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ESR of Gd and Er impurities in the metallic Van Vleck compound TmH_2

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The present investigation deals with the metallic system TmH_2. Susceptibility measurements of pure TmH_2 indicate that the major component of the susceptibility is the Van Vleck or polarization susceptibility of the Tm ions over a rather large low-temperature range up to about 30 K. However, superimposed on this susceptibility is a Curie-like contribution due to the presence of a small percentage of Tm atoms with a magnetic ground state. Their origin is intrinsic, due to vacancies or interstitial occupation of the H atoms. The ESR of rare-earth impurities (Gd and Er) diluted in the matrix TmH_2 is used to probe the magnetic behavior of this metallic singlet ground-state system. ESR measurements at X-band frequency and at low temperature ($T<35$ K) have been carried out on powder samples of $Tm_{1-x}Gd_xH_2$ (with the Gd concentration in the range 0.001–0.01) and on a $Tm_{0.99}Er_{0.01}H_2$ sample. The observed resonance characteristics (g value, linewidth) of the Gd and Er impurities show a much more complex behavior, with temperature and impurity concentration, than that previously observed in thulium and praseodymium monopnictides. We have considered the effects of the exchange interactions that couple the impurities both with the thulium host ions and with the conduction electrons of the host matrix, extending the Hasegawa description of the spin dynamics of a metallic system to the present case of three coupled spin systems. We analyze and discuss our experimental results within such a theoretical framework where the main physical information deduced is the following. (a) For both Er and Gd, the impurity-Tm exchange interaction is negative, corresponding to an antiferromagnetic coupling; (b) the spin-dynamical regime of the Gd–conduction-electron system is a regime of partial bottleneck; (c) from a linewidth contribution increasing exponentially with temperature we obtain an energy smaller than what is expected if it is attributed to the relaxation induced by the population of the first Van Vleck Tm excited state; (d) the temperature and concentration dependence of the Gd g value show unusual results indicating a complex behavior in the spin dynamics.

I. INTRODUCTION

Similar to other rare-earth (RE) and rare-earth-like dihydrides, TmH_2 has a face-centered-cubic CaF_2 structure. However, its low-temperature magnetic properties differ from other magnetic rare-earth dihydrides, as it has a singlet ground state. Therefore at low temperatures it is a weakly coupled Van Vleck (VV) paramagnet.[1] This was first shown by Burger *et al.*[2] from resistivity measurements. Recent susceptibility,[3] NMR[3] and neutron-diffraction[4] experiments have confirmed that the ground state is indeed a singlet.

In this work we studied the electron spin resonance (ESR) of Gd impurities in $Tm_{1-x}Gd_xH_2$ with $x=0.001$, 0.005, and 0.01 and of Er impurities in $Tm_{1-x}Er_xH_2$ with $x=0.01$. These impurities replace the Tm and therefore, their crystal electric field has a cubic symmetry with eight tetrahedral hydrogen nearest neighbors and 12 Tm next-nearest neighbors. The ground state of Er in the rare-earth-like dihydrides ScH_2 and YH_2 was found to be a Γ_7 doublet and therefore its ESR line, due to the cubic environment, is isotropic.[5] Accordingly, we expected, and indeed found, that Er in TmH_2 would have a Γ_7 ground state. As for Gd, due to its interaction with the conduction electrons, its $S_{7/2}$ ground state ESR spectrum is exchange narrowed into a single line.[6] Thus the ESR of these two impurity atoms will be mainly influenced by their exchange interaction with the conduction electrons[6] and with the magnetic Tm atoms[7,8] and can be investigated even in powdered samples. The exchange interaction will create an internal magnetic field that will affect the position of the resonance line known as the g shift. It will also affect the relaxation time of these ions that is observed via their linewidth.[6-8]

In Van Vleck systems the susceptibility χ per mole can be expressed as the sum of two contributions[1]

$$\chi=N_A g_J^2 \mu_B^2 \sum_{i=1}^{2J+1} [2|\langle i|J_z|j\rangle|^2/(E_j-E_i) + |\langle i|J_z|i\rangle|^2/T]P(i) , \quad (1)$$

with the Boltzmann statistical weights:

$$P(i)=\exp(-E_i/k_BT)\Big/\sum_{i=1}^{2J+1}\exp(-E_i/k_BT)\ .$$

The first term within the brackets is the VV-like contribution and the second term is the Curie-like term. For Tm, $J=6$, and the ground state for TmH_2 was found to be a singlet Γ_2 with the first excited state, a triplet Γ_5,[2] located about 170 K above it.[3,4] At low temperatures, only the ground state is occupied and therefore only the VV term will contribute to the susceptibility. In this temperature region, χ is temperature independent. Above a certain temperature the excited states will start to populate and both terms will contribute to the susceptibility.[1]

The ESR of Gd in Van Vleck systems has been reported in the pnictides PrX and TmX where X=P, As, Sb, and Bi.[7,8] In these compounds large g shifts were observed and found to be a linear function of the susceptibility of the host compound (when the temperature was varied) implying that the g shift is due to the exchange interaction between the Gd and the rare-earth ions. At low temperatures (when only the singlet ground state is occupied), the spin-lattice relaxation of the Gd induced by the host atoms is zero. However, at higher temperatures when the excited states start to be populated, the host atoms will induce a spin-lattice relaxation via the Tm-Tm or Pr-Pr exchange interaction.[7,8] In this temperature region a rapid increase of the linewidth with temperature is observed; it is nearly exponential when plotted as a function of $1/T$.[7] This is due to the Boltzmann factor that governs the population of the excited state. A similar ESR behavior is expected for rare-earth ions with a doublet ground state interacting with the VV host rare-earth ions. However, very little has been published on this matter. The only work we are aware of is the ESR of Nd and Yb with a Γ_6 doublet ground state in a few VV pnictides at $T=1.8$ K, where significant g shifts were observed.[9] As no temperature dependence of the spectra was included in this report, it was not possible to obtain information on the g shift and linewidth behavior at higher temperatures.

