Resistivity study of β-TbH$_{1.93+x}$: Observation of an anomaly near 150 K similar to that found in α-R H$_x$ solid solutions

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The electrical resistivity of β-TbH$_{1.93+x}$ is shown to exhibit an anomaly near 150 K whose amplitude increases with increasing x. A quenched-in $\Delta\rho_q$ recovers in the anomaly region. The phenomenon is very similar to the 160-K anomaly in some α-R H$_x$ systems and is attributed to short-range ordering of H atoms on octahedral sites or to localized precipitation of nuclei of the H-rich phase.

The heavy lanthanides, from Gd to Lu, form dihydrides (β phase) with a relatively wide stability region: 1.9 $\lesssim H/R \lesssim$ 2.2. They crystallize in the fluorite structure, such that in the ideal stoichiometric case all tetrahedral interstices (T sites) of the fcc metal lattice are occupied by hydrogen atoms, while the octahedral sites (O sites) are filled with any excess concentration of H atoms. In reality (see, e.g., Ref. 1), the ideal composition RH$_2$ already contains up to several percent of occupied O sites, the origin of which is controversial and seems to be related to the history of the specimens.[1,2]

In this paper we present results which are part of a major study of the physical properties of rare-earth hydrides. Thus, the contribution of the optical phonons, due to hydrogen vibration, to the electrical resistivity has been investigated in the nonmagnetic hydrides of the rare earths Sc, Y, and Lu (Ref. 2) as well as in the magnetically ordered systems based on Gd, Dy, Tm, and Er.[3] A special effort has been devoted to the investigation of the magnetic properties of several dihydrides, in particular, of TbH$_{2+x}$ (Refs. 4 and 5)—shown[1] to possess complex commensurate and noncommensurate structures, which depend strongly on the excess concentration x. While investigating the manifestations of the magnetic transitions upon the resistivity of this system,[6] we have discovered an unexpected anomaly in the region of 150 K, which seems to have striking similarities with that observed in the solid solutions (α phase) of hydrogen with several rare earths: Lu,[7] Tm,[8] Er.[9]

The specimens used for the measurements were prepared from 99.9-at.% terbium foil of 100 μm thickness (main metallic impurities: 200 at.% ppm Y, 10 Cu, 10 Ni), cut into 20 × 1-mm^2 strips and contacted with four spot-welded platinum leads. The samples were then hydrogenated by direct absorption at 600 °C in a strictly controlled procedure involving essentially two steps: (1) preparation of the "ideal" dihydride corresponding to the upper limit of the isothermal plateau at the absorption temperature (for which there is a resistivity minimum); (2) addition of the excess concentration x of hydrogen (for details see Ref. 2). Their composition and characteristics are given in Table I. The absolute ρ values are good to ±5%, due to uncertainties in the determination of the geometrical shape factor, but the relative reproducibility on a (ρ, T) pair is 10^{-4} and the measurement

precision better than 10^{-9} Ω cm. An immediate inference drawn from the data in Table I is the contribution of the excess hydrogen to ρ:

$$\Delta\rho/\Delta x \text{ (at 273 K)} = 1.7 \pm 0.1 \ \mu\Omega \text{ cm/1\% } x.$$

The ideal dihydride composition (in the sense of an exclusive T-site occupation) in our experiment is TbH$_{1.93 \pm 0.01}$.

In Fig. 1 we present the $\rho(T)$ dependences of the above samples (omitting the magnetically perturbed region below ~ 50 K), which clearly exhibit a change in slope around 150 K for $x > 0$. On the other hand, the $\rho(T)$ curves outside the anomaly area are rather parallel and yield, thus, for the thermal coefficient an x-independent value of $\Delta\rho/\Delta T$ (at 273 K) = $(7 \pm 0.5) \times 10^{-8}$ Ω cm/K. For a better visualization of the anomaly phenomenon, we have plotted in Fig. 2 the difference quotients as a function of temperature derived from the data in Fig. 1. The ideal dihydride, $x = 0$, shows a smooth transition from the magnetically perturbed high-slope region below 50 K to the constant-slope region of the Grüneisen law at medium T (100–200 K), followed by another area with increasing slope above 200 K indicating the beginning of the conduction-electron coupling to the optical phonons.[10] The presence of excess hydrogen on O sites, $x > 0$, results in a break in the $\rho(T)$ curves, which is centered at or slightly below $T = 150$ K and the amplitude of which increases with increasing x.

The curves in Fig. 2 are the result of two types of experiment: (1) $\rho(T)$ taken with increasing temperature after slow cooling of ~ 0.5 K/min (relaxed specimens), giving

TABLE I. Specimen characteristics.

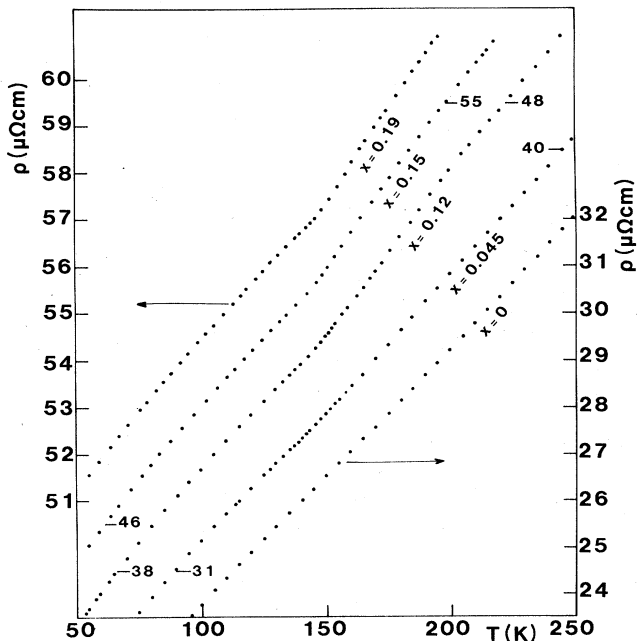| Specimen	ρ (100 K) ($\mu\Omega$ cm)	ρ (273 K) ($\mu\Omega$ cm)
TbH$_{1.92}$	23.8	33.5
TbH$_{1.94+0.045}$	31.7	41.7
TbH$_{1.93+0.12}$	40.2	51.3
TbH$_{1.93+0.15}$	48.5	60.1
TbH$_{1.93+0.19}$	54.5	66.3

