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Spin-disorder resistivity and crystalline field effects in TmH_2

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An analysis of the electrical resistivity $\rho(T)$ of TmH_2 yields the spin-disorder resistivity ρ_m and its temperature dependence. ρ_m is constant at high temperatures ($\rho_m = 2.8$ $\mu\Omega$ cm, a value which is much smaller than for pure Tm); at low temperatures, $\rho_m(T)$ decreases and tends to zero. This result can be interpreted on the basis of a nonmagnetic ground state separated from the first excited state by a gap of 150 K.

INTRODUCTION

The exchange interaction between a conduction electron spin s and a localized rare-earth magnetic ion of angular momentum J can be written as

$$\mathscr{H} = -(g-1)\Gamma\delta(\mathbf{r}-\mathbf{R})\mathbf{s}\cdot\mathbf{J} , \tag{1}$$

where g is the Landé factor, r and R the respective positions of the conduction electron and of the ion, and Γ the amplitude of the exchange integral. This interaction has two main consequences: it leads first to a magnetic ordering of the rare-earth ions due to the induced long-range oscillating polarization; second, the scattering of conduction electrons by this interaction gives rise in the paramagnetic state ($T > T_C$) to the so-called spin-disorder resistivity.[1] This resistivity ρ_m is proportional to Γ^2 but it varies also with the number of conduction electrons [see Eq. (5)]. A precise measurement of ρ_m, for a given magnetic ion embedded in different metallic hosts can thus give valuable information on the Γ coupling and on the electronic structure. One also expects ρ_m to be sensitive to crystalline-field effects (CFE), i.e., to the electrostatic fields of all charges situated in the vicinity of the magnetic ion: these fields may split the magnetic ground state into several substates, and, hence, modify the coupling with the conduction electrons.[2] One thus expects ρ_m to give information on the strength, sign, and symmetry of the crystalline field.

The present work will be concerned with the compound TmH_2. This study is part of a systematic investigation of the transport and magnetic properties of rare earth (RE) hydrides. The interest for these systems arises because these properties, as well as the electronic structure, differ largely in the hydrides from what is observed in the pure metals. For instance, it is known that a large fraction of the conducting states are pulled down below the d band by the strong potential of the proton:[3,4] The result is that there remains only one conduction electron per rare-earth atom in the hydride instead of three in the pure metal. At the same time one observes a drastic decrease of the magnetic transition temperatures for all the dihydrides.[5] For instance, T_C of GdH_2 is near 20 K while it is ~300 K in pure Gd; similarly, T_C is ~56 K in pure Tm while no transition is observed[6] in TmH_2 above 2 K. It thus becomes important to understand whether this is only due to a modification of the number of conduction electrons or if the value of Γ is itself modified. As far as crystalline-field effects are concerned, they have been observed in a number of RE hydrides by specific-heat,[7-9] Mössbauer spectroscopy,[10,11] and neutron diffraction[12] measurements (for a review see also Ref. 13); more specifically for TmH_2, the magnetic susceptibility tends to a constant at low temperatures which indicates that there is no magnetic moment at all in the $T \to 0$ limit.[6]

THEORETICAL ANALYSIS OF THE SPIN-DISORDER RESISTIVITY ρ_m

The value of ρ_m is given by the following formula:

$$\rho_m = \frac{m}{ne^2}\frac{1}{\tau} \tag{2}$$

(n is the number of conduction electrons per unit volume). The relaxation time τ is given by

$$\frac{1}{\tau} = \frac{mk_F}{\pi\hbar^3}\left[\sum_{i,j} NM_{ij}^2(k_\pm \to k'_\pm)f_{ij} + \sum_{i,j} NM_{ij}^2(k_\pm \to k'_\mp)f_{ij}\right] , \tag{3}$$

where N is the number of scattering centers per unit volume, M_{ij} are matrix elements describing the scattering of a conduction electron k into a state k' by the potential given in formula (1), the indices ± label the spin state of the conduction electron while i,j characterize the initial and final substate of the magnetic ion, and

$$f_{ij} = \frac{2}{1+\exp[(\varepsilon_j - \varepsilon_i)/kT]}$$

is a statistical factor involving the change in energy for the considered process.