The interaction with the conduction electrons should lead to a g shift that is proportional to the strength of the exchange interaction and the density of states of the conduction electrons,[6] and a linear thermal broadening due to the Korringa mechanism.[10] This simple behavior is expected for the so-called unbottlenecked case where the conduction spin-lattice relaxation rate is large compared to other relaxation channels. However, as shown by Hasegawa[11] other possible situations may occur due to the exchange of magnetization between the impurity spin system and conduction-electron spin system. This exchange of magnetization is effective when the g values of both systems are close, and can lead to a partial or a complete bottleneck state.[6] The average g value of the spins of the conduction electrons is about 2. For Er, in cubic symmetry with a Γ_7 ground state, $g=6.77$, and therefore no bottleneck is expected. In contrast, the g value for Gd is 1.993, and therefore a partial or a full bottleneck can occur that influences the ESR spectrum. The magnetization of the impurity system is proportional to the Gd concentration, and therefore a change in the bottleneck conditions is obtained when the Gd concentration is varied.[6] Korringa relaxation in the pnictide VV system was not reported;[7,8] it could be either that the linewidth broadening was too small or that the broadening induced by the rare-earth host ions interfered with the observation. Korringa broadening was observed for Gd in the VV system $PrIn_3$.[8]

In this work we show that the points discussed above have to be taken into account when analyzing the experimental results. We found that although the Er ESR results can be analyzed in a straightforward way, the Gd results are more complicated. In addition, we found that it was not possible to obtain a stoichiometric TmH_2 compound, as a small percentage of the Tm atoms had a magnetic moment at low temperatures. This could affect the ESR behavior in particular for the Gd case.

In the following, we will first describe the sample preparation and the experimental setup, followed by the experimental results. We will then introduce the theoretical part needed for the analysis. The discussion of the experimental results is presented in the last part of our work.

II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The compounds of Tm doped with Gd or Er were prepared in an arc furnace. A 3 at. % Gd master alloy was used to prepare the $Tm_{1-x}Gd_x$ compounds $(0.01>x>0.001)$. The concentration was reduced by alloying it with pure Tm in the proper ratios. The $Tm_{0.99}Er_{0.01}$ alloy was prepared by melting the two elements in one stage. The purity of the elements was 99.9%.

The hydrides are prepared by direct pressure absorption of hydrogen at about 600 °C. At this temperature the H atoms occupy essentially the two available tetrahedral interstitial sites per Tm atom, but there is also possible formation of a H solid solution within the octahedral sites. For this reason one has to subsequently outgas the hydride at a lower temperature (≅550 °C) under a low pressure ($\cong 10^{-7}$ Torr); under such conditions the system Tm-H is stable for the dihydride and unstable for the solution of H in the dihydride.[12]

We carried out a series of ESR measurements at X-band frequency ($f \cong 9.2$ GHz) on powder samples, studying the resonance spectrum as a function of temperature in the range 4–40 K. In our experimental setup the temperature is fixed by means of a helium-gas-flow cryostat (Oxford Instruments) which enables one to vary the temperature T continuously from liquid-helium temperature up to room temperature. A standard field-modulation technique is used so that the detected signal corresponds to the field derivative of the absorbed microwave power. Our ESR experimental results will be described in the next section.

III. EXPERIMENTAL RESULTS

A. Susceptibility of TmH_2

Figure 1 displays the measured magnetic susceptibility $\chi(T)$ of a TmH_2 powder sample, where $\chi(T)$ represents $M(T)/H$ (the magnetization $M(T)$ having been measured in the constant field $H=5$ kOe with a vibrating sample magnetometer). $\chi(T)$ is seen to increase with decreasing temperature from $T=300$ K down to about 40 K, below which it flattens out except for the presence at very low temperatures ($T<10$ K) of a small Curie-like component which will be discussed below. The nearly constant low-temperature $\chi(T)$, as taken at $T=20$ K, is found to be $\cong 0.067$ emu/mol or 2.76×10^{-3} emu/cm^3. This may be attributed to the low-temperature Van Vleck susceptibility of the singlet ground-state Tm ions. The plot of $1/\chi$ versus T, which is also shown in Fig. 1, gives in the high-temperature range a mean slope corresponding to a magnetic moment of $\cong(7.7\pm 0.3)\mu_B$, i.e., a value very close to that of a free Tm atom.

As previously mentioned, at very low temperatures ($T<10$ K), a Curie-like component is evidenced in $\chi(T)$; this component is likely to be related to the presence of a small concentration of Tm ions having a magnetic ground state. The estimated concentration of these magnetic Tm ions is of the order of 1 at. %. Their origin is most probably related to a stoichiometry problem, the exact H concentration y being perhaps slightly different from the value 2: for instance, the presence of a small concentration of octahedral H atoms (in excess of 2) may change the local symmetry of the Crystal Field and thus lead to a magnetic ground state; if y is slightly smaller than 2, then there may be also a small fraction of Tm atoms having magnetic properties.

B. Description of the ESR results

As mentioned before, we carried out a series of ESR measurements at X band on powder samples, studying the resonance spectrum in the low-temperature range ($T<40$ K). The samples studied, containing diluted rare-earth impurities, are the following: (i) for TmH_2 with Er impurities we looked at a $Tm_{0.99}Er_{0.01}H_2$ powder sample; (ii) for the $Tm_{1-x}Gd_xH_2$ system we studied samples corresponding to three different Gd concentrations x: $x=0.01$, 0.005, and 0.001.

For the samples studied, the resonance data to be presented and discussed in the following concern the *g factor* (deduced from the field for resonance H^{res} through the condition $\omega=\gamma H^{\mathrm{res}}$, where $\gamma=g\mu_B/h$ is the gyromagnetic ratio of the precessing moments) and the *linewidth* ΔH ($\Delta H=1/\gamma T_2$ when the linewidth originates solely from an intrinsic relaxation mechanism of the transverse magnetization). The quantities H^{res} and ΔH_{pp} have been derived, respectively, from the field H_0 (intersection of the signal with the baseline) and the peak-to-peak linewidth ΔH_{pp} after a correction relevant to the observed A/B value. These corrections have been made assuming they are the same as the ones expected for a Lorentzian line shape corresponding to the same A/B ratio. The correction factors, needed to extract the true resonance parameters, are a unique function of the A/B ratio and they have been previously tabulated[13] for the case of an intrinsic Lorentzian line shape.

