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Observations of magnetic and structural ordering in TbH_{2+x} compounds through electrical resistivity measurements

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We present detailed resistivity measurements $\rho(T)$ in the magnetically ordered state of TbH_{2+x}. Three types of behavior are observed: (i) for $x \simeq 0$, we find a classical antiferromagnetic transition with a well-defined drop of the spin-disorder resistivity below $T_N \simeq 18$ K; (ii) for $x > 0$, the total resistivity $\rho(T)$ goes progressively through a minimum and a maximum with decreasing temperature, indicating an incommensurate type of ordering which starts at temperatures above T_N; (iii) for $x \geq 0.15$ and for samples presenting a structural transition within the H sublattice, we observe a sharp transition at 38 K, with a smoother minimum at about 55 K. These results can be attributed to modifications of the electronic structure and of the mean free path with x, and to the existence of uniaxial crystalline field effects related to structural short-range and long-range order in the H sublattice.

INTRODUCTION

Investigations of the magnetic properties of TbH_{2+x} compounds have been done through neutron diffraction,[1-3] susceptibility,[2,4,5] and specific-heat measurements[6] and they show a rather complex behavior. Near the stoichiometric composition a classical antiferromagnetic behavior is observed (with $T_N \simeq 16$ K), exhibiting a well-defined maximum in the susceptibility and a sharp specific-heat anomaly. But the situation becomes quickly more complicated for finite x values; incommensurate structures are found by neutron diffraction with an onset temperature above T_N, the susceptibility peak is replaced by a kink, while the large specific-heat peak disappears and is replaced by smaller humps or peaks at higher temperatures. More surprisingly, the kink in the susceptibility does not coincide with the largest specific-heat anomaly.[6]

There are thus several unexpected peculiarities concerning the evolution with x of the magnetic properties of TbH_{2+x}, among which one can mention are (i) the fact that the magnetic ordering temperatures increase with x while one expects rather the opposite trend because of the simultaneous decrease of the number of conduction electrons; (ii) the fact that the ordering temperatures are apparently higher, for finite x values, in TbH_{2+x} than in GdH_{2+x} (Refs. 2 and 5); and (iii) the fact that the onset of magnetic ordering is very progressive, again for finite x, with no clear specific-heat anomaly. All this raises interesting questions concerning the relation between the magnetic ordering and the evolution with x of the electronic and atomic structure. This evolution takes place between the two limits $x = 0$ (or pure dihydride) and $x = 1$ (pure trihydride). As concerns the electronic structure one deals in the first limit with a monovalent metal and in the second limit with an insulator,[7,8] but for the present studies, which are restricted to the range $x \leq 0.2$, we are definitely always near the metallic limit. As concerns the atomic structure, the host metal lattice is always fcc (for $x \leq 0.2$), with H occupying the tetrahedral interstitial sites in the $x = 0$ limit; for finite x values, H begins to occupy the octahedral sites and forms a solid solution which is stable up to $x \simeq 0.3$, but there is at present little information concerning the stability of this solid solution in the low-temperature range ($T < 300$ K).

In the present work, we present resistivity measurements which are very sensitive to magnetic ordering through the spin-disorder resistivity term $\rho_m(T)$;[9] in particular, they can be sensitive to the commensurate or incommensurate nature of the ordering: ρ_m decreases always in the first case while it increases in the second one when crossing the magnetic transition temperature, because of the superzone boundary effects related to the opening of new gaps in the electronic structure by the incommensurate ordering.[10] At the same time, it is possible to see if there are correlations between the magnetic ordering and any structural ordering, especially in the H sublattice, as the resistivity $\rho(T)$ is sensitive to both.