One can give ρ_m the following form:

$$\rho_m = \sum_i \rho_{ii}p_i + \sum_{\substack{i,j\\ j\neq i}} \rho_{ij}p_i f_{ij} . \tag{4}$$

Here p_i are the probabilities for the RE ion to be in the substate i of energy ε_i; ρ_{ii} and $\rho_{ij}=\rho_{ji}$ are, respectively, the elastic and inelastic contribution to the spin-disorder resistivity. In the absence of CFE all the $2J+1$ substates i (where $i=m_J$ the magnetic quantum number) are degenerate so that $p_i=1/(2J+1)$ and $f_{ij}=1$. All contributions in Eq. (4) are then elastic and one obtains for ρ_m the well-known result

$$\rho_m^0=\frac{\hbar k_F}{4\pi Z}\left[\frac{m\Gamma}{e\hbar}\right]^2(g-1)^2J(J+1) \qquad (5)$$

(where Z is the number of conduction electrons per atom).

The energy pattern $\varepsilon_i(x,W)$ for a Tm ion (with $J=6$) surrounded by a system of point charges with cubic symmetry has been calculated[14] and is given in Fig. 1: It is expressed in terms of two parameters x and W which are related to the strength and sign of the crystal fields. If one considers that this crystal field is mainly due to the nearest-neighbor H ions, then it can be shown easily that x should be always positive and that W will be negative for the hydridic (or H^-) model and positive for the protonic (or H^+) model.

The calculated energy pattern is formed from six energy levels ε_i of symmetry Γ_1, Γ_2, Γ_3, Γ_4, $\Gamma_5^{(1)}$, and $\Gamma_5^{(2)}$, each of these substates being in fact a linear combination of the initial $|m_J\rangle$ substates. One can then see that there are four possible candidates for the ground state: Γ_2 or Γ_3 for the hydridic model and Γ_1 or $\Gamma_5^{(1)}$ for the protonic one. We will consider only the hydridic model, because there is large evidence in its favor for several hydride systems, both experimentally[7,11] and theoretically.[4] If we consider now, for instance, the Γ_2 state, its eigenfunction is of the form $a_1|6\rangle+b_1|2\rangle+b_1|-2\rangle+a_1|-6\rangle$: This is clearly a nonmagnetic state, and if it is the ground state one expects ρ_m to go to zero in the limit $kT \ll \Delta E$, where ΔE is the energy difference between this ground state and the first excited state; the same is true also for the Γ_3 substate which is the ground state if $x>0.81$. One expects thus ρ_m to be always zero in the limit $T\to 0$ for the hydridic model (with the possible exception $x=0.81$).

In Fig. 2, we report the calculated variation of $\rho_m(T/\Delta E)$ normalized to the T equals infinity value given by formula (5); case 1 corresponds to $x=0.4$, a value also used for TbH_2;[15] for case 2, we have simplified the energy pattern by taking $\varepsilon_1=0$, $\varepsilon_2=\Delta E$, $\varepsilon_3=\varepsilon_4=\varepsilon_5=\varepsilon_6=(1+\alpha)\Delta E$, where α is an adjustable parameter; for all cases we use the eigenfunctions corresponding to $x=0.4$. The whole calculation is somewhat complex because it needs the determination of 21 terms ρ_{ii} and ρ_{ji}; their numerical values, normalized to ρ_m^0, are given in Table I.

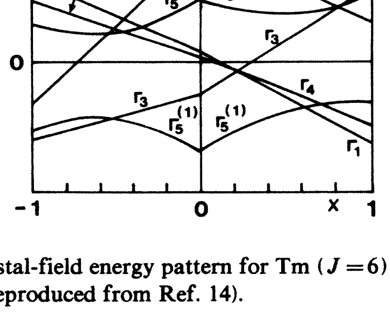

FIG. 1. Crystal-field energy pattern for Tm ($J=6$) in a cubic environment (reproduced from Ref. 14).

