

## Magnetic Behaviour of Some (RE)Ru<sub>2</sub>H<sub>x</sub> Hydrides

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**Abstract** Experimental results of low temperature (1.5 - 50K) AC magnetic susceptibility and DC magnetization on some (RE)Ru<sub>2</sub>H<sub>3</sub> hydrides (RE = several rare earths) are reported and discussed. All the parent compounds investigated here order ferromagnetically. After H<sub>2</sub> absorption the ferromagnetic order remains. However, a significant reduction of the Curie temperature was found to occur in the corresponding hydrides. This hydrogen induced effect will be discussed in terms of a weakening of the RE-RE exchange interaction in the hydrides as compared with that of the parent compounds.

### 1. INTRODUCTION

It is well known that atomic hydrogen dissolves in many metals and intermetallic compounds occupying interstitial sites in the host lattice. The rare earth intermetallic compounds of nd-transition elements, for instance, have attracted considerable interest from both the scientific and technological points of view due to their ability to absorb large amounts of hydrogen at room temperature and moderate pressures<sup>1-3</sup>. Indeed, several physical properties of the (RE)B<sub>2</sub>H<sub>x</sub> hydrides (B=nd-transition element) such as thermodynamical, structural, hydrogen diffusion, electrical and magnetic properties have been extensively studied, mainly during the last few years, by a variety of techniques<sup>4, 5, 6</sup>.

Frequently, it is found that when the intermetallic host takes up hydrogen, significant changes take place in their properties listed above as a consequence of the formation of new hydride phases. Concerning the magnetic properties, it is also known that the basic magnetic coupling mechanism in rare earth intermetallic compounds, containing the nd-transition elements, is that of indirect exchange coupling between the rare earth ions, usually assumed to be of Rudermann-Kittel -

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-Kasuya-Yosida (RKKY) type, arising from the exchange interaction between a RE spin  $S$  and conduction electron spin  $s$  given by

$$H_{\text{ex}} = -2J(0)\vec{S}\cdot\vec{s} \quad (1)$$

where  $J(0)$  is the  $q=0$  value of the exchange constant.

When treated in the molecular field approximation, the RKKY interaction leads to a ferromagnetic Curie temperature

$$T_c \sim (\Gamma/3k_B)(g_i-1)^2J(J+1) \quad (2)$$

where  $\Gamma$  is the coupling constant between RE ions,  $J$  is the total angular momentum and  $g_i$  the ionic  $g$ -value. Then, despite the negligible overlap between the  $4f$  orbitals of the neighbouring RE ions (localized moments), several rare earth metals as well as intermetallic compounds order magnetically due to the strong RKKY coupling arising from the exchange interaction (1). In fact, most of the compounds belonging to the series  $(\text{RE})\text{Ru}_2$ , for example, order either ferro or antiferromagnetically at appropriate temperatures.

Jacob et al.<sup>7</sup> have shown that  $\text{GdRu}_2$  and  $\text{GdRh}_2$  intermetallic compounds absorb hydrogen to form  $\text{GdRu}_2\text{H}_3$  and  $\text{GdRh}_2\text{H}_3$  hydrides, respectively. They observed a marked reduction in the ferromagnetic transition temperature in these hydrides relative to that of the uncharged starting compounds. On the other hand, H. de Graaf et al.<sup>8</sup> reported recently on Mossbauer and magnetization measurements on  $\text{GdCu}_2$  and  $\text{GdCu}_2\text{H}_x$  which show that the parent compound orders antiferromagnetically, while its hydride becomes ferromagnetic. A weaker and a stronger RE-RE exchange coupling were respectively invoked to explain those somewhat contrasting changes in the magnetic behaviour of  $(\text{GdRu}_2, \text{GdRh}_2)$  and  $\text{GdCu}_2$ , due to hydrogen uptake.

