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Spin-disorder resistivity in the paramagnetic state of the heavy rare-earth dihydrides

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We present systematic measurements of the paramagnetic spin-disorder resistivity ρ_m in Gd, Tb, Dy, Ho, and Er dihydrides. We observe that ρ_m is strongly affected by crystalline-field effects especially as concerns DyH_2 and ErH_2. The absolute values of ρ_m are much smaller than in the corresponding pure metals, an effect which can be attributed in part to modifications, with hydrogen, of the electronic band structure, but it implies also a reduction of the fundamental exchange interaction between conduction and localized electron spins.

INTRODUCTION

The magnetic properties of rare-earth (RE) systems are mainly a consequence of the local exchange interaction between conduction-electron spins **s** and RE spins **S**, i.e.,

$$\mathcal{H} = -\Gamma\delta(\mathbf{r}-\mathbf{R})\mathbf{s}\cdot\mathbf{S} \ . \tag{1}$$

(**r** and **R** are the respective positions of the conduction-electron and RE spins and Γ the interaction constant.)

This interaction results in magnetic ordering below a temperature T_N (proportional to Γ^2) which involves also the well-known Ruderman-Kittel-Kasuya-Yosida (RKKY) function related to the long-range and oscillating character of the conduction-electron spin polarization.[1] But it gives also rise, in the paramagnetic state ($T > T_N$) to the so-called spin-disorder resistivity ρ_m given by Ref. 1:

$$\rho_m = (\hbar k_F / 4\pi Z)(m\Gamma / e\hbar^2)^2 (g_J - 1)^2 J(J+1) \ . \tag{2}$$

(k_F is the Fermi wave vector, Z the number of conduction electrons per atom, g_J the Landé factor, and $J = L + S$ the total angular momentum quantum number.)

This expression involves only Γ and some features of the band structure such as Z and the density of states $N(\varepsilon_F) = (mk_F/2\pi^2\hbar^2)$, possibly permitting an easier quantitative analysis of it. One of the main purposes of this work is to compare the absolute values of ρ_m in the hydrides and in the corresponding pure metals; there is, in fact, between these two systems a drastic change in electronic structure: For instance, the pure metals have three conduction electrons while the dihydrides have only one; this is so because a large fraction of the conduction-electron states is pulled down, below the d band, by the strong protonic potential leading to the formation of full low-lying metal-hydrogen bonding bands.[2,3] There remains then only one electron in the conduction band with a pure d character.

Complications for ρ_m (but also for T_N) may stem from crystalline-field effects due to the electrostatic charges surrounding a given RE ion. These fields may split the $2J+1$ degeneracy of the ionic state giving rise to a number of energy levels ε_i. This situation has been analyzed in detail[4] for crystal fields of cubic symmetry (which is the case for the dihydrides); the corresponding Hamiltonian involves two parameters W and x: The first one is a scaling factor depending on the sign and amplitude of the surrounding charges while the second reflects the ratio of the fourth- and sixth-degree crystal fields. The main consequence of these crystal fields is to modify the structure of the ground state, with essentially a decrease of the associated magnetic moment and spin-disorder resistivity; as concerns ρ_m, it becomes temperature dependent even in the paramagnetic regime, when $k_B T \simeq \Delta E_{ij}$, where $\Delta E_{ij} = \varepsilon_j - \varepsilon_i$ measures the crystalline-field energy splitting. The new expression for $\rho_m(T)$ is then given by

$$\rho_m(T) = \sum_i \rho_{ii} P_i + \sum_{i \neq j} \rho_{ij} P_i f_{ij} \ . \tag{3}$$

(P_i is the probability for the RE ion to be in the substate i of energy ε_i, while f_{ij} is a statistical factor.)

A detailed analysis of formula (3) is given in Ref. 5 for the case of TmH_2 (see also Refs. 6 and 7). Formulas (3) and (2) converge of course in the limit $k_B T \gg \Delta E_{ij}$.

EXPERIMENTAL ANALYSIS OF THE ELECTRICAL RESISTIVITY $\rho(T)$

The measured resistivity $\rho(T)$ comprises several terms, i.e.,

$$\rho(T) = \rho_r + \rho_m + \rho_{\mathrm{ph}}(T) \ . \tag{4}$$

ρ_r is the residual resistivity, ρ_{ph} is the phonon resistivity resulting from both acoustical and optical phonons. A precise determination of ρ_m requires therefore first a knowledge of ρ_r and ρ_{ph}. The residual resistivity is determined at $T \ll T_N$ and it turns out to be always quite small, i.e., $\rho_r \leq 0.5 \pm 0.1$ $\mu\Omega$ cm; these low values indicate that our dihydrides RH_x are always very near to the stoichiometry $x = 2$.