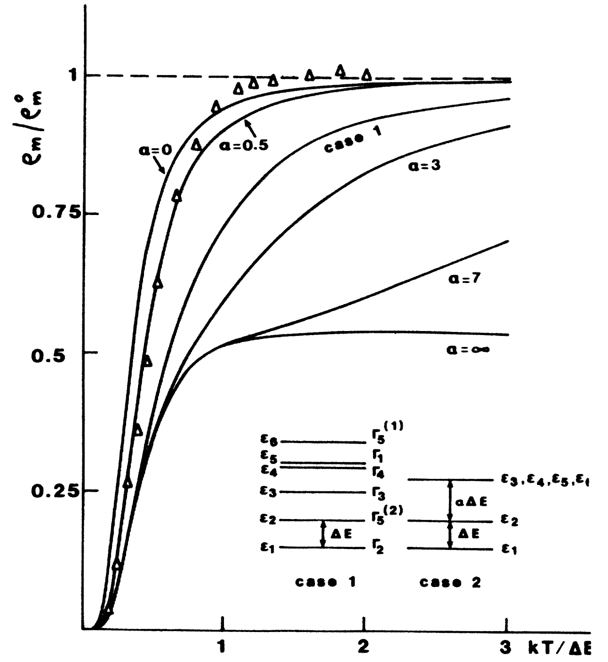

FIG. 2. Calculated thermal variation of $\rho_m(T)$ for different crystal-field energy patterns. Case 1 corresponds to Fig. 1 with $x=0.4$. For case 2, we use a simplified and adjustable pattern given in the insert. The experimental points are taken from Fig. 5 with $\rho_m^0=2.8$ $\mu\Omega$ cm and $\Delta E=150$ K.

EXPERIMENTAL RESULTS

Details concerning the preparation of TmH_2 are given in a previous work.[16] The experimentally measured resistivity $\rho_{\text{expt}}(T)$ contains in principle four different terms:

$$\rho_{\text{expt}}(T)=\rho_r+\rho_m(T)+\rho_{\text{ac}}(T)+\rho_{\text{op}}(T) \ . \qquad (6)$$

The first term is the residual resistivity related to any imperfection in the TmH_2 lattice; the second term is the spin-disorder term, while the third and fourth terms describe the scattering of the electrons by, respectively, the acoustical and optical phonons. It seems *a priori* difficult to sort out easily the $\rho_m(T)$ term, but we will show how this is possible. In the liquid-helium range of temperatures we measure a constant resistivity of 0.19 $\mu\Omega$ cm: Such a low value cannot be attributed to the spin-disorder resistivity (its value is 10.2 $\mu\Omega$ cm in pure Tm;[17] the only possibility is then to attribute it to the residual term, a point of view which is reinforced by the observation of a similar residual resistivity in the nonmagnetic LuH_2.[18] In previous work[16] we have also estimated the optical contri-

TABLE I. Numerical values of (ρ_{ij}/ρ_m^0) for the case $x=0.4$.

j \ i	1	2	3	4	5	6
1	0	0.993	0	0	0	0.006
2	0.993	0.032	1.268	0.694	0	0.012
3	0	1.268	0	0.143	0	0.589
4	0	0.694	0.143	0.036	1	1.126
5	0	0	0	1	0	0
6	0.006	0.012	0.589	1.126	0	1.265

bution to the resistivity stemming from the H vibrations: It is negligible below 150 K and amounts to about 0.8 $\mu\Omega$ cm at 300 K. We have subtracted ρ_r and $\rho_{op}(T)$ from the measured resistivity, and in Fig. 3 we represent the corresponding quantity:

$$\rho(T)=\rho_{ac}(T)+\rho_m(T)\ . \tag{7}$$

One can note immediately the linear behavior of $\rho(T)$ above 200 K which is perfectly in line with the acoustical contribution stemming from the vibrations of the Tm atoms. Nevertheless one can see also that $\rho(T)$ does not follow exactly the expected Grüneisen behavior at lower temperatures. To see this more quantitatively, we report in Fig. 4 the variation of $d\rho/dT$ for TmH_2 and LuH_2, which, except for the $4f$ shell, are supposed to have exactly the same electronic and atomic structure. It is immediately visible that LuH_2, which is nonmagnetic, because it has a filled f shell, obeys the Grüneisen behavior (with a Debye temperature Θ_D of 240 K) over the whole temperature range while strongly increased values of $d\rho/dt$ are observed in TmH_2 below roughly 200 K which can be only related to $\rho_m(T)$. We determine in fact this $\rho_m(T)$ by using the observed slope at $T>200$ K and by taking the same Θ_D as for LuH_2; this way we obtain the curve labeled $\rho_{ac}(T)$ in Fig. 3. It remains then to identify $\rho_m(T)$ through the difference $\rho(T)-\rho_{ac}(T)$ which is done in Fig. 5. It appears immediately that $\rho_m(T)$ is nearly constant and equal to 2.8 ± 0.05 $\mu\Omega$ cm above 200 K, a result which can be expected according to formula (5), but one observes also that $\rho_m(T)$ drops sharply below 150 K. It is hardly necessary to say that this drop cannot be attributed to magnetic ordering, a T_C of 150 K being completely incompatible with the observed values[5] in GdH_2 ($\sim$20 K) or in HoH_2 ($\sim$5 K) for which one expects higher T_C values than for TmH_2. The observed drop can then only be attributed to CFE.