EXPERIMENTAL PROCEDURE

The pure dihydrides, with H in the tetrahedral interstitial sites of the fcc CaF_2-type lattice, are prepared by direct absorption at approximately 600 °C (for details see Ref. 11). This should lead to the ideal composition $x = 0$ corresponding to the upper limit of the isothermal plateau. But this way we obtain, in fact, compositions $x = -0.08$ (or $TbH_{1.92}$) if we use 99.9% purity grade terbium and $x = -0.04$ (or $TbH_{1.96}$) for 99.99% purity grade terbium. This apparent stoichiometric deficit can be explained if one admits that a small fraction of the tetrahedral sites is not available to the H atoms because they are blocked by the presence of impurities, or because there are small damaged regions, at the surface perhaps, which are strongly polluted by oxygen and nitrogen. If we measure the residual resistivity ρ_r of such samples (at 1.5 K), we obtain very low values (≤ 0.5 $\mu\Omega$ cm) even for the $TbH_{1.92}$ sample, indicating that their effective composition must be very near to $x=0$. For this reason, we assume that these materials are effectively stoichiometric and we count the excess hydrogen concentration x taking them as base line. It is sometimes stated[2] that hydrogen, for a measured $x=0$ stoichiometric composition, occupies a given fraction of octahedral sites with a corresponding concentration of empty tetrahedral sites. We would like to emphasize that this can well be the result of preparation conditions, because at 600 °C (or above) there is enough thermal energy to excite H from tetrahedral to octahedral sites, especially in the presence of a finite H pressure; to avoid this we anneal, after the preparation at 600 °C, our samples at 500 °C in a vacuum of 10^{-7} Torr: under such conditions, the dihydride is stable while the H atoms in the octahedral sites are unstable.

The importance of the purity of the initial Tb metal appears also in the preparation conditions of the $2+x$ compounds: for 99.99% pure Tb, the additional H concentration x can be absorbed at room temperature under a pressure ≤ 1 Torr, while for the 99.9% pure Tb one has to heat the dihydride up to 300 °C under a pressure of about 10 Torr. In all cases, we observe a drastic increase of the residual resistivity ρ_r, indicating that the added H occupies octahedral sites. We observe, nevertheless, some discrepancies also in ρ_r, which is higher in the 99.99% pure samples than in the 99.9% pure samples for the same nominal x. A possible origin may be the presence of a small fraction of precipitated, nearly insulating γ phase ($\simeq TbH_3$) which can modify the effective x and also the value of ρ_r through a percolation factor: such a behavior has been observed in LuH_{2+x} for $0<x\leq 0.3$ and will be published in a forthcoming article. Despite these uncertainties concerning the exact x value, we will show in the following that there are three different, well reproducible types of magnetic behavior in TbH_{2+x}.

The electrical measurements are performed using the four-point dc method, with a relative precision $\leq 10^{-8}$ Ω cm; the samples are in the form of strips with a thickness of about 200 μm; the transformation from resistance to resistivity introduces uncertainties due to the geometry which are of the order of a few percent.

RESULTS

We observe, in fact, three distinct types of resistive behavior.

(1) $x\simeq 0$ (pure TbH_2). The resistivity presents in this case a well-defined transition (Fig. 1) starting at $T_N=18$ K (there is a small precursor anomaly at 20-21 K indicated by a second arrow in Fig. 1, whose amplitude is very small). The drop of the spin-disorder resistivity ρ_m is very large and equal to 15.3 Ω cm. This behavior is typical of a commensurate transition and agrees with the findings from neutron diffraction. The absolute value of ρ_m (for $T>T_N$) is discussed together with other rare-earth dihydrides, in a separate article.[12]

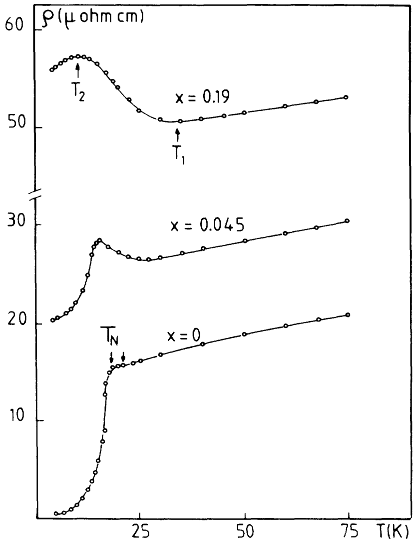

FIG. 1. Thermal variation of the low-temperature total resistivity $\rho(T)$ for three concentrations x of octahedral hydrogen with 99.9% pure Tb. The second arrow for the $x=0$ case indicates the position of a very small anomaly not really visible in the figure. The temperatures T_1 and T_2 correspond, respectively, to the minimum and maximum of $\rho(T)$ when $x>0$.