The phonon resistivity has been determined quantitatively in a number of preceding investigations;[8] the acoustical contribution is in all cases very similar to the one observed in the nonmagnetic dihydride LuH_2, a fact which facilitates its quantitative evaluation; the optical contribution is always small and different from zero only for $T > 150$ K. The preparation of the hydrides is done using standard techniques and details are given in previous work.[8]

RESULTS

As a typical example, we will first analyze the case of DyH_2, for which we will see that there are marked crystalline-field effects. On Fig. 1 we plot the measured resistivity $\rho(T)$ for which one can distinguish three temperature regions.

(1) $T > 130$ K: In this region, one can represent $\rho(T)$ exactly by a law of the form $\rho = \rho_0 + \rho_{\text{ph}}(T)$ where ρ_0 is a constant resistivity comprising ρ_r and ρ_m.

(2) $5 \leq T \leq 130$: In that region one sees that $\rho(T)$ drops below the preceding law, represented by the dashed curve. It means in fact that $\rho_m(T)$ begins to decrease as soon as $T < 130$ K.

(3) $T < 5$ K: Magnetic ordering begins to occur (see inset of Fig. 1), $\rho_m(T)$ drops to zero leaving only ρ_r in the limit $T \rightarrow 0$.

Similar behavior, somewhat less pronounced, is observed for all the other dihydrides. In all cases, we are able to isolate the $\rho_m(T)$ contribution and we will now present the corresponding values along the RE series.

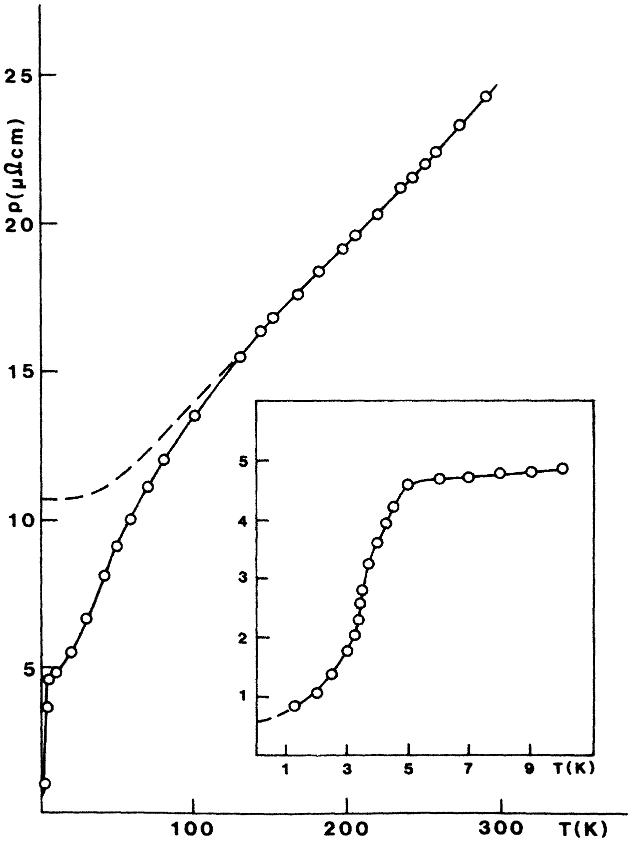

FIG. 1. Variation of the total resistivity $\rho(T)$ for DyH_2. The dashed curve corresponds to the phonon resistivity with a constant spin-disorder resistivity ρ_m; the inset gives the magnetic ordering transition.