This paper reports on some results of AC magnetic susceptibility and magnetization measurements carried out on the series  $(\text{RE})\text{Ru}_2\text{H}_3$  (RE representing Tb, Dy, Ho, and Er), as well as their preparation method, as part of a more extensive program designed to investigate the entire  $(\text{RE})\text{Ru}_2\text{H}_3$  series using both magnetic susceptibility and electron spin resonance techniques.

It will be shown (section 3) that the series of hydrides studied here,  $(RE)Ru_2H_3$ , where RE represents Tb, Dy, Ho or Er, is a further example of  $T_c$  reduction, suggesting that a RE-RE exchange weakening induced by hydrogen absorption comes about in these hydrides.

## 2. EXPERIMENTAL METHODS

The samples of  $(RE)Ru_2$  were prepared by arc melting the high purity constituent elements under argon atmosphere in a Zr-gettered arc furnace. Weight losses during the arc melting procedure were found to be negligible. The samples were then wrapped in Ta foils, sealed inside evacuated quartz tubes and annealed at  $1050^\circ\text{C}$  for 48 hours to ensure homogeneity. Powder x-ray diffraction data were taken using a GE-XRD diffractometer ( $\text{CuK}_\alpha$  radiation). The results of the x-ray analysis on the uncharged samples demonstrate that they possess the correct hexagonal single Laves phase structure and lattice parameters as determined by Compton and Matthias<sup>9</sup>.

A sequence of steps for the hydrides preparation was followed, including (1) outgassing of the starting sample at about  $500^\circ\text{C}$  in vacuum of approximately  $10^{-3}$  torr; (2) reactor with ultrahigh purity hydrogen at about 30 atmospheres and at room temperature using a conventional high pressure stainless steel reaction of constant volume. Each sample was kept into the high pressure system for about 36 hours; (3) the hydrogen concentration of the several hydrides was determined by using the ideal gas law, from the initial and final hydrogen pressures, the working temperature and the known volume of the apparatus; (4) after that, each hydride was removed from the reactor and the amount of absorbed hydrogen was determined again by the method of mass difference between the hydride and the corresponding parent compound. The x-ray diffraction and magnetization measurements on each hydride were carried out immediately after the hydrogenation procedure in order to prevent against any take out of hydrogen that could occur if the hydrogenated samples were exposed to ambient atmosphere.

Finally, AC magnetic susceptibility data were taken using a conventional  $20H_z$  biphas impedance bridge and the magnetization measurements were performed between 1.5 and 50K in magnetic fields up to 12 KGauss with a type Foner vibrating sample magnetometer.

### 3. RESULTS AND DISCUSSION

Fig. 1(a-b) shows plots of AC susceptibility  $\chi_{ac}$ , as a function of temperature in zero applied magnetic field for  $\text{HoRu}_2$  (1-a),  $\text{ErRu}_2$  (1-b) and their respective hydrides. As may be seen from the figures, sharp peaks characteristic of paramagnetic to ferromagnetic transition occur in both the compounds and the corresponding hydrides. Furthermore, these data clearly show that the magnetic transition temperature,  $T_c$ , decreases in the hydrides as compared with  $T_c$  of the associated parent compounds. Similar features were also observed in all intermetallic compound-hydride couples under discussion here.