(i) *Er impurities.* The variation with temperature of the g factor and of the linewidth ΔH for the $Tm_{0.99}Er_{0.01}H_2$ sample is displayed in Fig. 2. It is first to be noticed that the g value observed for the Er resonance line indicates that the ground state of the Er^{3+} ion, in the TmH_2 cubic host, is a Γ_7 Kramers doublet. More precisely, if we refer

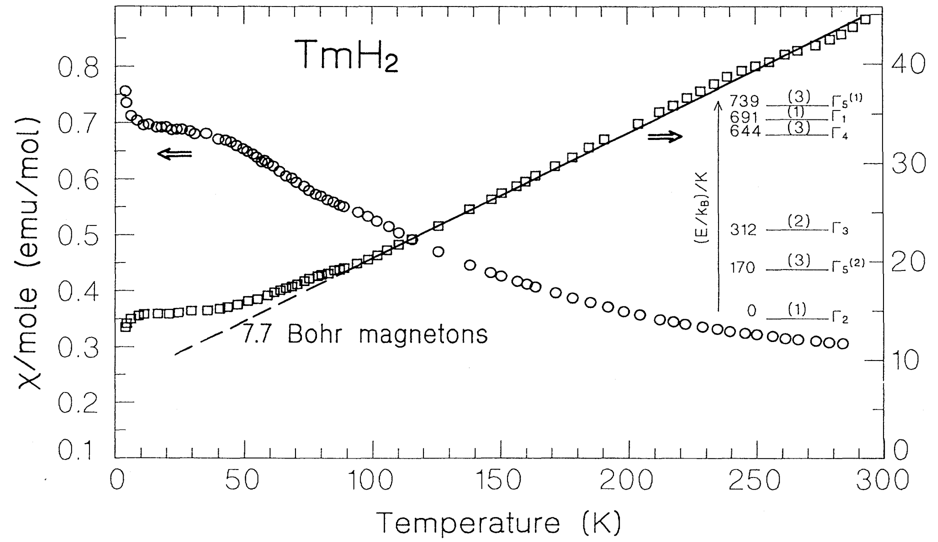

FIG. 1. Variation with temperature of the magnetic susceptibility χ of TmH_2 (left scale) and plot of $1/\chi$ vs T (right scale) where the slope of the dashed line in the high-temperature range gives a magnetic moment of $\cong 7.7\pm 0.3\mu_B$ per Tm ion. Inset: Crystal-field energy-level scheme adopted for Tm^{3+} ions on sites of cubic symmetry in TmH_2 as obtained by Winter, Shaltiel, and Dormann (Ref. 3).

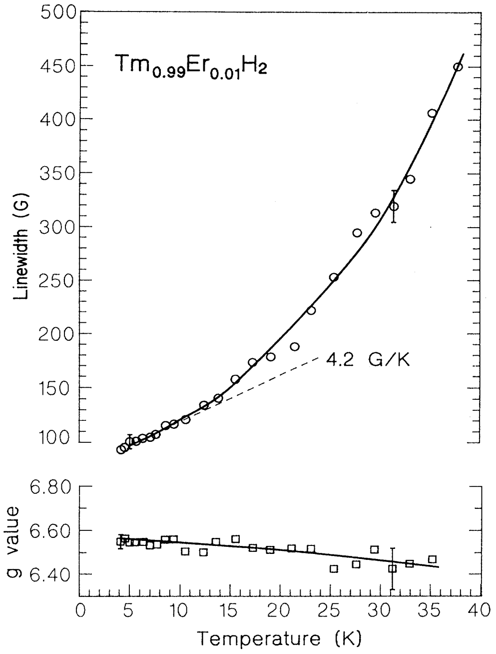

FIG. 2. Variation with temperature of the g value and of the linewidth for $Tm_{0.99}Er_{0.01}H_2$. The solid line through the data points is a guide to the eye. The low-temperature linear increase (dashed line) of the linewidth corresponds to a slope of 4.2 G/K.

the observed Er line position to $g=6.77$, the g factor of Er for a Γ_7 ground state in a cubic environment, we see that the observed value at $T=4.2$ K (which is $g=6.55\pm0.03$) corresponds to a negative g shift $\Delta g=-0.22$. The g factor is weakly temperature dependent, tending to decrease with increasing temperature in the high-temperature range of measurements ($T>24$ K). Concerning the temperature variation of the linewidth one may note the following: it shows a linear increase with temperature, in the range 4–13 K, with a slope of 4.25 G/K (see the dashed line in Fig. 2); a much more rapid increase is seen at higher temperatures. This rapid increase of the Er linewidth is likely to be associated with the relaxation mechanism of the rare-earth impurities discussed in the Introduction, namely, the exchange-induced relaxation of the impurities by the Tm host-ion spin fluctuations. These Er resonance results will be discussed and analyzed in Sec. IV. Finally, it is worth mentioning that in *pure* TmH_2 (with commercial, 99.9% pure Tm) an Er resonance line may be observed due to the presence of a small concentration of Er impurities ($x<0.001$): the resonance results are very similar to the ones reported above for the $x=0.01$ sample, indicating that the Er resonance characteristics are not very much Er concentration dependent.