For GdH_2, we plot $\rho_m(T)$ on Fig. 2; here one expects, as is indeed the case, a temperature-independent ρ_m since there are essentially no crystal-field effects, mainly because of the absence of an orbital moment; the absolute value $\rho_m = 29 \pm 2$ $\mu\Omega$ cm (the uncertainty stems only from the difficulty to determine the geometrical factor of the samples) is about four times smaller than in pure Gd.[1]

The case of TbH_2 should be *a priori* more complex: It corresponds to $J = 6$ and the corresponding ground state (see Table I) and should be nonmagnetic if one attributes the crystal field to the surrounding nearest-neighbor H atoms. This is so both if H is charged positively (protonic model) or negatively (hydridic model); we will in fact only consider the latter H^- model because there is enough evidence in its favor both theoretically[3] and experimentally[9-11] for various dihydrides. The observed $\rho_m(T)$ for TbH_2 is quite large (Fig. 2) and essentially temperature independent for $T > 70$ K, but there is nevertheless a well-defined and appreciable decrease for $T_N < T < 70$ (with $T_N \simeq 18$ K), indicating that the ground state is somewhat less magnetic than the free isolated Tb ion. It is interesting to note that TmH_2, which was investigated in a previous paper,[5] has also $J = 6$, but here one observes effectively a nonmagnetic ground state with $\rho_m = 0$ for $T < 10$ K. We will see in the discussion the possible reasons for the differences between TbH_2 and TmH_2.

The variation of $\rho_m(T)$ for DyH_2 is represented in Fig. 3, where one can see the large drop from $\rho_m = 10.1$ $\mu\Omega$ cm above 130 K to $\rho_m = 4$ $\mu\Omega$ cm just above T_N; it will be shown later on that this drop is entirely in agree-

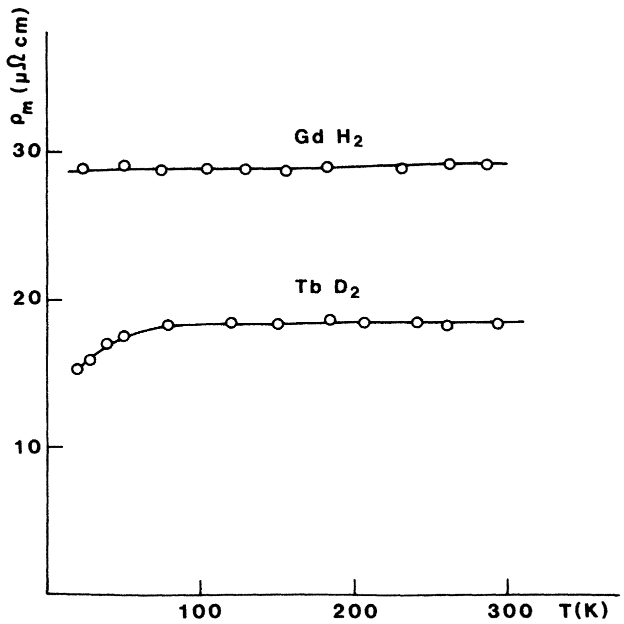

FIG. 2. Temperature variation of the spin-disorder resistivity $\rho_m(T)$ for GdH_2 and TbD_2.

TABLE I. Spin-disorder resistivity ρ_m in RH_2. The theoretical values, taking GdH_2 as reference, are given in column 1. In column 2, we give the measured ground-state resistivity for $T \sim T_N$; the experimental and theoretical ground-state resistivity ratios are given in columns 4 and 5 for the known or possible ground states (column 3). Column 6 gives the measured ground-state magnetic moments normalized to the free-ion value; in the last column, we report the value of ρ_m measured at high temperature ($T=300$ K).

	ρ_m^{th} ($\mu\Omega$ cm)	ρ_m^{GS} ($\mu\Omega$ cm) (expt.)	Ground state	$\rho_m^{\text{GS}}/\rho_m^{\text{th}}$ (theory)	$\rho_m^{\text{GS}}/\rho_m^{\text{th}}$ (expt.)	μ^{GS}/μ_0 (expt.)	ρ_m^{HT} ($\mu\Omega$ cm)
GdH_2	29	29	Free ion	1	1	1	29
TbH_2	19.3	15.3	Γ_2 ($x<0.81$)	0			
			Γ_3 ($x>0.81$)	0	0.79	0.82(10)	18.4
			$\Gamma_2+\Gamma_5^{(2)}+\Gamma_3$ ($x=0.81$)	0.76			
DyH_2	13	4	Γ_7	0.37	0.31	0.38(9)	10.1
HoH_2	8.35	5.8	$\Gamma_5^{(2)}$ ($x<-0.54$)	0.44	0.69	0.64(10)	5.8
			$\Gamma_3^{(2)}+\Gamma_4^{(2)}$ ($x>-0.4$)	0.63			
ErH_2	4.7	1.5	Γ_6	0.30	0.32	0.31(8)	3.2
TmH_2	2.15	0	Γ_2,Γ_3	0	0	0	2.8

ment with the expected ground-state configuration.