In order to identify the exact nature of the observed transitions, we have also made magnetization measurements as a function of both the temperature and the applied magnetic field for all the parent compounds and hydrides we have selected to investigate. Fig. 2(a-b) show typical Arrott's plots<sup>10</sup> ( $M^2$  vs.  $HM$  isotherms) for  $\text{HoRu}_2$  (2-a) and  $\text{HoRu}_2\text{H}_3$  (2-b) obtained by measuring the magnetization as a function of the applied magnetic field up to nearly 12 KGauss for several temperatures above and below the magnetic transition temperature. Arrott's plots were constructed for all the samples studied and the reciprocal magnetic susceptibilities  $\chi^{-1}$ , in the limit of zero applied field, were given as a function of temperature by the intercepts on  $HM$  axis when extrapolated to  $M^2=0$ . Plots of  $\chi^{-1}$  versus temperature for  $\text{ErRu}_2$ ,  $\text{DyRu}_2$  and their hydrides as obtained from their corresponding Arrott's plots are displayed in figs. 3 and 4. The full lines are least square fits of Curie-Weiss Law to the data with effective magnetic moments  $\mu_{ef}$  of  $(9.5 \pm 0.2)\mu_B$  per Er ion and  $(10.7 \pm 0.2)\mu_B$  per Dy ion. The  $\mu_{ef}$  values for all the charged and uncharged samples were found identical to those predicted for the Hund's rule ground state of the associated rare earth ion within the experimental error. In table 1 are summarized the  $\mu_{ef}$  values and the magnetic transition temperatures determined for the (RE)  $\text{Ru}_2$  compounds and corresponding hydrides we have investigated together with the data obtained for  $\text{GdRu}_2$  and  $\text{GdRu}_2\text{H}_3$  by Jacob et al.<sup>7</sup>. We would like to remark at this point that all  $T_c$  values that we measured for the intermetallic parent compounds are in perfect agreement with those previously reported by Wilhelm and Hillenbrand<sup>11</sup>.

In order to check the correctness of our measurements, we have

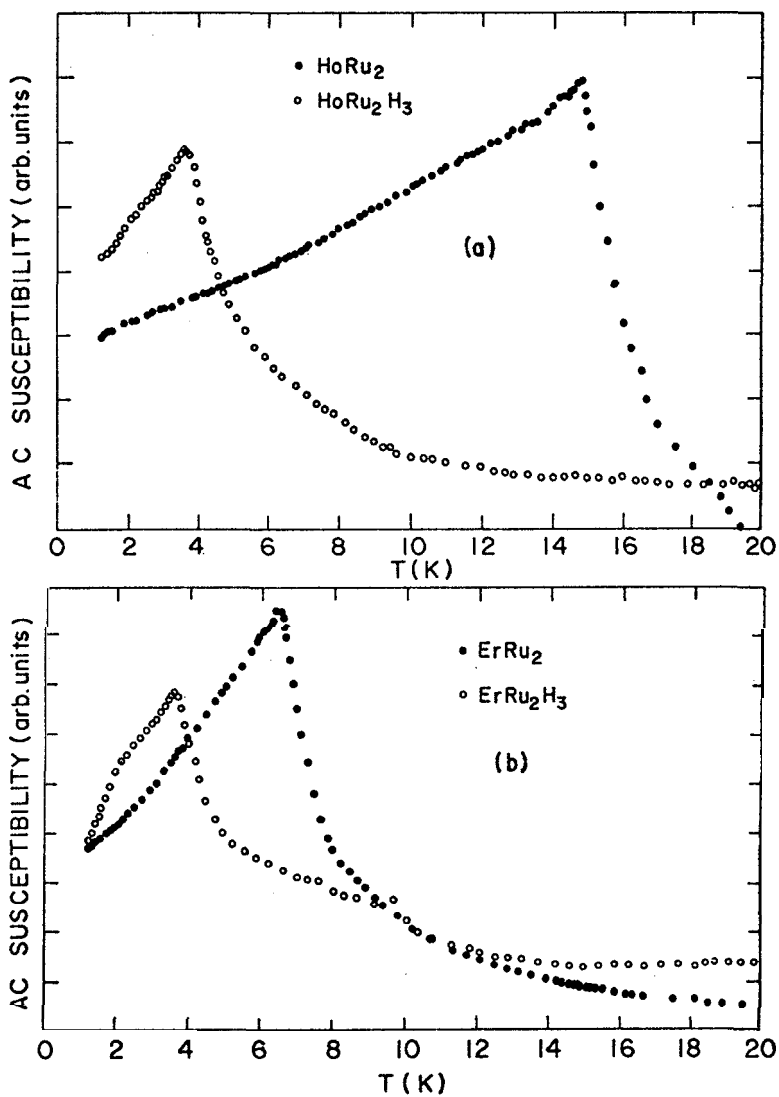


Fig.1 - AC magnetic susceptibility vs. temperature for  $\text{ErRu}_2$  (a),  $\text{HoRu}_2$  (b) and their corresponding hydrides.