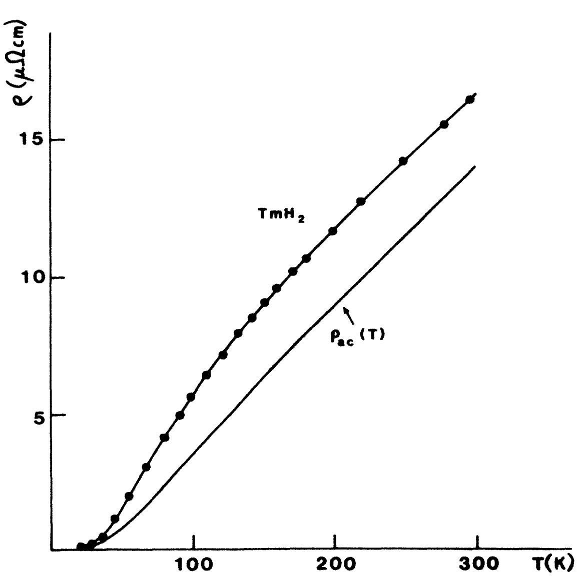

FIG. 3. The upper curve represents the variation of the measured resistivity after subtraction of the residual and the optical contribution; the lower curve is the best-fit calculated acoustical contribution (see text).

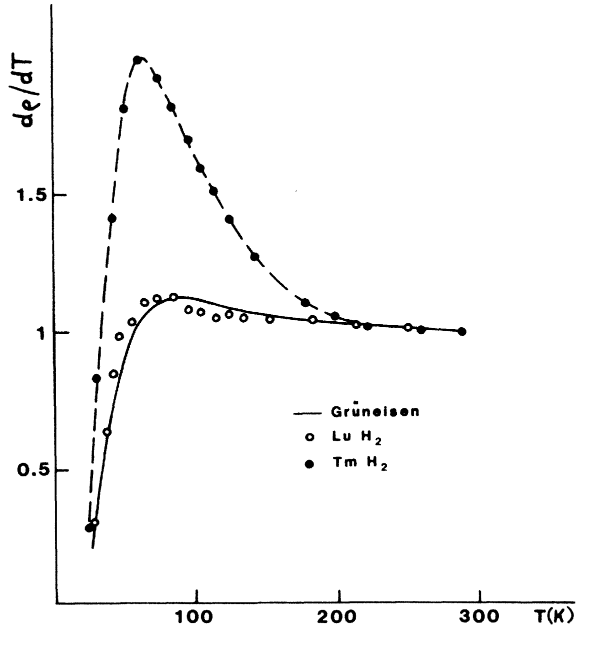

FIG. 4. Thermal variation of $d\rho/dT$ for TmH_2 and LuH_2. The continuous curve represents the Grüneisen function with $\Theta_D=240$ K (the values are normalized to unity for $T=290$ K); the broken curve serves to guide the eye through the experimental points of TmH_2.

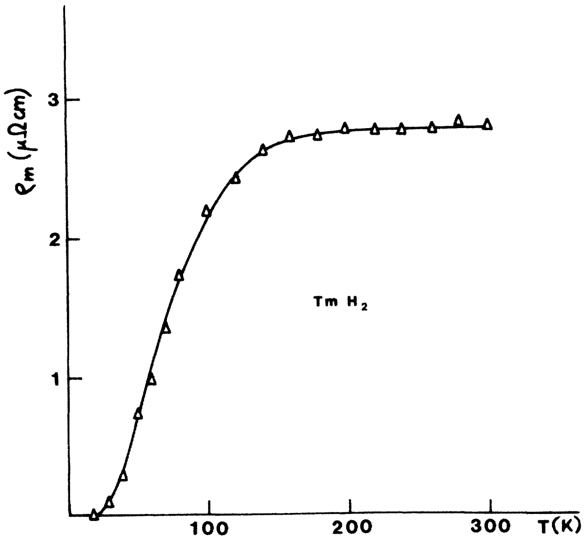

FIG. 5. Thermal variation of the measured spin-disorder resistivity obtained by subtracting the estimated $\rho_{ac}(T)$ from $\rho(T)$ [see text and formula (7)].