The case of HoH_2 is apparently more classic (Fig. 3): ρ_m is nearly constant for $30 \le T \le 300$. Below 30 K one observes a slight increase of ρ_m; similar increases are observed in TbH_{2+x} (Ref. 12) (with $x>0$) and in the pure dihydrides of Pr and Sm (unpublished work from our laboratory). A possible explanation is to relate it to an incommensurate precursor small magnetic ordering which is observed in some dihydrides and termed as "intermediate magnetic structure,"[13] but there may be other explanations like the Kondo effect or the electron scattering from an aspherical Coulomb potential;[14] in the present state it is difficult to decide among these different possibilities.

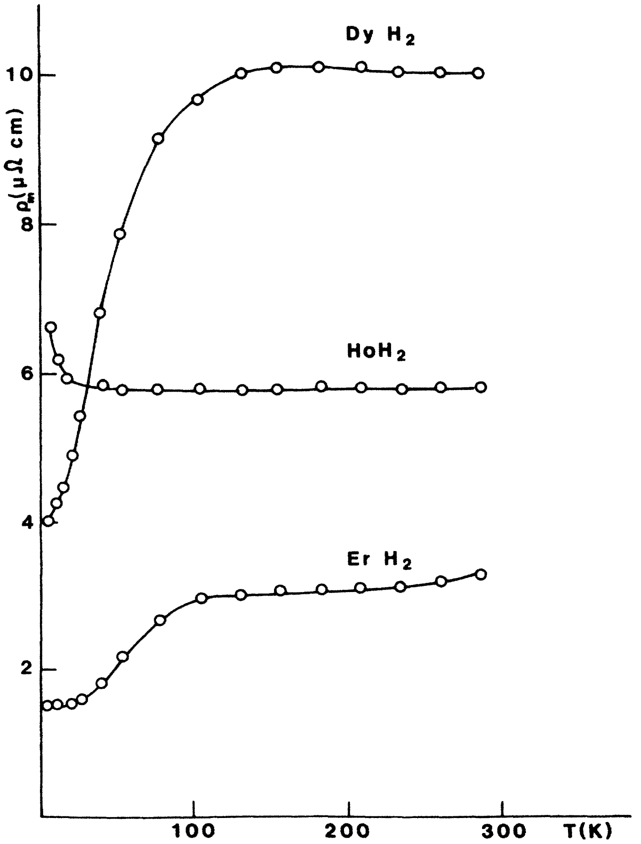

FIG. 3. Temperature variation of the spin-disorder resistivity $\rho_m(T)$ for DyH_2, HoH_2, and ErH_2.

The case of the ErH_2 (Fig. 3) is very similar to that of DyH_2. ρ_m increases from 1.5 $\mu\Omega$ cm above T_N ($=2.3$ K) to about 3.2 $\mu\Omega$ cm at room temperature. The main part of the increase occurs between 30 and 130 K though there seems to be a slight but continuous increase of ρ_m even above 130 K, which is perhaps not finished even at 300 K.

DISCUSSION

For the quantitative analysis of our data we take ρ_m of GdH_2 as a reference value and compare the measured values with a model where we take Γ and the band-structure parameters as strictly constant for all dihydrides. This defines a theoretical spin-disorder resistivity labeled as ρ_m^{th}, the values of which are given in Table I and Fig. 4 (dashed curve). The values of ρ_m measured at high temperature ($T=300$ K), i.e., ρ_m^{HT} are also given in Table I and Fig. 4. The overall variation of ρ_m^{HT} follows reasonably well the de Gennes law but it is to be remarked nevertheless that the observed values for DyH_2, HoH_2, and ErH_2 are somewhat below theoretical expectations, indicating perhaps that the crystal-field effects are not saturated at this temperature.