(2) $x>0$ (up to $x=0.19$ for 99.9% pure Tb; up to $x\simeq 0.10$ for 99.99% pure Tb). The addition of a finite concentration x of hydrogen, entering now into the octahedral sites, results in a sharp increase of the residual resistivity, indicating that, to a first approximation, there is scattering of the electrons by the statistical solution of hydrogen on the octahedral sites. But as is visible in Fig. 1, there is at the same time a spectacular variation of the resistive behavior with temperature. Upon cooling, the total resistivity goes first through a minimum at a temperature T_1 which is higher than the preceding T_N value: this can be attributed to an incommensurate transition, but it is to be noted that the appearance of this ordering is very progressive and smooth without real discontinuity in $\rho_m(T)$; at lower temperatures, $\rho(T)$ goes through a maximum at a temperature T_2 which is smaller than T_N. The corresponding decrease of $\rho(T)$ is rather sharp for small x, but it becomes progressively broadened for larger x. The existence of such a drop below T_2 is, of course, not necessarily an indication that there is a second magnetic ordering transition, but it can be in line with the incommensurate transition occurring at higher temperatures which modifies the resistivity $\rho(T)$ according to the following formula:[10]

$$\rho(T)=[\rho_0(T)/1-\delta M] . \tag{1}$$

$\rho(T)$ is the total resistivity in the absence of incommensurate ordering, i.e.,

$$\rho_0(T)=\rho_r+\rho_{ph}(T)+\rho_m(T,M) ,$$

where ρ_r is the residual resistivity, $\rho_{ph}(T)$ the phonon resistivity, and ρ_m the spin-disorder resistivity; M is the incommensurate order parameter and δ a parameter describing the modification of the electronic structure by the occurrence of new gaps; below the incommensurate phase transition ($T_I \simeq T_1$) one has also

$$\rho_m(T)=\rho_m(T_I)[1-M^2] \ .$$

It is the denominator of formula (1) which gives an increase of $\rho(T)$, while, for the numerator, one expects only a decrease of $\rho(T)$ which can be at the origin of the maximum at T. In Fig. 2, we show the variation of T_1 and T_2 as a function of the residual resistivity ρ_r which is, in principle, proportional to x.

In Fig. 3, we outline the total resistivity $\rho(T)$ in a larger temperature range, up to room temperature; for $x=0$, no anomaly is observed, the variation of $\rho(T)$ being dominated at $T>T_N$ essentially by the phonon contribution. But for $x=0.19$, one observes a well-defined anomaly around 170 K which had been discussed in an earlier article:[13] this anomaly is very similar to the one observed in α solid solutions of hydrogen in pure hexagonal rare earths,[14] where it is attributed to short-range ordering in the H sublattice through the formation of H pairs surrounding a rare-earth (RE) atom. Tentatively one can admit that this is also the case in the dihydride for the H solid solution on the octahedral sites, which has been proved indirectly in one of our preceding works using electron irradiation.[15] But this structural anomaly is very small and it is difficult to see *a priori* if it has an influence on the magnetic ordering.

(3) $x>0.19$ (for 99.9% pure Tb); $x>0.10$ (for 99.99% pure Tb). Here it is better to investigate first the high-temperature region, outside the magnetic ordering T range (Fig. 4). A large resistivity drop is observed in the 99.99% pure sample for $T<250$ K ($x=0.2$), $T<230$ K ($x=0.175$), and $T<215$ K ($x=0.15$). An analogous drop (below 180 K) has been observed[15] for a 99.9% pure sample of composition $\mathrm{TbH}_{1.93+x}$ with $x=0.215$.

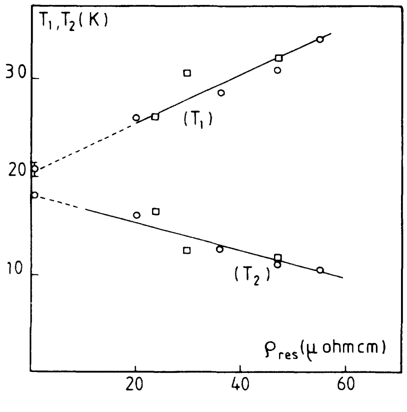

FIG. 2. Variation of T_1 and T_2 as a function of the residual resistivity ρ_r for 99.9% pure Tb (○) and 99.99% pure Tb (□). It is to be remarked that T_1 seems to extrapolate at $\rho_r=0$ towards the small anomaly indicated in Fig. 1 by a second arrow.

