. T. Taylor, Philos. Mag. 2, 1079 (1957).

[19]M. Behar and R. M. Steffen, Phys. Rev. Lett. 29, 116 (1972).

[20]H. Bernas, *Conference on Implantation* (Société Française de Physique Vittel, Paris, to be published).

[21]H. Bernas, M. O. Ruault, and B. Jouffrey, Phys. Rev. Lett. 27, 859 (1971).

[22]H. De Waard, Proc. IAEA, Conference on Mössbauer and its Applications, 1972, p. 123 (unpublished).

[23]P. E. Rider, K. A. Gschneidner, Jr., and O. D. Mac Masters, A. I. M. E. 233, 1488 (1965).

[24]V. Allali, D. Donze, and A. Treyvaud, Solid State Commun. 7, 1241 (1969).

[25]J. Flouquet, Phys. Rev. Lett. 27, 515 (1971).

[26]B. Cornut (private communication).

[27]A. Benoit, J. Flouquet, and J. Sanchez (unpublished).

[28]C. J. Gorter, Physica (Utr.) 14, 504 (1948).

[29]I. Lagendijk, L. Niesen, and W. J. Huiskamp, Phys. Lett. A 30, 326 (1969).

[30]N. R. Steenberg, Phys. Rev. 95, 982 (1954).

[31]R. E. Walstedt and A. Narath, Phys. Rev. B 6, 4118 (1972).

[32]D. Spanjaard and F. Hartmann, J. Phys. F 3, 1178 (1973).

[33]G. Williams and L. L. Hirst, Phys. Rev. 185, 407 (1969).