(ii) *Gd impurities.* The variation with temperature of the g factor and of the linewidth ΔH for the three different $Tm_{1-x}Gd_xH_2$ samples studied is displayed in Figs. 3, 4, and 5 for, respectively, the Gd concentrations $x=0.01$, $x=0.005$, and $x=0.001$. It may be noted at first

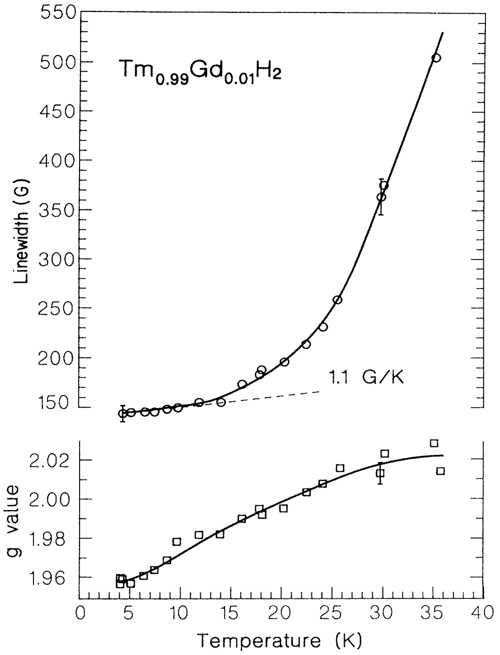

FIG. 3. Variation with temperature of the g value and of the linewidth for $Tm_{0.99}Gd_{0.01}H_2$. The solid line through the data points is a guide to the eye. The low-temperature linear increase (dashed line) of the linewidth corresponds to a slope of 1.1 G/K.

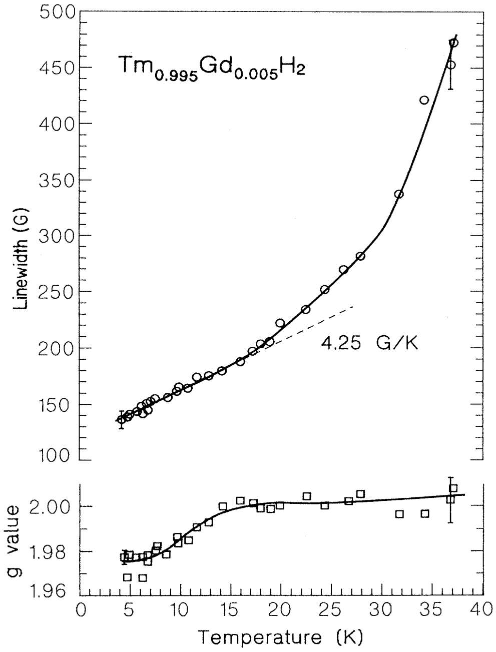

FIG. 4. Variation with temperature of the g value and of the linewidth for $Tm_{0.99}Gd_{0.005}H_2$. The solid line through the data points is a guide to the eye. The low-temperature linear increase (dashed line) of the linewidth corresponds to a slope of 4.25 G/K.

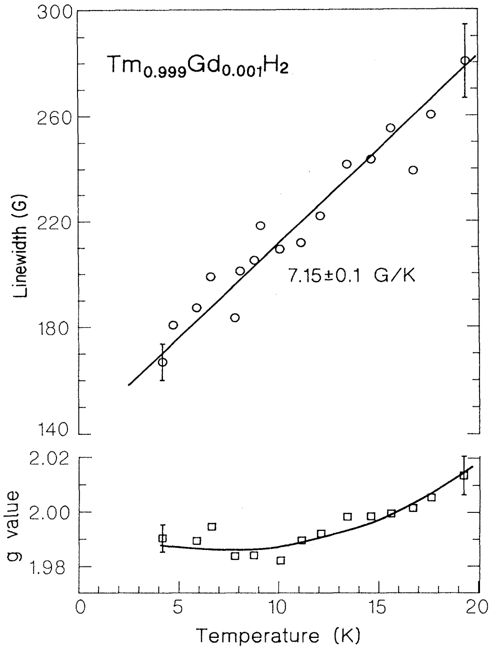

FIG. 5. Variation with temperature of the g value and of the linewidth for $Tm_{0.999}Gd_{0.001}H_2$. Within the temperature range of measurements the linewidth increases linearly with temperature (solid line) with a slope of 7.15 G/K.

that the Gd resonance characteristics and their temperature variation depend substantially on the Gd concentration. It is observed that, in the low-temperature range (typically from 4 to 15 K), the linewidth increases linearly with temperature. It is a qualitative feature common to the three samples, but it is found that the slope of this linear temperature variation is concentration dependent, increasing with decreasing Gd concentration (rising from 1.1 G/K for $x=0.01$–7.1 G/K for $x=0.001$). At higher temperatures (typically $T>15$ K) the linewidth increases much more rapidly than linearly with temperature. This nonlinear temperature-dependent contribution to the linewidth is to be associated with the relaxation of the Gd impurities by the Tm host ions.

Concerning the g values, one may refer the observed Gd resonance line positions to $g=1.993$, the g value of a Gd^{3+} ion in an insulating material. Then the following points may be stressed from our experimental results. At the lowest temperature ($T=4$ K), the observed g value corresponds for the three Gd samples to a negative g shift, as in the Er impurity case, but its absolute value is found to be Gd concentration dependent. Another important qualitative feature is to be pointed out: a substantial temperature variation of the g factor is observed within the temperature range of measurements. It corresponds to a monotonic increase of g with increasing temperature, a phenomenon evidenced for the three different samples.

IV. ANALYSIS AND DISCUSSION

A. Theoretical framework

The crystal-field Hamiltonian for rare-earth (RE) ions in a cubic field has the form[14]

$$\mathcal{H}_{\rm CF}(\mathbf{J})=B_4O_4(\mathbf{J})+B_6O_6(\mathbf{J}) , \qquad (2)$$

where $O_4(\mathbf{J})$ and $O_6(\mathbf{J})$ are the equivalent operators of the 4th and the 6th degree, respectively; B_4 and B_6 are the crystalline parameters of the fourth and sixth degree, respectively. $\mathbf{J}$ is the total angular momentum of the rare-earth ion. The wave functions and energy levels of the $2J+1$ states were calculated and tabulated as a function of two parameters W and x, by Lea, Leask, and Wolf[15] (LLW), where $B_4=Wx$ and $B_6=W(1-|x|)$. The temperature dependence of the undoped TmH_2 was measured by Winter, Shaltiel, and Dormann,[3] who found that at low temperatures, up to about 30 K, the susceptibility was constant, indicating that the ground state is a VV singlet. Fitting the susceptibility to the calculated values of LLW and Eq. (1) they obtained the energy scheme for Tm, shown in Fig. 1, with $x=0.53$ and $W=-3.905$, where the ground state is a Γ_2 with a Γ_5 (Ref. 2) triplet state 170 K above it. At low temperatures Winter, Shaltiel, and Dormann found a small Curie-like contribution attributed to the presence of a small percentage of Tm ions with a magnetic ground state. Our measurements of the susceptibility of an undoped TmH_2 sample show similar results (Fig. 1). Again a small additional Curie-like contribution is observed; they are attributed to 1 at. % Tm atoms with a magnetic ground state.