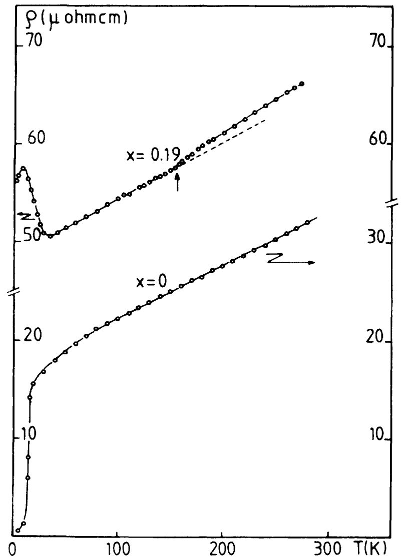

FIG. 3. Variation of the total resistivity $\rho(T)$ in the temperature range $1.5<T<300$ K for the $x=0$ and $x=0.19$ samples. A small anomaly is clearly visible for the $x=0.19$ sample around 170 K.

This drop, which can be related only to a structural modification, is stopped for all three 99.99% pure samples below roughly 165 K, probably because of a lack of thermal diffusion below this temperature. It is to be noted also that samples which are slowly cooled and heated through the transition (relaxed samples) show a well-

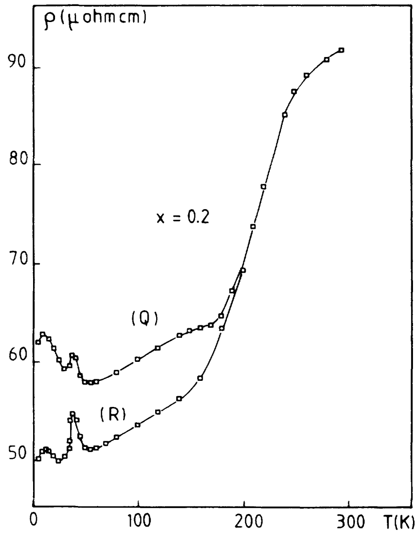

FIG. 4. Variation of the total resistivity for a 99.99% pure TbH_{2+x} sample with $x=0.2$. (R) indicates a slowly cooled or relaxed sample and (Q) the same sample, but quenched from room temperature into liquid nitrogen. The measurements are done in both cases with increasing temperatures by starting at 1.5 K.

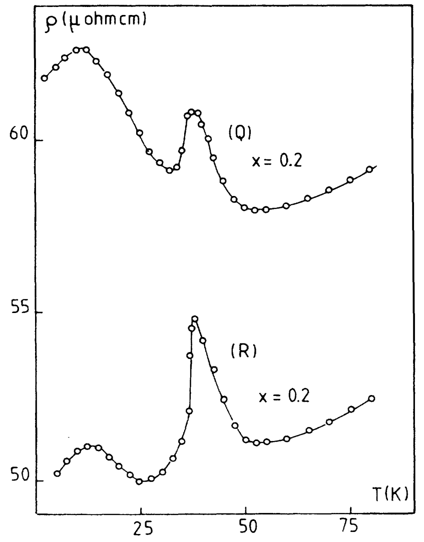

FIG. 5. Enlarged view of the total resistivity variation in the range $2 < T < 80$ K for the same samples as in Fig. 4.

defined hysteresis (not shown in Fig. 4), indicating that this structural transition is probably of first order. It can be attributed either to a precipitation of the high resistivity γ phase or, more probably, to a long-range ordering of H atoms (and the corresponding vacancies) inside the octahedral sublattice. We shall discuss this point later on and we shall see that this structural modification has profound effects on the low-temperature magnetic behavior (Figs. 4 and 5). In fact, one observes now two types of transitions: one which is reminiscent of the behavior in Fig. 1 ($x > 0$) with two temperatures T_1 and T_2 which are typically in the same range as in Fig. 1; and a second magnetic transition at higher temperatures, starting with an increase of $\rho(T)$ below 55 K and showing a sharp maximum (especially for $x = 0.2$) around $T = 38$ K (Fig. 5).