In a first part of the discussion we will concentrate on these absolute values of ρ_m^{th} which are about four times smaller than the values observed in the pure RE (Fig. 4). In order to do this it is convenient to separate the contribution to ρ_m related to the band-structure parameters and the one related to the scattering mechanism (or the scattering lifetime τ), i.e.,

$$\rho_m = \frac{m}{ne^2}\frac{1}{\tau}\,, \qquad \frac{\hbar}{\tau} \simeq N(\varepsilon_F)\Gamma^2 \tag{5}$$

[$n=(Z/\Omega)$ is the number of conduction electrons per unit volume, Ω the atomic volume, $N(\varepsilon_F)$ the density of states]. The term $A=(m/ne^2)$ is related only to band-structure parameters; in the free-electron approximation it varies like $1/Z$, i.e., it is three times larger in the dihydrides than for the pure metal; outside this approximation one must replace m/n by a quantity[8] proportional to $1/N(\varepsilon_F)v_F^2$, which can be estimated by looking at detailed band-structure calculations.[2,3,15,16] Very roughly one finds that the density of states and the bandwidth are about two times smaller in the dihydrides as compared to the pure metals. From this one can deduce that $A(RH_2)/A(R)\simeq 3.1\pm 0.2$, a value which is very near to the free-electron approximation (R is a rare-earth ion). One sees thus that the decrease of $\rho_m(RH_2)$ as compared to $\rho_m(R)$ is in fact opposed to the variation of A, implying that $1/\tau$ decreases by a factor of more than 10; this spectacular reduction of $1/\tau$ cannot be explained just by a variation of $N(\varepsilon_F)$ but implies also a reduction of Γ^2 by a factor of more than 4 to 6 i.e. Γ must be reduced by more than a factor of 2. It is to be remarked that a similar decrease is observed as concerns the phonon resistivity when one goes from R to the RH_2: In that case one has $(\hbar/\tau)=\lambda k_B T$, where λ is the electron-phonon coupling parameter. Here one finds that λ is reduced by a factor of about 10,[8] indicating a striking parallelism between the variation of ρ_m and $\rho_{\text{ph}}(T)$.

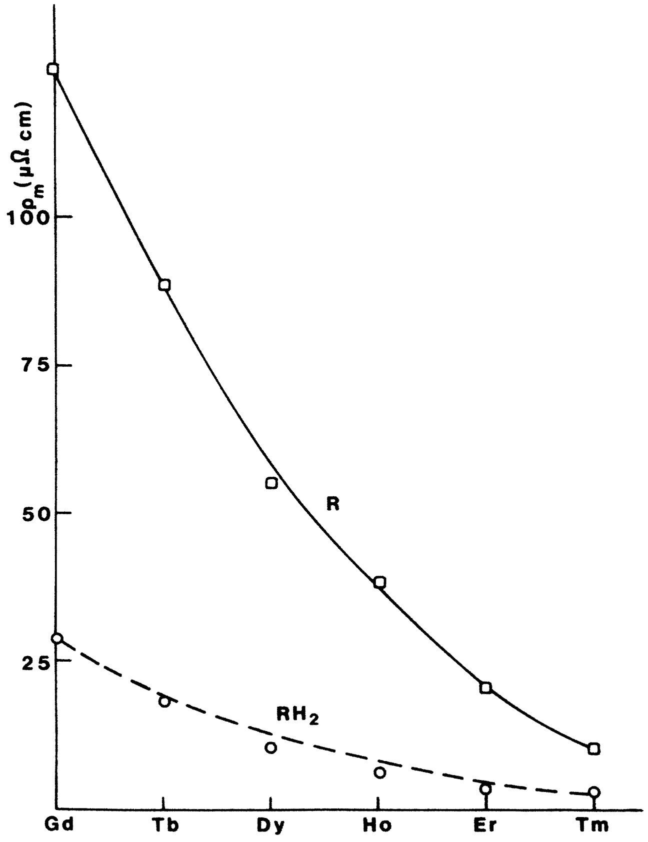

FIG. 4. Spin-disorder resistivity ρ_m of pure R and RH_2 measured at 300 K. The dashed curve follows the variation of the de Gennes factor.

One may now wonder what the reason is for this decrease of Γ; from band-structure calculations it is known that the remaining d conduction electron in the dihydride has a nearly pure e_g character while in the metal one has d electrons of e_g and t_{2g} character as well as of $s+p$ character. Our results indicate that the Γ coupling is weaker for the e_g electrons and it would be interesting to confirm this from a theoretical point of view.

We will now analyze the crystal-field effects and for this we begin with the low-temperature part, i.e., when $T\simeq T_N$ or $T<\Delta E_{ij}$; the corresponding ground-state spin-disorder resistivities ρ_m^{GS} are indicated in Table I together with the observed and calculated ratios $\rho_m^{\text{GS}}/\rho_m^{\text{th}}$. The calculated values are obtained using the ground-state configuration corresponding to the hydridic model with the wave functions given in Ref. 4. The exact ground states, which depend on the value of x, are experimentally established for DyH_2 and ErH_2 (Refs. 9–11) but there remains some uncertainty as concerns TbH_2, HoH_2, and TmH_2.

