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Pressure-induced metallization in Erbium trihydride

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ABSTRACT

Electrical resistivity and Raman spectra of ErH_3 were studied in a diamond anvil cell under high pressure up to 140 GPa in the temperature range 4–300 K. A crossover from a semiconductor-like to a metallic temperature dependence of resistivity at fixed pressures was observed at about 50 GPa. In the pressure range 80–140 GPa a resistivity maximum was observed at the $R(T)$ dependencies. The temperature corresponding to this maximum linearly increased with pressure increase, reaching 26 K at 140 GPa. No superconductivity was observed in the studied pressure-temperature range.

1. Introduction

All rare-earth metals (REMs), counting Sc and Y, react with hydrogen under ambient or relatively mild conditions, forming hydrides with composition H/Me = 2–3. With the exception of Eu and Yb, which are irregular members of the family, the behavior of REMs in a hydrogen atmosphere is universal. The dihydrides of all regular REMs and the trihydrides of La, Ce and Pr have an fcc lattice of metal atoms. The metal lattice in the trihydrides of Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu, Y and Sc at ambient pressure is hcp. However, if sufficient pressure is applied to these trihydrides, their metal lattice can also be transformed into an fcc one [1]. This transformation occurs via an intermediate phase with a long-period stacking sequence of alternating hcp and fcc layers [2].

The electrical properties of REM trihydrides differ significantly from that of REM dihydrides – the former are narrow bandgap semiconductors, whereas the latter are metals at their respective stoichiometry. Thus, a composition alteration between H/Me = 2 and 3 in REM hydrides results in a metal-to-semiconductor transition. As demonstrated in Ref. [3] for yttrium hydride, this unique property can be used in a design of switchable mirrors for visible light.

The semiconductor-to-metal transition in REM trihydrides can be driven not only by composition change, but also by a pressure application. It was predicted that the high pressure fcc phases of YH_3 [4], ErH_3 [5,6] and HoH_3 [6] should be metallic. Moreover, ab-initio calculations predicted the fcc trihydrides of rare-earth metals to be superconductors, particularly, for fcc-YH_3 the superconductive transition temperature could reach 40 K [7].

Later IR absorption [8] and electrical resistivity [9] measurements on YH_3 under high pressure were interpreted as the metallization at the pressures 25 and 70 GPa respectively. According to Ref. [2] the formation of fcc-YH_3 is complete at 22 GPa, thus, the semiconductor-to-metal transition is not associated with the formation of the fcc phase, but occurs for fcc-YH_3 alone.

A resistivity maximum was observed above 40 GPa and below 15 K at the $R(T)$ dependencies for YH_3 at constant pressures, but no superconductivity was detected [9]. The origin of this anomaly was unknown.

Because no other REM trihydrides were studied by electrical transport measurements under high pressure, it is unclear, if the metallization scenario of YH_3 is typical for other REMs. To verify this we performed the resistivity measurements of ErH_3, which metallization was predicted in [5,6], at pressures ~ 140 GPa. Raman spectroscopy was used to observe the structural changes in the sample.

2. Experimental

Erbium metal of 99.9% purity was first annealed in a vacuum of about 10^{-3} T at 400 °C for 4 h, and then exposed to the hydrogen gas at a pressure of about 100 bars at 200 °C for 24 h. The XRD pattern of the resulting ErH_3, measured with the Empyrean diffractometer using CuKα radiation, is shown in Fig. 1. The lattice parameters for ErH_3 well agree with the literature data for stoichiometric trihydride [10], and no impurity phases were detected to an accuracy of 5 wt%.

The diamond anvil cell (DAC), beveled at 7–8° to a culet of 30 µm was used. A mixture of CaF_2 and epoxy resin was used to insulate four van der Pauw electrodes made of 2 µm platinum foil from each other and from the supporting stainless steel gasket. The samples were