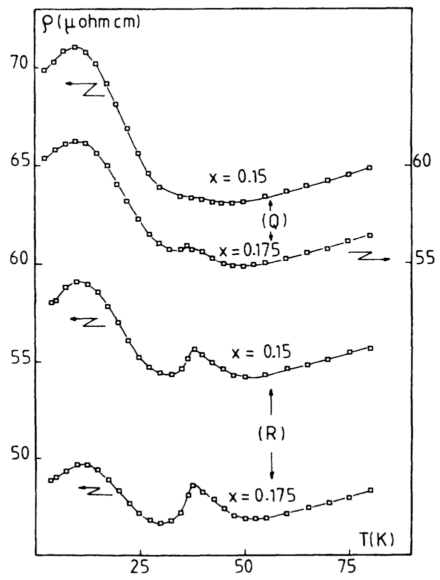

FIG. 6. Variation of the low-temperature resistivity for two 99.99% pure samples with $x = 0.175$ and $x = 0.15$ in the relaxed and quenched state.

The correlation with the structural transformations above is demonstrated in Figs. 5 and 6; one can partially block the high-temperature structural transformation by quenching the sample from room temperature to liquid nitrogen temperature (quenching rate $\simeq 10^4$ K/min). This gives rise to a higher residual resistivity; at the same time one observes a damping of the higher magnetic transition occurring between 35 and 55 K, while the lower one around T_1, T_2 is amplified.

DISCUSSION

The antiferromagnetic behavior of $\mathrm{TbH_2}$ ($x = 0$) does not raise many fundamental questions. The corresponding transition temperature and spin-disorder resistivity are smaller than in $\mathrm{GdH_2}$ (Refs. 16, 5, and 12) in qualitative agreement with the de Gennes law. The value of the antiferromagnetic modulation vector Q is different compared to $\mathrm{GdH_2}$, and the corresponding problem has been discussed recently[17] in relation with the electronic structure of the RE dihydrides and the different nesting possibilities.[7] The influence of the crystal field on ρ_m, present in $\mathrm{TbH_2}$ but not in $\mathrm{GdH_2}$, has also been discussed.[12]

The incommensurate behavior, characterized by the temperatures T_1, T_2 is much more interesting, and one has to understand why the corresponding transition temperature $T_I = T_1$ increases with x and takes up values which are higher than in GdH_{2+x}. *A priori,* one may consider the relation between T_N (or T_I) and the global electronic structure variation. It is given by

$$T_N \text{ (or } T_I) \simeq Z N(\varepsilon_F) \Gamma^2(Q) \qquad (2)$$

[Z is the number of conduction electrons per atom, $N(\varepsilon_F)$ is the Fermi level density of states, and $\Gamma(Q)$ is the Fourier transform of the long-range Ruderman-Kittel-Kasuya-Yosida (RKKY) type of interaction energy].

In principle, an increase in x results in a decrease of Z, of $N(\varepsilon_F)$ (Refs. 7 and 8), and probably also of $\Gamma(Q)$ (see Ref. 12). It is to be remembered also that, in all cases, one has a lower ordering temperature for the trihydride.[5]

For all these reasons, one always expects T_N or T_I to decrease with increasing x. But this is not the case for TbH_{2+x} (see Fig. 2 as concerns $T_I \simeq T_1$). A further question of importance concerns the reason leading to a commensurate-incommensurate passage; one possibility is to relate it to modifications of the nesting conditions with the x evolution of the electronic structure: this would lead to a thermal variation of the modulation vector $Q(T)$ but, unfortunately, there have existed no measurements of it up to now. A second possibility is to relate it to the mean free path which decreases strongly as

x increases; it is known in the pure RE metals that this can also modify the Q value.[18] It is impossible for the moment to distinguish between these two reasons.