In this work we have used the ESR of Er and Gd impurities as probes to investigate the magnetic properties of the host TmH_2 metal. The spin Hamiltonian $\mathcal{H}$ with spin $\mathbf{S}_I$ for Gd or Er impurities in TmH_2 can be expressed as the sum of several terms:

$$\mathcal{H}=\mathcal{H}_Z+\mathcal{H}_{I,\rm Tm}+\mathcal{H}_{I,\rm CE} , \qquad (3)$$

where $\mathcal{H}_Z$ is the Zeeman term, $\mathcal{H}_{I,\rm Tm}$ is the isotropic exchange interaction between the impurity spin $\mathbf{S}_I$ and the Tm spin $\mathbf{S}_{\rm Tm}$, and similarly $\mathcal{H}_{I,\rm CE}$ is the exchange interaction of the impurity spin and the spins of the conduction electrons. Specifically, we can write

$$\mathcal{H}_Z=g_I\mu_B(\mathbf{H}\cdot\mathbf{S}_I) , \qquad (4)$$

where g_I is the isotropic g value and $\mathbf{H}$ is the external magnetic field.

$$\mathcal{H}_{I,\rm Tm}=\mathcal{J}_{I,\rm Tm}\sum_j \mathbf{S}_I\mathbf{S}_{{\rm Tm},j}=(g_{J,\rm Tm}-1)\mathcal{J}_{I,\rm Tm}\sum_j(\mathbf{S}_I\mathbf{J}_{{\rm Tm},j}) , \qquad (5)$$

where $\mathbf{S}_{\rm Tm}$ and $\mathbf{J}_{\rm Tm}$ are the spin and the total angular momentum of the Tm ion respectively, and $\mathcal{J}_{I,\rm Tm}$ is the exchange-interaction constant between the impurity ion and the Tm ion. The sum is over the $Z=12$ Tm nearest neighbors. $g_{J,\rm Tm}$ is the Tm Landé g factor.

$$\mathcal{H}_{I,\rm CE}=\mathcal{J}_{I,\rm CE}\mathbf{S}_I\langle \mathbf{s}\rangle , \qquad (6)$$

where $\langle \mathbf{s}\rangle$ is the average spin of the conduction electrons, and $\mathcal{J}_{I,\mathrm{CE}}$ is the exchange-interaction constant between the impurity ions and the conduction electrons. Higher-power spin terms due to the crystal-field contribution are not included: in Er with a doublet Γ_7 ground state, these terms do not occur; in Gd they are neglected as the interaction with the conduction electrons averages out the various transitions into a single line.

The effect of the exchange-interaction terms is to create an effective internal field that will shift the position of the resonance line and give an effective g value different than g_I. The difference between these two g values is known as the g shift, Δg.

The conduction electrons in the molecular-field approximation will induce a g shift, $\Delta g_{I,\mathrm{CE}}$:[6]

$$\Delta g_{I,\mathrm{CE}}=g_I[(g_{J,I}-1)/g_{J,I}]\mathcal{J}_{I,\mathrm{CE}}\rho(E_F)\ , \tag{7}$$

where $\rho(E_F)$ is the density of states at the Fermi level and $g_{J,I}$ is the impurity Landé g value. Similarly the exchange interaction with the Z Tm nearest atoms will induce a g shift:

$$\Delta g_{I,\mathrm{Tm}}=g_I[(g_{J,I}-1)/g_{J,I}][(g_{J,\mathrm{Tm}}-1)/g_{J,\mathrm{Tm}}]Z \times\mathcal{J}_{I,\mathrm{Tm}}\chi_{\mathrm{Tm}}/(\mu_B^2 N_A)\ , \tag{8}$$

where χ_{Tm} is the susceptibility per mole and N_A is Avogadro's number. The total g shift Δg_I is the sum of the two g shifts

$$\Delta g_I=\Delta g_{I,\mathrm{Tm}}+\Delta g_{I,\mathrm{CE}}\ . \tag{9}$$

The exchange interaction will also induce the relaxation of the impurity spin system. The dynamics of this relaxation and its relation to other spin systems is schematically shown in Fig. 6 for the three spin systems: the impurities, the Tm atoms, and the conduction electrons. The arrows indicate the relaxation path, and includes the relaxation of the three systems to the lattice.

The simplest situation is the unbottlenecked case,[6,11] where the relaxation rate of the impurity spins $1/T_{I,\mathrm{CE}}$ and $1/T_{I,\mathrm{Tm}}$ into the conduction electrons and the Tm spin systems, respectively, are small compared to $1/T_{\mathrm{CE,L}}$, the relaxation rate of the conduction electrons to the lattice. Here the total relaxation of the spin system can be written as the sum of the relaxations into the other systems:

$$1/T_I=1/T_{I,\mathrm{CE}}+1/T_{I,\mathrm{Tm}}+1/T_{I,L}\ . \tag{10}$$

The relaxation rate to the lattice $1/T_{I,L}$ (via phonons) can be neglected in the temperature range where our measurements were carried out. This is well known, and was also confirmed from our measurements of the linewidths of Er or Gd in $\mathrm{LuH_2}$ which showed that $1/T_{I,L}$ is negligible with respect to $1/T_{I,\mathrm{CE}}$ (see the following paragraphs).