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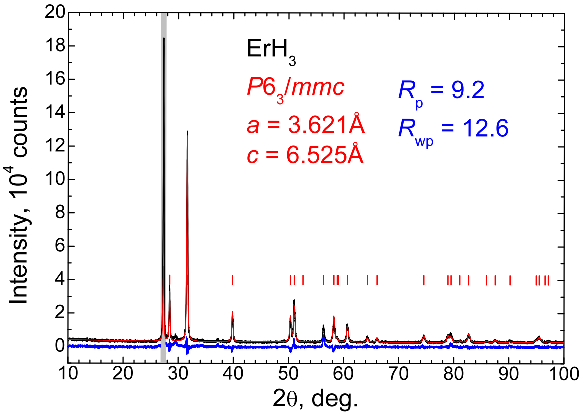

Fig. 1. (Color online) XRD pattern of the initial ErH_3 sample (black), its Rietveld fit (red) and fit residue (blue). Ambient conditions, CuKα radiation. Due to a strong texture the (002) peak was excluded from the refinement, as shown by the gray shadowed area.

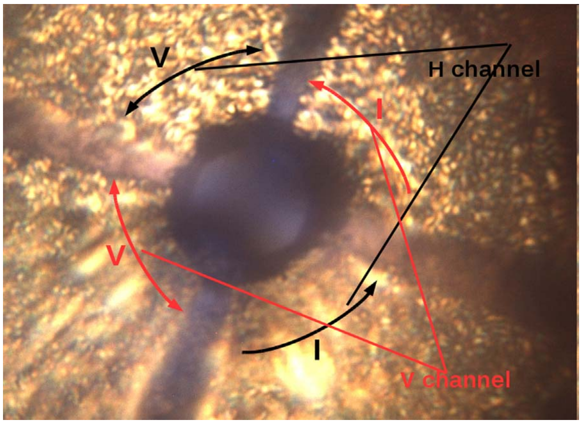

Fig. 2. (Color online) Layout of the sample and the platinum electrodes in the DAC. Channel H indicates channel for current – the current was put through these electrodes, and the voltage measured with two other electrodes (V channel).

loaded into a 20 μm hole drilled in a gasket preindented from 250 to a 5 μm thickness. The layout of the sample in the DAC is shown in Fig. 2. For the channel H means channel for current – the current was put through these electrodes, and the voltage measured with two other electrodes (another channel).

No pressure transmitting medium was used. The pressure was determined by the diamond edge scale [11]. The Raman spectra were excited by a 632.8 nm He–Ne laser line and recorded by a Raman spectrometer equipped with a nitrogen-cooled CCD and notch filters.

3. Results and discussion

Typical Raman spectra of ErH_3 for different pressures are shown in Fig. 3. The peak at 500 cm^{-1} disappears gradually in the pressure range 0–5 GPa. At about 13 GPa the peaks at 650 and 850 cm^{-1} disappear suddenly, and a new peak at 900 cm^{-1} emerges. Such changes are due to the formation of the intermediate phase between the hcp and fcc ones. At further pressure increase, all Raman peaks disappear gradually in the range 13–30 GPa, which is a result of a continuous transformation of the intermediate phase into the fcc one. At higher pressures no Raman signal can be recorded from the sample as a consequence of decreasing penetration depth of the laser beam into the sample, caused by gradual metallization. Similar pressure evolution of Raman spectra were reported for YH_3 [12].

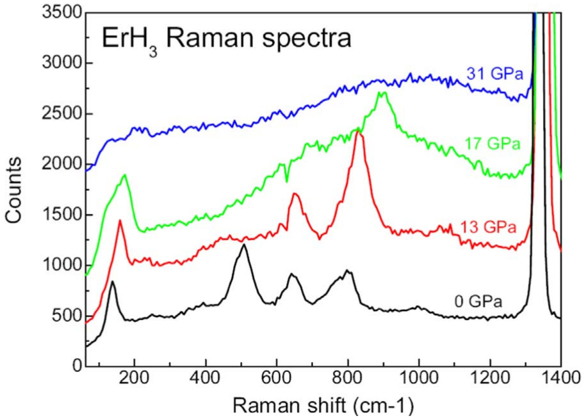

Fig. 3. Raman spectra of ErH_3 measured at different pressures and room temperature.

