

Effect of Hydrogen on the Magnetic Properties of Tm

Takashi ITO, Kazuyoshi ITO, Kaoru MIZUNO, Sam LEGVOLD*
and Bernard J. BEAUDRY*

Department of Physics, Shimane University, Matsue, Shimane 690, Japan

**Ames Laboratory and Department of Physics, Iowa State University,*

Ames, Iowa 50011, U. S. A.

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The influence of hydrogen on the magnetic structures in thulium was determined by measuring the temperature dependence of the low field magnetization over the temperature range from 4.2 to 90 K. Results show that the magnetic ordering temperatures decrease with increasing hydrogen concentrations up to the limit of simple solubility of 7.7 at. % H. The magnetization curves for the samples up to 5.2 at. % H show the thermal hysteresis in the ferrimagnetic region. On the basis of the indirect exchange theory, the hydrogenation effects for the density of states at the Fermi energy are discussed.

§1. Introduction

Recently much attention has been given to the behavior of metal hydrides due to the interests in the basic physical properties and in the application as hydrogen storage materials. Especially rare earth metal hydrides have important technological applications in many industries and hence it is surprising that many of the fundamental properties are rather poorly understood. The magnetic properties of the rare earth metals, as well as in their hydrides, have been explained through the indirect exchange interaction between the 4f electrons via polarization of the conduction electrons.

Several investigators have observed that during hydrogenation the elemental lanthanide system loses its metallic conduction.¹⁻⁴⁾ These results implied that the conduction electron band was being depopulated during the hydrogenation process. Band structure calculations have been performed for rare earth metal hydrides⁵⁻⁸⁾ and found that during hydrogenation a new band was formed, lying at a lower energy than the conduction band of the host metal, and electrons are progressively transferred from the conduction band into this new band, which is mainly hydrogenic in nature. The density of states at the Fermi energy is lower than that of the host metal, and hence magnetic ordering should either be suppressed during the hydrogenation process. The hydrogen in the lanthanide hydrides is tending toward the anionic model. It is interesting to study the influence of hydrogen on the magnetic structures in thulium in order to have the information of the hydrogenation effect for the density of states at the Fermi energy. In the present work, low field magnetization measurements have been made on Tm-H system.

§2. Sample Preparation

The metals used in this study were prepared in bulk form starting with the highest purity Ames Laboratory polycrystalline Tm metal. The major impurities in the starting Tm, given in ppm atomic, were O=1060, C=564, N=456, H=167, F=35, Ho=20 and Ce=10. All other metallic impurities were less than 10 ppm atomic. After electropolishing the solid piece of Tm metal was placed in a Pt boat and reacted with hydrogen gas in a standard pressure, high vacuum system using UH_3 as gas source. The system was pumped down to 2×10^{-7} torr before heating the metal to 600°C and after this temperature was attained hydrogen was admitted to the system. The quantity of hydrogen which reacted was determined from the pressure change in the system of known volume.

§3. Magnetization Results

The low field magnetization was measured in the temperature range from 4.2 to 90 K. Rectangular parallelepipeds about $2.5 \times 2.5 \times 5$ mm were mounted in a vibrating sample magnetometer and an applied field of 1 kOe was used so that suitable signal intensity would be forthcoming. The magnetic structure of Tm has been studied using neutron diffraction by Koehler *et al.*⁹⁾ The incommensurate sinusoidal CAM structure sets in at a T_N of 58 K and there is squaring off of the sinusoidal modulation between 40 and 32 K at which the seven layer ferrimagnetic sets in. Magnetic measurements on single crystal Tm have been reported by Richards and Legvold.¹⁰⁾

In Fig. 1, we give the 1 kOe isofield results for the *c*-axis Tm single crystal. Here the Néel temperature T_N is defined as the cusp of the curve and the ferrimagnetic transition temperature T_c as the point of inflection. The cooling and warming curves show a thermal hysteresis near the squaring off of the sinusoidal modulation. The ferrimagnetic transition temperatures obtained by the cooling and warming process are 33.5 and 35.6 K, respectively. In the incommensurate sinusoidal structure region the curve does not show a thermal hysteresis and the Néel temperature is 57.6 K.

In Fig. 2, we show similar magnetization data for 4.3 at. % H in Tm. The ferrimagnetic transition temperatures obtained by the cooling and warming process are 15.7 and 20.0 K, respectively. The Néel temperature is 53.2 K. Compared with the results of pure Tm in Fig. 1, it is clear that the addition of H causes a downward shift of the Néel temperature and the ferrimagnetic ordering temperatures. Low isofield magnetization data for 7.3 at. % H in Tm are shown in Fig. 3. It can be seen that the thermal hysteresis does not appear in all the temperature range.