The relation via the conduction electrons is the Korringa relaxation:

$$1/(\gamma T_{I,\mathrm{CE}})=\Delta H_{I,\mathrm{CE}} =\pi k_B(T/\mu_B)g_I[(g_{J,I}-1)/g_{J,I}]^2[\mathcal{J}_{I,\mathrm{CE}}\rho(E_F)]^2. \tag{11}$$

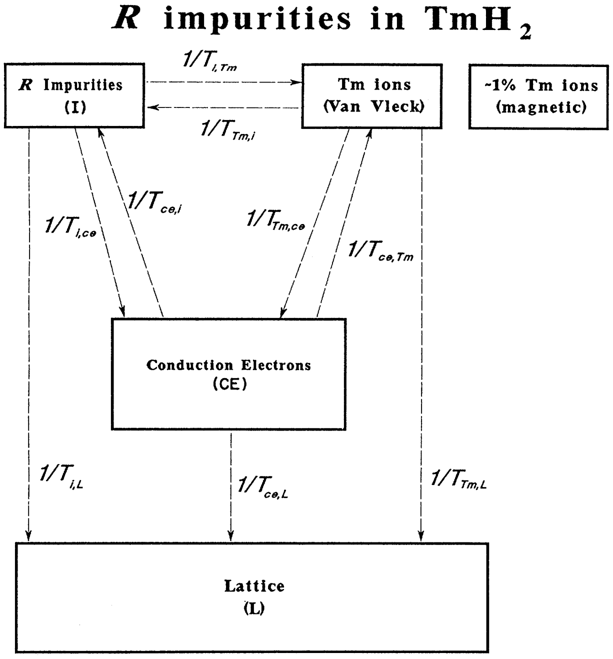

FIG. 6. Schematic diagram illustrating the three coupled-spin systems considered for the description of the spin dynamics, as discussed in the text (Sec. IV). A fourth spin system that arises from intrinsic Tm ions with a magnetic ground state is shown without its relaxation paths.

At low temperatures when only the Tm singlet state is occupied, the relaxation via the Tm spin system is virtually zero, and therefore, in this temperature region the temperature dependence of the linewidth ΔH is determined only by the Korringa rate. At higher temperatures when the Tm excited states start to populate, the relaxation path via the Tm spin system becomes effective. Detailed calculation of this relaxation has been carried out for Gd in the pnictide Van Vleck compounds. They show that the linewidth is given by[7,8]

$$1/(\gamma T_{I,\mathrm{Tm}})=\Delta H_{I,\mathrm{Tm}}=\sum_j k_j\exp(-\Delta E_j/kT)\ , \tag{12}$$

where k_j is a function of $\mathcal{J}_{I,\mathrm{Tm}}$ and various matrix elements within the Tm states; $\exp(-\Delta E_j/kT)$ is the statistical factor. At low temperatures only the first excited state will contribute to the relaxation and therefore from a Sieverts plot (of ΔH versus $1/T$), the position of the first excited state can be extracted.

When the unbottlenecked conditions are not satisfied, a more complicated situation prevails.[11] This may occur when the g value of the conduction electrons, which is around 2.0, is close to the g value of the impurities. This is the case for Gd ($g=2.00$) but not for Er with a Γ_7 ground state ($g=6.77$). For a two-spin system of the conduction electrons and the impurity ions, the bottlenecked condition has been analyzed in detail.[6] However, little has been reported for the case of a three-spin system in the bottleneck regime, and the transition to the unbottlenecked state.

B. Analysis and discussion of the experimental results

1. Analysis and discussion of the resonance of Er impurities

Resonance results relative to a $Tm_{0.99}Er_{0.01}H_2$ sample have been described in the preceding section and are shown in Fig. 2 (g value and linewidth versus temperature). We have already noted that the value observed for the Er line position indicates that the ground state of the Er^{3+} ion, in the TmH_2 cubic host, is a Γ_7 Kramers doublet.

Let us now consider the dynamics of the Er moments with respect to their exchange couplings, to the conduction-electron spins on one hand and to the Tm ions on the other hand. For the Er–conduction-electron system one can infer, due to the large difference of the resonant field values at X band frequency, that we are in the case of the weak-coupling regime (Korringa limit). One can suppose it is also the case for the Er–Tm-ion system. Consequently, the experimental resonance parameters (g shift, linewidth) should be analyzed in terms of the expressions given by Eqs. (9)–(11).

We can then proceed to the analysis of the observed resonance parameters of the Er line as follows. At the lowest temperatures, the linewidth shows a linear increase with temperature, in the range 4–13 K, with a slope of 4.25 G/K. This linear increase is to be associated with the Korringa relaxation of the Er towards the conduction electrons, theoretically described by Eq. (11), which gives

$$|\mathcal{J}_{\mathrm{Er,CE}}\rho(E_F)|=2.2\times 10^{-2}(\pm 10\%)\ .$$

To calculate $\rho(E_F)$ we make use of the value of the electronic contribution to the specific heat γ_e for LuH_2 which we assume to be close to that of TmH_2, $\gamma_e=2.27$ mJ/mol K^2.[16] From $\gamma_e=(2\pi^2/3)k_B^2\rho(E)(1+\lambda)$ [the factor 2 appears because $\rho(E)$ is calculated per atom spin], where λ is the electron-phonon enhancement factor, and using the value of $\lambda=0.13$,[16] we obtain $\rho(E)(1+\lambda)\approx 0.4$ state/eV atom spin. It follows that the value of the exchange integral deduced from the Korringa relaxation rate is $|\mathcal{J}^{\Delta H}_{\mathrm{Er,CE}}|=55$ meV.

From the Korringa linewidth the sign of this exchange interaction is not obtained. Preliminary results of ESR of Er in LuH_2 gives a negative g shift. From Eq. (7) and the value of $\mathcal{J}_{\mathrm{Er,CE}}$ we obtain $\Delta g_{\mathrm{Er,CE}}=-0.025$.

From Fig. 2, we see that the observed g value, at 4.2 K, is $g_{\mathrm{obs}}=6.55\pm 0.03$, which corresponds to a *negative relative g shift:*

$$\Delta g_{\mathrm{Er}}=-0.22(+-10\%)\ ,$$

where we refer the Er position to $g=6.77$, the g-factor value of Er for a Γ_7 ground state in a cubic environment.