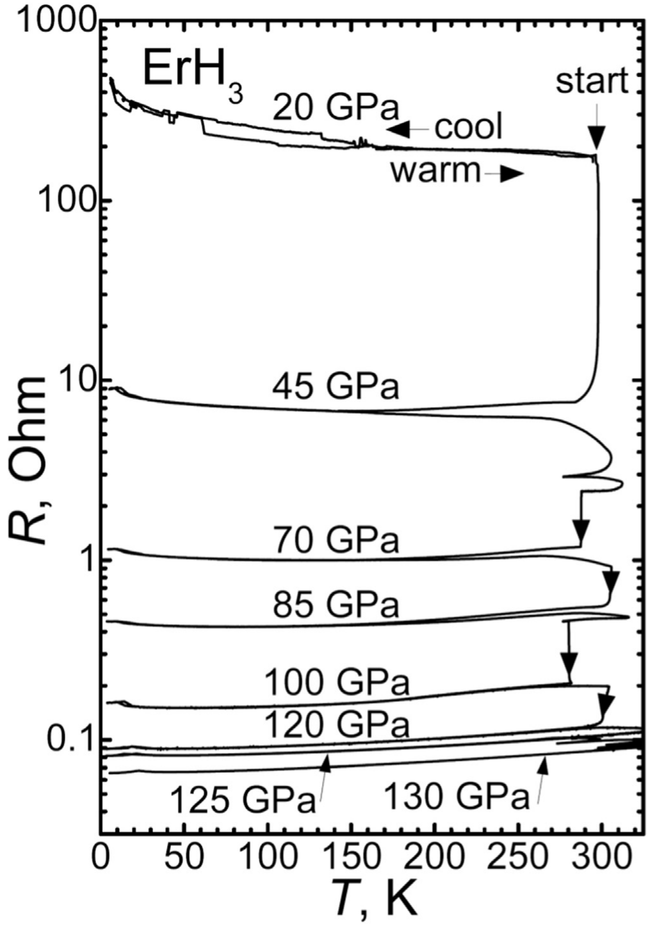

Fig. 4. (Color online) Temperature dependence of the electrical resistance of ErH_3 during compression in the DAC.

The electrical resistance measurements were measured starting from 20 GPa. At this pressure the formation of the fcc-ErH_3 is complete [13], thus, the resistivity of only fcc phase can be studied. The pressure was increased in steps at ambient temperature, and the $R(T)$ dependencies were recorded when cooling the DAC cell to 4 K and warming it to room temperature at fixed pressures, as shown in Fig. 4.

The $R(T)$ at 20 GPa had typical semiconductor-like behavior. We noticed a significant photoconductivity at this pressure, responsible for sudden jumps in R. At 45 GPa and above the photoconductivity disappeared. Small hysteresis between cooling and warming was observed in $R(T)$ for most pressures, indicating pressure drift during the cooling-warming cycle. At 70 GPa and above the $R(T)$ dependence became weak, and no significant increase in R could be observed at 4 K comparing to ambient temperature. Thus, we regard the sample state as metallic from this point, and we estimate the metallization pressure in ErH_3 as 50(20) GPa.