Figure 4 shows the magnetic ordering temperatures T_N and T_c versus hydrogen content for all the Tm-H samples. The Néel temperatures decrease linearly with increasing hydrogen concentration up to 7.7 at. % H in Tm and constant above it. The

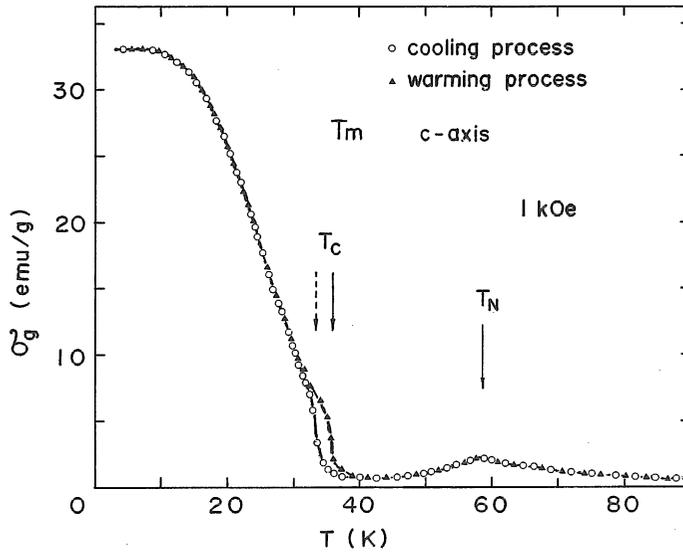


Fig. 1. Isofield magnetization versus temperature at 1 kOe for *c*-axis Tm.

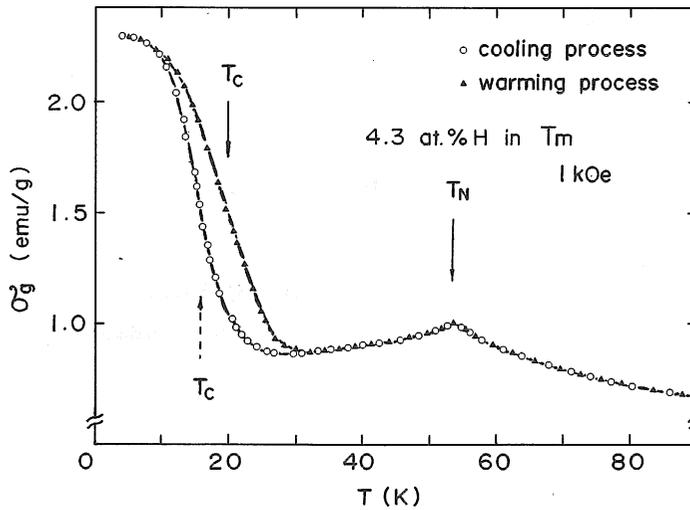


Fig. 2. Isofield magnetization versus temperature at 1 kOe for 4.3 at. % H in Tm.

solubility of hydrogen in Tm is 7.7 at. % and this result is consistent with the result of Beaudry *et al.*¹¹⁾ The values of $\Delta T_N/\Delta c$ and $\Delta T_N/T_N \cdot \Delta c$ are -1.05 (deg/at. % H) and -1.83×10^{-2} (1/at. % H), respectively. The ferrimagnetic ordering temperatures show the thermal hysteresis up to 5.2 at. % H, and decrease with increasing hydrogen concentration until the hydrogen interstitial solubility limit.

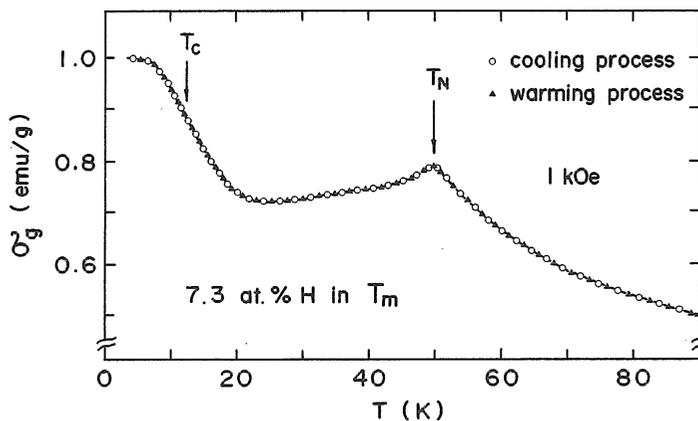


Fig. 3. Isofield magnetization versus temperature at 1 kOe for 7.3 at. % H in Tm.