FIG. 1. Temperature dependence of the electrical resistivity of different TbH$_{2+x}$ specimens. The numbers drawn for the three intermediate concentrations indicate the ordinates (in $\mu\Omega$ cm) at both extremities of the corresponding $\rho(T)$ curve, using the same scale as for the other samples.
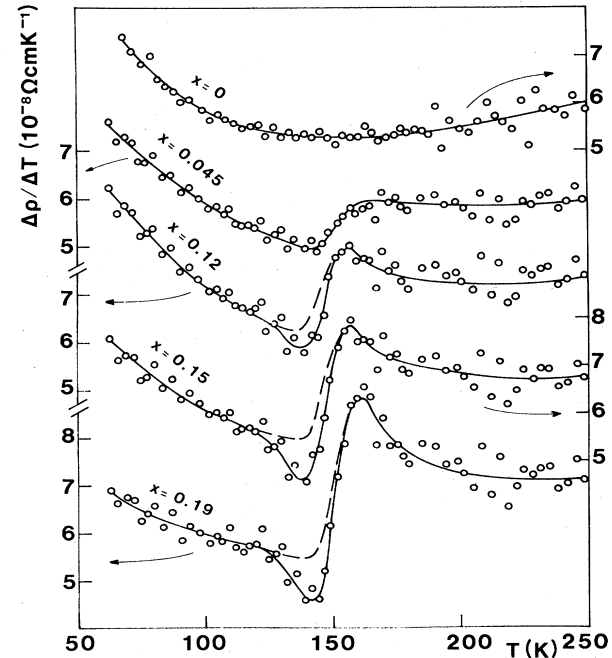

FIG. 2. Calculated slopes of the $\rho(T)$ dependences from Fig. 1. The dashed curves correspond to relaxed specimens, the full curves (drawn through the data points) to quenched specimens.

the dashed curves; (2) $\rho(T)$ obtained after a fast cooling ~ 5 K/min across the anomaly (quenched specimens). Experiment (2) led to a residual-resistivity increase $\Delta\rho_q$, which recovered right in the region of the anomaly yielding the pocket at 140 K in the differentiated curves of Fig. 2. Finally, the manifestation of the optical phonons (at the origin of the increasing slope at higher temperatures for $x = 0$) seems to be gradually suppressed in the x-doped samples.

The most striking feature of the phenomenon is its qualitative and quantitative similarity with the already mentioned anomaly in some α-RH$_x$ systems, which we shall try to summarize.

(a) The anomaly temperature, which is 150 K in our case, is 160–170 K in the α phase.

(b) The x dependence of the anomaly amplitude is, for comparable x, three to four times stronger in the α phase than in the β phase; however, we have to remember that the slopes themselves upon which the anomaly is superposed are also three to four times larger in the α phase, reflecting the stronger coupling of the conduction electrons to the acoustic phonons (cf. Refs. 2, 3, and 10).

(c) The production of a $\Delta\rho_q$ in rapidly cooled specimens recovers in the anomaly region.

As the anomaly in the α phase was explained[8, 9, 11] by short-range ordering of the statistically distributed hydrogen atoms at 160–170 K, lowering the resistivity of the system, it is tempting to draw also an analogy in the interpretation of the newly observed anomaly in the β phase. Indeed, we are dealing in the latter case with a solid solution of hydrogen atoms in the hydride and in the former case with a solid solution of H atoms in the metal. An extension of the interpretation to the β phase could, therefore, be a short-

range ordering phenomenon of the H atoms on O sites; for example (again in analogy to the α phase), the formation of H-H pairs on neighboring O sites in the $\langle 110 \rangle$ directions. Another possibility is a kind of frustrated precipitation of TbH$_3$ nuclei out of the β-phase solution; the analogy for the RH$_x$$_-$ anomaly would then correspond to a precipitation of RH$_2$ nuclei out of the α-phase solution. It is, in fact, interesting to note that, in both cases, the precipitation into the hydrogen-rich phase is related with a structural transformation:

$$\text{hcp } \alpha\text{-}R\,\text{H}_x \rightarrow \text{fcc } \beta\text{-}R\,\text{H}_{2+x} \rightarrow \text{hcp } \gamma\text{-}R\,\text{H}_{3-x}.$$

This means that additional energy is required to transform the lattice; this energy could be unavailable at the low temperatures of the experiment leading to only localized precipitation of nuclei of the H-rich phase.

Two further observations on the α-phase systems remain to be tested and experiments in this direction are planned in the near future.

(1) The isotope effect (when replacing H by D) on the anomaly temperature: the latter was 5 to 10 K higher in D-loaded samples of the α phase.

(2) The influence of a low-temperature subthreshold electron irradiation, which, in principle, should give a similar result as the quench, but should also exhibit an isotope effect on the produced $\Delta\rho_{\text{irr}}$.

It should be interesting to investigate the phenomenon with other methods such as specific heat, neutron and x-ray scattering, internal friction, etc., and on other systems, in view of the larger variety of the available β-RH$_{2+x}$ compounds (when compared to α-RH$_x$) stable at low temperatures.

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