DISCUSSION

Several interesting conclusions can be drawn from the observed result. First of all, the absolute value of ρ_m at high temperature is about four times smaller in TmH_2 than in pure Tm; considering formula (5) it is immediately visible that this cannot be attributed to the decrease of Z as one goes from Tm (for which $Z=3$) to TmH_2 (for which $Z=1$) as this would predict just the opposite trend. Evidently a modification of the coupling constant Γ or of the effective mass m must be involved; this is most probably related to a different nature of the remaining electron in the conduction band. It is quite obvious that this electron interacts only weakly,[4] for symmetry reasons, with the H atoms sitting in the tetrahedral sites, while the two other conduction electrons being pulled down in the low energy bands interact strongly with them. One can then imagine that both types of electrons also interact differently with the Tm ion and its spin, leading to different Γ values.

The second point on which we should like to insist is that $\rho_m(T)$ goes effectively to zero in the $T=0$ limit: This means that the ground state is really a nonmagnetic one in agreement with the considerations developed in the theoretical section.

We have tried to fit the observed thermal variation of $\rho_m(T)$ with the theoretical expectation of Fig. 2; we find that the experimental variation cannot be fitted by the case 1 model, and one can show that no agreement is obtained with either energy pattern given in Fig. 1. In fact we obtain the best agreement for the case 2 model with $\alpha \sim 0.5$; it means that the excited energy levels are more crowded together than given by Fig. 1. Several possible explanations can be proposed for this discrepancy. It is important first to underline that the calculations in Ref. 14 are done for point charges and that only nearest neighbor CF interactions are taken into account; for these reasons it is better to consider Fig. 1 (only) as a qualitative approach to the CF problem. This theoretical model neglects also any ion-ion interaction which may give rise to internal magnetic fields: Such a term is considered, for instance, in the case of TbH_2 (Ref. 19) or for Tb based compounds (Ref. 20) where it is shown to be of fundamental importance. Despite all these approximations it remains that ΔE, the energy difference between the first two eigenstates is ~ 150 K, an order of magnitude also observed in other RE dihydrides.[14]

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[1] P. G. de Gennes and J. Friedel, J. Phys. Chem. Solids. **4**, 71 (1958).
[2] V. U. S. Rao and W. E. Wallace, Phys. Rev. B **2**, 4613 (1970).
[3] M. Gupta and J. P. Burger, Phys. Rev. B **22**, 6074 (1980).
[4] D. Misemer and B. N. Harmon, Phys. Rev. B **26**, 5634 (1982).
[5] W. E. Wallace, *Hydrogen in Metals I*, edited by G. Alefeld and J. Völkl (Springer-Verlag, Berlin, 1978), p. 169.
[6] Z. Bieganski and B. Stalinski, J. Chem. Phys. **39**, 1285 (1963).
[7] Z. Bieganski and B. Stalinski, Phys. Status Solidi A **2**, K161 (1961).
[8] J. Opyrchal and Z. Bieganski, Solid State Commun. **20**, 261 (1976).
[9] Z. Bieganski and B. Stalinski, J. Less-Common Met. **49**, 421 (1976).
[10] J. M. Friedt, G. K. Shenoy, B. D. Dunlap, D. G. Westlake, and A. T. Aldred, Phys. Rev. B **20**, 251 (1979).
[11] G. K. Shenoy, B. D. Dunlap, D. G. Westlake, and A. E. Dwight, Phys. Rev. B **14**, 41 (1976).
[12] H. Shaked, D. G. Westlake, J. Faber, and M. H. Mueller, Phys. Rev. B **30**, 328 (1984).
[13] R. R. Arons, in *Numerical Data and Functional Relationships in Science and Technology*, Vol. 12, Pt. C of *Landolt-Börnstein New Series*, edited by K. H. Hellwege (Springer-Verlag, Berlin, 1982), p. 372.
[14] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).
[15] H. Shaked, J. Faber, M. H. Mueller, and D. G. Westlake, Phys. Rev. B **16**, 340 (1977).
[16] J. P. Burger, J. N. Daou, P. Vajda, and A. Lucasson, J. Less-Common Met. **103**, 381 (1984).
[17] G. S. Anderson and S. Legvold, Phys. Rev. Lett. **1**, 322 (1958).
[18] J. N. Daou, A. Lucasson, P. Vajda, and J. P. Burger, J. Phys. F **14**, 2983 (1984).
[19] H. Shaked and J. Faber, Phys. Rev. B **16**, 4982 (1977).
[20] B. K. Cooper and O. Vogt, Phys. Rev. B **1**, 1211 (1970).