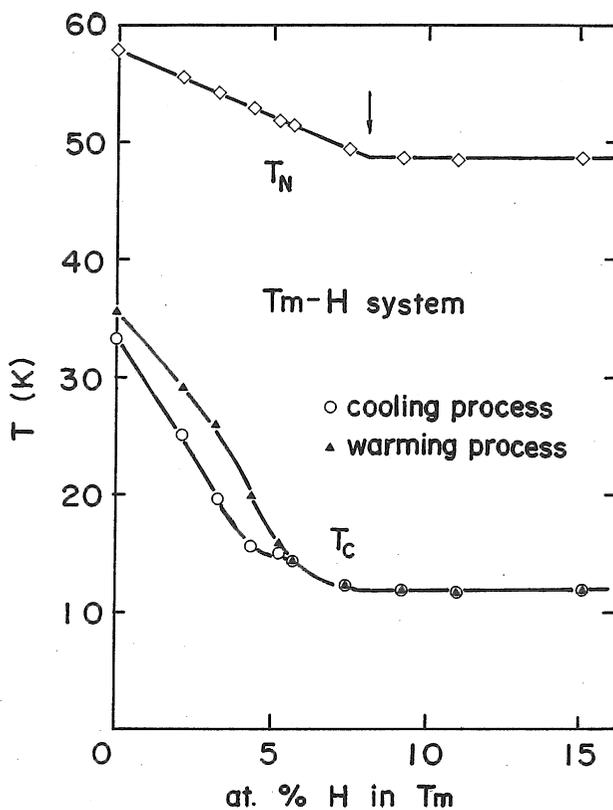


Fig. 4. Magnetic ordering temperatures T_N and T_c versus hydrogen content for all the Tm-H samples.

§4. Discussion

The elements Tm were selected from the heavy rare earth series because Gd, Tb and Ho have very limited room temperature hydrogen solubility while up to 7.7 at. % H can be dissolved in Tm according to the work of Beaudry *et al.*¹¹⁾ Daou *et al.*⁴⁾ have measured the temperature dependence of the electrical resistivity for Tm-H system and observed that during hydrogenation Tm loses its metallic conduction. Band structure calculations have pointed out for rare earth metal hydrides that during hydrogenation a new band was formed and electrons are progressively transferred from the conduction band into this new band and hence the density of states at the Fermi energy is lower than that of the host metal.

In a molecular field approximation the Néel temperature is given by the following equation:

$$kT_N = \frac{2}{3} (g-1)^2 J(J+1)J(Q) + \frac{2}{5} K_2 \left(J - \frac{1}{2} \right) \left(J + \frac{3}{2} \right). \quad (1)$$

The last term in Eq. (1) is the anisotropy energy and is assumed to be much less than the exchange energy. On the other hand, if the magnetocrystalline anisotropy effect is ignored for hydrogenation, the Néel temperature may be written in the following form on the basis of the indirect exchange theory:¹²⁾

$$T_N \propto I^2 N(E_F) \Sigma E(2k_F R_{On}), \quad (2)$$

where $N(E_F)$ is the density of state per atom at the Fermi level, $F(2k_F R_{On})$ is the Ruderman-Kittel oscillation function and I is the $s-f$ exchange integral. Rocher¹³⁾ has calculated that the Ruderman-Kittel sum varied only little with the small change in volume such as it results from the introduction of hydrogen:¹⁴⁾ 1×10^{-3} (1/at. % H). In an isotropic system, the hydrogenation effect for I are expected to be small,¹²⁾ and $\partial \ln T_N / \partial c$ is given from Eq. (2) by

$$\frac{\partial \ln T_N}{\partial c} = \frac{\partial \ln N(E_F)}{\partial c}. \quad (3)$$

The value of $\partial \ln T_N / \partial c$ obtained is -1.83×10^{-2} (1/at. % H). During hydrogenation the density of states at the Fermi energy is lower as the same value from Eq. (3). This result is consistent with the result of the electrical resistivity measurement.⁴⁾ The ferrimagnetic ordering temperatures show the thermal hysteresis and decrease not linearly with increasing hydrogen concentration. These complex results may be explained by the change of magnetization process and of magnetic structure.

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