We will first examine the cases of TbH_2 and TmH_2, two ions which possess the same $J=6$ value and for which one expects a nonmagnetic ground state (Γ_2 if $x<0.81$ or Γ_3 if $x>0.81$) with $\rho_m^{\text{GS}}=0$. This is the case for TmH_2 (Ref. 5) but not for TbH_2; it is to be noted also that TbH_2 has a finite magnetic ordering temperature at $T_N=18$ K while there is no magnetic ordering in TmH_2. In order to understand this difference it is important to realize how nonmagnetic ground-state systems react to a magnetic field like, for instance, the internal molecular

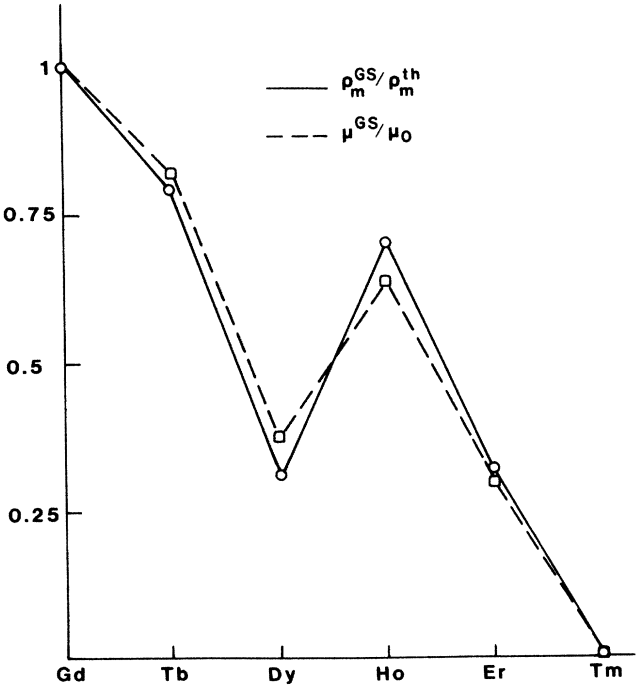

FIG. 5. Experimental ground-state spin-disorder resistivity and ground-state magnetic moment; both quantities are normalized to the theoretical free-ion value.

field due to RKKY-type interactions; it is known that magnetic fields tend to mix the ground state and the excited magnetic states with the possible formation of an induced magnetic state. But this induced magnetism appears only beyond a threshold condition which depends on the ratio between the strength of the exchange field and the strength of the crystal field;[17] this ratio is essentially a function of $\Gamma S/L$ where S and L are, respectively, the spin and orbital quantum numbers (with $J=L+S$) and Γ is the exchange integral [formula (1)]. If one admits that Γ is the same for all RE then one can remark that the above ratio is five times larger for Tb ($S=3$, $L=3$) than for Tm ($S=1$, $L=5$) so that TbH_2 may be beyond the threshold criterion while TmH_2 is not. This model is thus able to explain the drastic differences between TbH_2 and TmH_2 despite the fact that both ions have the same J value. One may now try to understand also the observed value for TbH_2 of $\rho_m^{GS}/\rho_m^{th}=0.79$; one calculates such a value (see Table I, column 5) if one considers that the three lowest energy levels (Γ_2, Γ_5, and Γ_3) are degenerate ($x=0.81$) or have very close energies because perhaps of the above-mentioned induced magnetism. Specific-heat measurements[18] have been analyzed supposing a nonmagnetic Γ_2 ground state separated by 30 K from the first excited Γ_5 state. Such an analysis is quantitatively somewhat different from our conclusions but it indicates also that the $\Gamma_2, \Gamma_5, \Gamma_3$ states are closer to each other than to the other states.

The ground states of DyH_2 ($x=0.24$) and ErH_2 ($x=-0.85$) have been determined through Mössbauer measurements[10,11] and are given in Table I; it is thus possible to calculate the ratios ρ_m^{GS}/ρ_m^{th} and to compare them to the observed values. One can see (Table I, columns 4 and 5) that the agreement is very good.