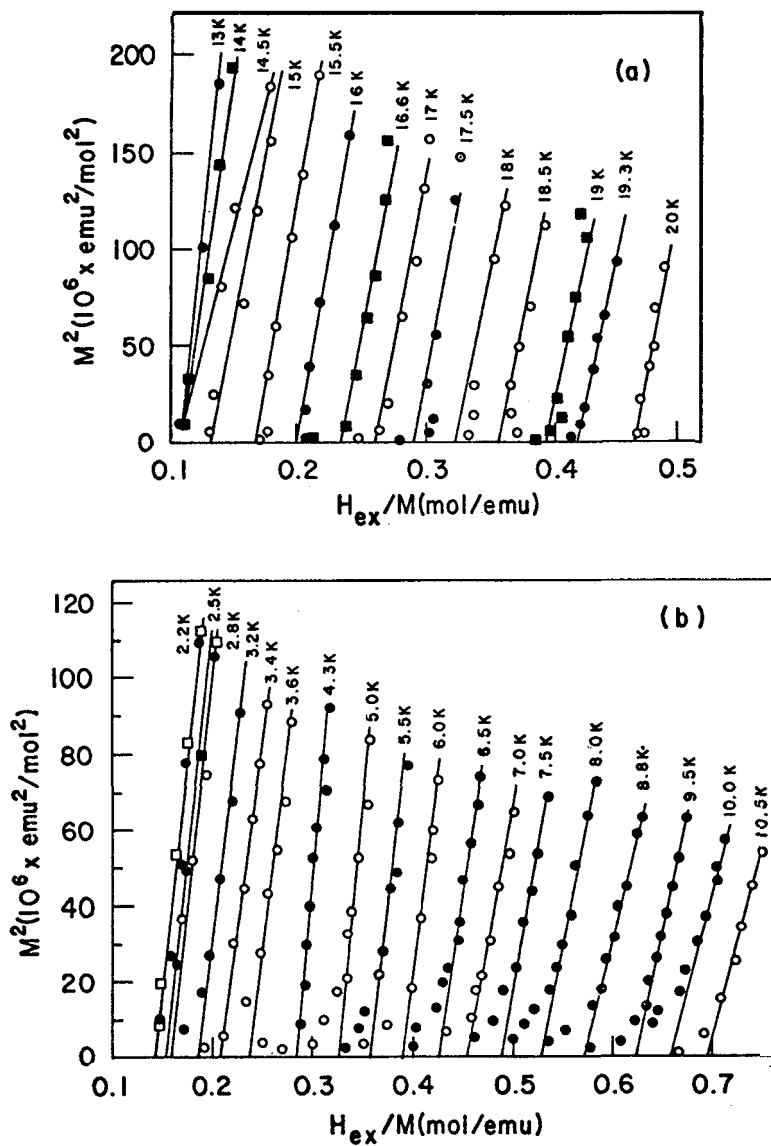


Fig.2 - Arrott's plots ( $M^2$  vs  $H_{ex}/M$ ) for  $\text{HoRu}_2$  (a) and  $\text{HoRu}_2\text{H}_3$  (b).