According to Eq. (9) one can then deduce the contribution to the Er g shift arising from the Er-Tm exchange interaction:

$$\Delta g_{\mathrm{Er,Tm}}=-0.195(\pm 10\%)\ .$$

The main qualitative physical result obtained is that the Er-Tm exchange interaction is *negative* and that its contribution largely dominates the g shift of the Er resonance line due to the large Van Vleck susceptibility of the Tm host ions. More precisely, taking the measured value (at $T\approx 20$ K) of TmH_2 (see Fig. 2), $\chi_{\mathrm{meas}}\approx 0.676\times 10^{-1}$ emu/mol, and identifying it to the low-temperature Van Vleck susceptibility of the Tm ions we would find $\chi^{\mathrm{VV}}_{\mathrm{Tm}}\approx 2.76\times 10^{-3}$ emu/cm^3. From Eq. (8), taking into account this value of $\chi^{\mathrm{VV}}_{\mathrm{Tm}}$, together with $g_{J,\mathrm{Er}}=\frac{6}{5}$ for Er, $g_{J,\mathrm{Tm}}=\frac{7}{6}$ for Tm, $N=0.247\times 10^{23}$ Tm atoms/cm^3 and $Z_0=12$ for the number of first Tm nearest neighbors of an Er impurity, it follows from Eq. (8) that the value of the exchange integral one can estimate from the g shift is $\mathcal{J}_{\mathrm{Er,Tm}}\approx -0.45\times 10^{-1}$ meV.

2. Analysis and discussion of the resonance of Gd impurities

Resonance results relative to three different $Tm_{1-x}Gd_xH_2$ samples, corresponding to the Gd concentrations $x=0.01$, 0.005, and 0.001, have been described in Sec. III and are shown, respectively, in Figs. 3, 4, and 5 (g value and linewidth versus temperature).

The results show that below 10 K, where the Korringa relaxation should dominate, the slope of linewidth against temperature depends strongly on the concentration and varies from 1.1 G/K for 1 at. % Gd to 7.1 G/K for 0.1 at. % Gd. This is an indication that we are in the bottleneck regime, as decreasing the impurity concentration opens the bottleneck and therefore makes the relaxation via the conduction-electron spin system more effective.

The analysis of the experimental results of Gd in TmH_2 are therefore more complicated than those of Er. Such a theoretical investigation deserves an approach geared to the differential details of the experimental results and has been left for future investigation. For the present we will point out some of the unique results that have to be taken into consideration in such an analysis.

(a) The dependence of ΔH on the Gd concentration. The Korringa contribution is proportional to $p(x,T)[\mathcal{J}_{\mathrm{Gd,CE}}\rho(E_F)]^2k_BT$, while the bottleneck one is proportional to $q(x,T)(\chi_{\mathrm{CE}}/\chi_{\mathrm{Gd}})$ (if $\chi_{\mathrm{Gd}}\gg\chi_{\mathrm{CE}}$), i.e., to qT/x.[13] The observed experimental variation of $\Delta H(x,T)$ can be related to both these terms.

(b) The g value measured at 4.2 K (the lowest temperature used in this work) for $x=0.01$ is 1.957 and it increases with decreasing concentration to 1.975 and 1.99 for $x=0.005$ and $x=0.001$, respectively. As the Korringa relaxation for $x=0.001$ is a factor of 6.5 larger [i.e., $p(x)$ increases when x decreases] than for $x=0.01$, we can assume that the latter is almost fully bottlenecked and therefore most of its g shift arises from the direct exchange interaction Gd-Tm. A negative g shift is obtained with $\Delta g=-3.6\times 10^{-2}$, using the value of the unshifted g equal to 1.993. Thus, as in the case of Er, the coupling has a negative sign. For a rough estimate using Eq. (8) and taking $\chi^{\mathrm{VV}}_{\mathrm{Tm}}=2.76\times 10^{-3}$ emu/cm^3, $g=2$ for Gd and $Z_0=12$, the number of Gd-Tm first nearest neighbors, we obtain for the exchange interaction $\mathcal{J}_{\mathrm{Gd,Tm}}=-0.098\times 10^{-1}$ meV, which corresponds to a weaker value than $\mathcal{J}_{\mathrm{ER,Tm}} = -0.45 \times 10^{-1}$ meV obtained above. The corresponding ratio is relatively large but one has to consider that the absolute values are very small, so that they may be very sensitive to the local distance (between Tm and Er,Gd) and the stresses surrounding the Er,Gd atoms.

(c) A possible explanation for the *increase* of the g value at 4.2 K with the decrease of the Gd concentration is to attribute this increase to the opening of the relaxation bottleneck of the Gd ions to the lattice via the conduction electrons. This however will necessitate a positive exchange interaction $\mathcal{J}_{\mathrm{Gd,CE}}$ [see (d) below].

(d) The temperature dependence of the g value. In all samples the Δg vary from negative values to positive ones with $g = 2.02$ at high temperatures. A possible explanation for this variation is to attribute it to the interaction with Tm in the excited states. However, a variation of the g shift is already observed for the 0.01 sample at 6 K (see Fig. 3). At this temperature the population of the first excited state that is situated at 170 K is negligible and therefore cannot influence the g value. A second possible explanation is to attribute it to an increase with temperature of the Korringa contribution with positive $\mathcal{J}_{\mathrm{Gd,CE}}$. This is in contrast to the negative exchange interaction with the conduction electrons observed for Er in $\mathrm{LuH_2}$.[17]

(e) Above a certain temperature, typically 15 K, there is a rapid increase of the linewidth with temperature compared with the weak lower-temperature linear increase. This nonlinearly temperature-dependent contribution to the linewidth is associated with the relaxation of the Gd impurities by the magnetic excited crystal-field states of the Tm host atoms [Eq. (12)]. Taking the linewidth data of Fig. 3, we have plotted $\ln(\Delta H - \Delta H_l)$ versus $1/T$ where ΔH_l corresponds to the linearly temperature-dependent contribution of the observed linewidth ΔH. This plot is displayed in Fig. 7 together with that for Er using the data of Fig. 2.