A further important feature concerns the nature of the incommensurate modulation: it is observed to be sinusoidal (or linear) in TbH_{2+x} (Ref. 2), while it is helicoidal (or planar) in GdH_{2+x}.[16] This strongly suggests that there must be an energy term in the Hamiltonian of the magnetic system which has an axial symmetry, and this may point towards a role played by crystalline field effects. It is known that in pure $R\mathrm{H}_2$ (where R represents any rare-earth element) the crystalline field energy can be larger than the RKKY interaction energy;[9,12] the cubic symmetry of the crystalline field in $R\mathrm{H}_2$ is modified by the octahedral H atoms, and one may question if it is the isolated H atoms or the short-range ordering among these H atoms which is responsible for the axial effect. *A priori*, it is difficult to see why there should be a single axis behavior for isolated H atoms.

A point on which we would like to insist is that such an anisotropy may increase T_N (or T_I) in a way given by

$$T_I \simeq T_I^0 + K(x) , \tag{3}$$

where K is a uniaxial magnetic anisotropy constant. A finite value of $K(x)$ could thus explain the difference in T_I observed for GdH_{2+x} (for which one expects $K=0$) and TbH_{2+x}. The possible importance of an axial anisotropy has also been put forward in Ref. 6. The local nature of this anisotropy can perhaps also explain the absence of a sharp well-defined magnetic transition.

But the most interesting feature is the third type of behavior represented in Figs. 4–6. A simple idea one can put forward is to consider that it is just an enhanced version of the preceding T_1,T_2 behavior because of the formation of a longer-ranged order in the H sublattice replacing the short-range order. For this, it is necessary to first set aside the hypothesis that it might be a γ phase precipitation: it is known, for instance, that TbH_3 is nonmagnetic above 4 K (Refs. 4 and 5), and from this it is very difficult to support this idea. Considering the possible long-range order in the H sublattice, there has existed up to now no neutron or x-ray studies for TbH_{2+x}, but long-range structural ordering has been observed in several light $R\mathrm{D}_{2+x}$ systems (R =La,Ce,Pr,Nd) at concentrations as low as $x \simeq 0.15$ (Refs. 19–22). The superstructure lines indicate a doubling of the basic CaF_2 periodicity which takes place only along one axis. This doubling concerns mainly the H sublattice (where it involves both the octahedral and the tetrahedral hydrogen). Detailed neutron scattering studies are thus clearly needed for TbH_{2+x} in order to establish the exact nature of this ordering, but its axial character is particularly in line with the observed sinusoidal modulation of the magnetization. It is known also that such sinusoidal modulations, which exist also in pure rare-earth metals (Er,Tm) are not stable at low temperatures because they do not optimize the RKKY interaction energy (they are, in fact, stabilized by their entropy), and this may be at the origin of the sharp transition in the resistivity at 38 K which follows the incommensurate onset at 55 K; the transition at 38 K suggests that the sinusoidal structure returns to a modulation optimizing more the interaction energy, perhaps an antiphase structure or even an antiferromagnetic one; such a transition may be triggered by magnetoelastic effects (as in pure rare-earth metals), but perhaps one should also remember that the mean free path l again becomes relatively large in the structurally ordered phase and that this may be by itself a trigger for the link between different modulations.

The fact that the (T_1,T_2) type of behavior is still present in the structurally ordered phase may be the result of the simultaneous presence of long- and short-range domains, a complete ordering being prevented by the lack of H mobility at low temperature. It remains also to understand why the long-range ordering occurs preferentially in the 99.99% pure Tb samples and less in the 99.9% pure Tb: this can perhaps be related to the first-order nature of such order-disorder transitions[21] so that their occurrence could be influenced by the metallurgical state of the samples.

CONCLUSION

Our main observation is that the antiferromagnetic ordering in TbH_2 transforms into an incommensurate ordering for TbH_{2+x}. This may be related to modifications with x of the electronic structure through modifications of the nesting conditions; a decrease of the electronic mean free path can lead also to the same result but, for the moment, there are no decisive arguments in favor of one or the other of these hypotheses. The sinusoidal (i.e., linear) nature of the modulation suggests strongly that there is an axial crystalline field which itself can be related to a short-range structural ordering within the H sublattice. The fact that the magnetic transitions are pushed to higher temperatures when long-range structural order sets in gives strong support to this idea.

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