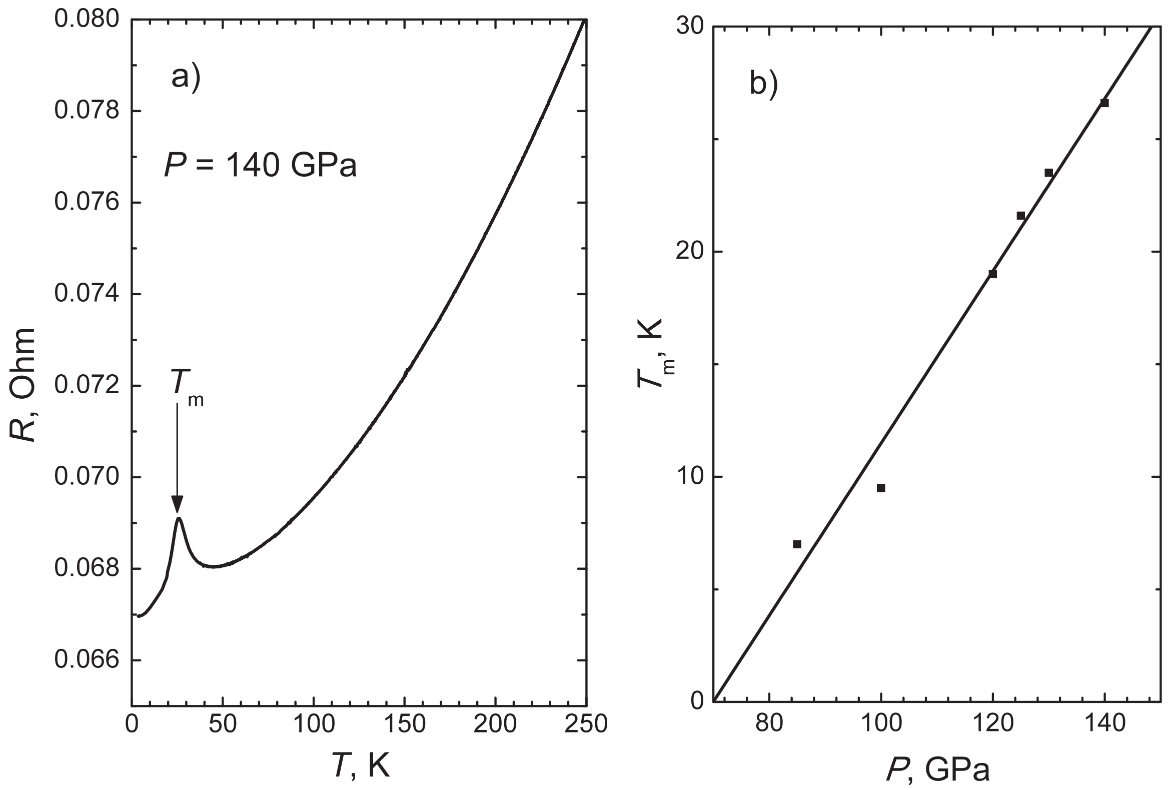

Fig. 5. (a, b) $R(T)$ dependence of ErH_3 at 140 GPa showing a characteristic maximum at T_m (left) and pressure evolution of T_m (right).

A small but reproducible maximum in the $R(T)$ dependencies was observed at 80 GPa and above. A detailed view of this feature at 140 GPa is shown in Fig. 5a. The pressure dependence of the corresponding temperatures $T_m(P)$ is shown in Fig. 5b. Similar anomaly was reported earlier for YH_3 [9].

Most REMs, as well as their di- and trihydrides are magnetically ordered at low temperatures. A detailed review of the magnetic ordering in REMs and their hydrides is given in Refs. [14,15] respectively. At ambient pressure pure erbium has three magnetically ordered phases: one ferromagnetic at the range $T = 0–20$ K, and two antiferromagnetic at $T = 20–54$ K and $T = 54–85$ K respectively. At their stoichiometry, erbium di- and trihydride are antiferromagnets with $T_N = 2.2$ K and 0.6 K respectively. Such low ordering temperatures result from low or zero electron density of states at the Fermi level of a system near the insulator-metal transition, which makes indirect exchange interaction between the localized 4f electrons mediated by the conduction electrons inefficient.

High pressure significantly increases the electron density of states at the Fermi level in ErH_3, manifesting in a resistance decrease by at least three orders of magnitude (see Fig. 4). At such conditions it is reasonable to suppose that a magnetic ordering temperature in ErH_3 should raise with pressure increase. The magnetic ordering temperature (e.g. the Néel point) typically manifests itself in a resistivity maximum, which provides a feasible explanation to the $R(T)$ anomaly in Fig. 5.

A disagreement between the theoretical predictions of superconductivity in the high pressure fcc phase of REM trihydrides [7] and experiment could be explained recalling that the calculations were non-spin-polarized.

4. Conclusions

We observed a gradual metallization of fcc-ErH_3 at a pressure of about 50 GPa by the means of Raman spectroscopy and electrical resistance measurements, similarly to the observation of fcc-YH_3 metallization in Ref. [9]. Such behavior should be typical for all late REM trihydrides. No superconductivity was observed in ErH_3 up to 140 GPa and down to 4 K. Instead of superconductivity, an anomaly was observed at low temperatures at the $R(T)$ dependencies, presumably indicating a magnetic ordering. Our results suggest the need of taking into account spin polarization of the localized 4f electrons of REM atoms in the ab-initio calculations for the better description of the ground state of REM compounds.

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