They show that the linewidth contribution varies with temperature (variation of the form $e^{-(\Delta E/kT)}$ with $\Delta E = 100$ K for the Gd sample and 80 K for the Er sample. Thus these values that should reflect the typical energy splitting of the first Tm triplet state are lower than the value of 170 K obtained from susceptibility[3] and neutron diffraction.[4] It should be mentioned that the NMR relaxation of the Tm nuclei in $\mathrm{TmH_2}$ shows a very similar behavior as a function of temperature as in the ESR of Gd and Er, but there ΔE is close to 170 K.[17] This is in contrast to results in TmSb where the value obtained for the position of the first excited state from ESR (Ref. 18) is in close agreement with inelastic-neutron-scattering data.[19] Thus there is a discrepancy between the energy associated with the first excited state of Tm, as observed by susceptibility, neutron scattering, and NMR of the Tm atoms, and that obtained from ESR. The results indicate that some mechanism is involved that lowers the energy. A possible explanation for this effect is that substitution of Er and Gd atoms introduces stresses around these impurities, lowering the energy level of the first excited state of their neighboring Tm atoms.

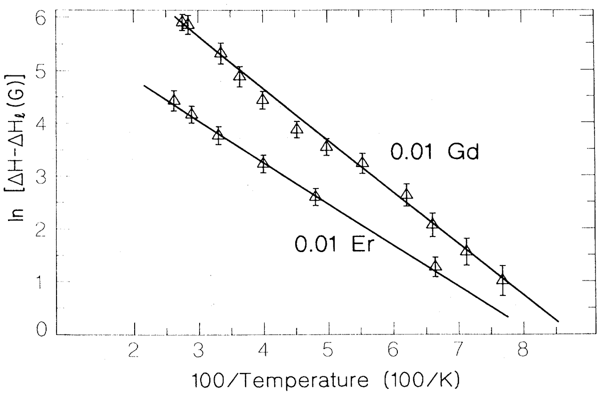

FIG. 7. Plot of $\ln(\Delta H - \Delta H_l)$ vs the inverse of the temperature for $\mathrm{Tm_{0.99}Er_{0.01}H_2}$ and $\mathrm{Tm_{0.99}Gd_{0.01}H_2}$ samples. ΔH is the observed linewidth (data of Figs. 2 and 3), and ΔH_l designates the extrapolated linewidth contribution which is increasing linearly with temperature.

(f) In the analysis of the ESR experiments one has to take into account, in addition to the three coupled spin systems, namely, the Gd spin system, the Van Vleck Tm spin system, and the conduction electrons, also the Tm atoms whose symmetry deviates from cubic symmetry. The presence of these Tm atoms is intrinsic, as it was found that stoichiometric $\mathrm{TmH_2}$, where all the H atoms occupy all the tetrahedral sites, does not form. So we either obtain $\mathrm{TmH_{2-x}}$ ($x \approx 0.01-0.02$) with vacancies in the tetrahedral H sites, or $\mathrm{TmH_{2+x}}$ where the H atoms occupy the octahedral sites.[20] In either case a small fraction of the Tm atoms do not possess cubic symmetry and have a magnetic ground state, as seen by the susceptibility at low temperatures. These fractions of Tm atoms will also influence the symmetry of near Tm atoms and therefore vary the position of the energy levels in these Tm neighboring atoms.[21] This may also effect the relaxation $T_{\mathrm{Gd,Tm}}$ or $T_{\mathrm{Er,Tm}}$ associated with the population of the Tm first excited states.

V. CONCLUSION

In summary, the present experimental investigation has been essentially concerned with a detailed study of the ESR of rare-earth impurities Er and Gd in $\mathrm{TmH_2}$. This method was used to probe the magnetic behavior of this metallic singlet ground-state system. Measurements of the susceptibility of the pure-metal host confirmed that it is to be associated with the Van Vleck susceptibility of the Tm ions over a large low-temperature range, indicating than the singlet state is well isolated in energy from the first excited state. However, a Curie-like contribution below 10 K indicates that about 1% of the Tm atoms do not have a singlet ground state. This is due to vacancies in the tetrahedral H sites and/or the occupation of octahedral H sites that induce a noncubic crystal field on the neighboring Tm atoms.

The observed resonance characteristics (g value, linewidth) of the Gd and Er impurities in $\mathrm{TmH_2}$ show a much more complex behavior, with temperature and impurity concentration, than the one previously observed in thulium and praseodymium monopnictides,[7,8] and cannot be analyzed only in terms of the effects induced by the exchange coupling between the impurity and Tm host ions, but also by their coupling with the conduction electrons. Therefore a three coupled-spin system has been used for the Hasegawa description of the spin dynamics in the present metallic system.

The main physical information that we extracted from the analysis of our ESR results are the following:

(i) The exchange interaction between the rare-earth impurities Er and Gd and the Tm host ions is negative in sign, corresponding to an antiferromagnetic coupling, as has been found in TmSb and TmBi compounds,[22] but the estimated magnitude of the exchange integral corresponds to a much weaker value than in the latter case.

(ii) The rapid increase of the linewidth observed typically above $T \approx 15$ K and departing from the low-temperature linear increase was found to increase exponentially with temperature for $Tm_{0.99}Gd_{0.01}$ and $Tm_{0.99}Er_{0.01}$ samples assuming an $e^{-(\Delta E/kT)}$ behavior. This energy corresponds to 100 K and 80 K for the Gd and Er, respectively, much lower than the energy of 170 K of the first Tm excited state obtained from susceptibility, NMR, and neutron diffraction.

(iii) We inferred from the Gd-concentration dependence of the low-temperature linear increase of the linewidth in the Gd samples that the spin-dynamical regime of the Gd–conduction-electron) system is a regime of partial bottleneck.

(iv) A strong temperature dependence of the g value observed already at 6 K cannot be associated with the position of the first excited state of the Van Vleck Tm atoms (170 K) indicating a more complicated behavior of the TmH_2 system, that may also be responsible for the concentration dependence of the g value.

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