This agreement is not as good for HoH_2 if one takes a Γ_5 ground state (valid for $x<-0.54$): The observed value for ρ_m^{GS} is higher than the calculated one; it means probably that this is not the correct ground state; for $x>-0.4$ one expects a $\Gamma_3+\Gamma_4$ ground state for which one obtains a better agreement. The real situation may even be more complex if one considers that the three states Γ_5, Γ_3, and Γ_4 have very close energies if $-0.54<x<-0.4$.

The crystalline-field effects in the ground state can also be measured through the observation of the ground-state magnetic moment μ^{GS} observed either by neutron diffraction[13] or by Mössbauer studies.[10,11] In column 6 of Table I and in Fig. 5, we see that the variation of μ^{GS}/μ_0 (where μ_0 is the free-ion magnetic moment) is qualitatively close to the variation of ρ_m^{GS}/ρ_m^{th}; this indicates that both quantities are affected in the same way by the crystalline field: The similarity of the Hamiltonians involved in the disorder resistivity ($\mathcal{H}\simeq-\Gamma\mathbf{s}\cdot\mathbf{S}$) and the magnetization ($\mathcal{H}=-g\mu_B\mathbf{H}\cdot\mathbf{S}$) are surely at the basis of this correlation. The nature of the ground state should also influence of course the value of the magnetic order temperature T_N, so that one may expect here also a deviation from the de Gennes law; T_N varies from 21 K for GdH_2 to 2.3 K for ErH_2 but it shows indeed marked deviations from the de Gennes law. If one compares, for instance, DyH_2 and HoH_2, one expects a higher T_N for DyH_2 while the experiments give $T_N=5.0$ K for DyH_2 and $T_N=6.5$ K for HoH_2 in fact, we observe that T_N varies qualitatively like ρ_m^{GS} for all cases.

For the high-temperature part (when $T\geq\Delta E_{ij}$) one expects that $\rho_m(T)$ approaches ρ_m^{th} and one may wonder if this is the case for $T=300$ K; in all cases, one observes indeed an increase (Figs. 2 and 3) of ρ_m with T (with the exception of HoH_2 for which one may assume that $\Delta E_{ij}>300$ K). The range of splitting energies (between the ground state and the first excited states) is of the order of 60 K for TbH_2, 120 K for DyH_2, 100 K for ErH_2, and 150 K for TmH_2; the corresponding values of W are then, respectively, 0.5 for TbH_2, 0.9 for DyH_2, 1.3 for HoH_2 (if one takes $\Delta E_{ij}\simeq400$ K), 2.5 for ErH_2, and $\simeq3$ for TmH_2 (if one takes $x\simeq0.6$). There seems thus to be a systematic increase of W from TbH_2 to TmH_2 for which we have no immediate explanation. The negative charge on the hydrogen (in the hydridic model) is very small and it is thus possible that there is an evolution of this charge along the RE series; it is also possible that the splitting is not only sensitive to the R-H interactions but also to the R-R interactions, including the magnetic interactions, which are known to change along the series. The fact[10] that the ground-state configuration for Er is different in ErH_2 and in YH_2 (with Er as an impurity) indicates also the possible importance of either the R-R interaction or of changes in the hydridic charge. There is also a problem concerning the values of x, the ratio between the fourth- and sixth-order terms in the crystal-field potential. As ρ_m^{GS} is sensitive to the nature of the ground state but not to the x value it is difficult to deduce it from our measurements. We have estimated it only for TbH_2 and HoH_2 for which we need a composite ground state formed by several levels in order to explain the absolute value of ρ_m^{GS}. This leads then to $x\simeq0.8$ for TbH_2 and $-0.4<x<0.6$ for HoH_2, which are in reasonable agreement with previous estimates;[19] for ErH_2 and DyH_2, we admitted the values determined by Mössbauer investigations,[10,11] i.e., respectively, $x=0.24$ and -0.85. These values are somewhat different from the values given in Ref. 19: This discrepancy may be related to the same reasons mentioned above concerning the variation of W along the RH_2 series.

CONCLUSION

In conclusion, our measurements show two main results. First of all, the spin-disorder resistivity, measured at high temperatures ($T\gg T_N$) is much smaller in RH_2 compared to the pure R, a result which cannot be explained only by the change in electronic structure; it implies also a strong reduction of the conduction-electron spin-localized spin interaction. Second, we observe at low temperatures ($T\simeq T_N$) large crystalline-field effects which give quantitative information on the exact nature of the ground state; reasonable agreement is obtained considering the hydridic H^- model.

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