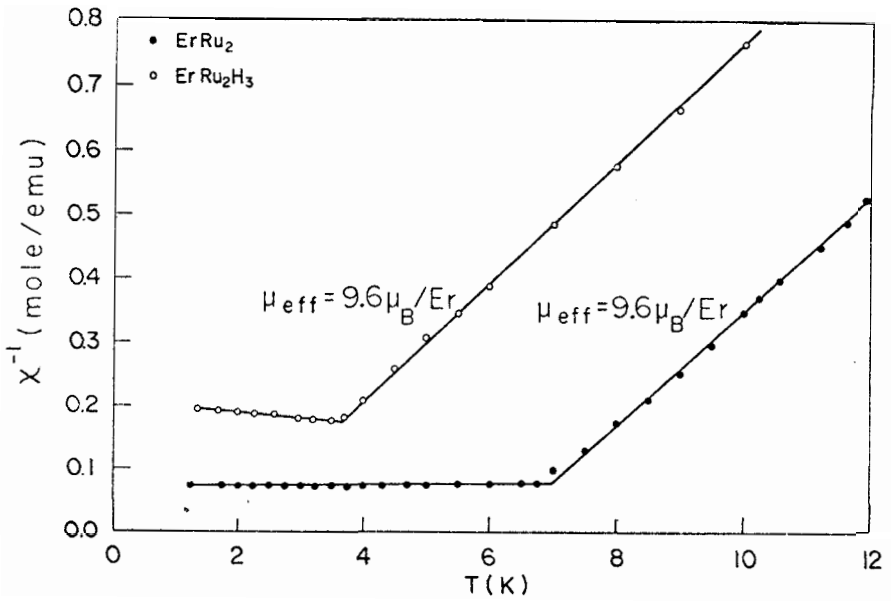


Fig.3 - Inverse magnetic susceptibility as a function of temperature for  $\text{ErRu}_2$  and  $\text{ErRu}_2\text{H}_3$ .

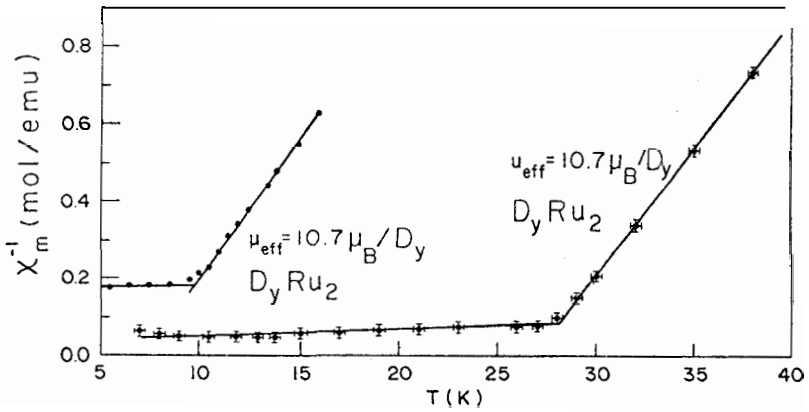


Fig.4 - Inverse magnetic susceptibility as a function of temperature for  $\text{DyRu}_2$  and  $\text{DyRu}_2\text{H}_3$ .

Table 1 - Ferromagnetic Curie temperature and effective Magnetic Moment of the (RE)Ru<sub>2</sub> compounds and their ternary Hydrides.

Compound/Hydrides	$T_c$ (K)	$\mu_{\text{eff}}$ ( $\mu_B/\text{ion}$ )
GdRu <sub>2</sub>	84, 83 <sup>(a)</sup>	6.8 ± 0.2
GdRu <sub>2</sub> H <sub>3</sub>	63.6, 65 <sup>(a)</sup>	6.6 ± 0.2
TbRu <sub>2</sub>	49.3	9.6 ± 0.2
TbRu <sub>2</sub> H <sub>3</sub>	13.6	9.5 ± 0.3
DyRu <sub>2</sub>	27.3	10.7 ± 0.2
DyRu <sub>2</sub> H <sub>3</sub>	9.8	10.7 ± 0.2
HoRu <sub>2</sub>	14.6	10.6 ± 0.2
HoRu <sub>2</sub> H <sub>3</sub>	2.6	10.5 ± 0.2
ErRu <sub>2</sub>	6.5	9.6 ± 0.2
ErRu <sub>2</sub> H <sub>3</sub>	3.6	9.6 ± 0.2

(a) Jacob *et al.*, ref. 7.

also investigated the magnetic properties of GdRu<sub>2</sub> and GdRu<sub>2</sub>H<sub>3</sub> using the Arrott's plots method and the results we got (see table 1) were quite similar to those published elsewhere<sup>7</sup>. The final experimental point that needs to be remarked is that the shapes of the magnetic isotherms for several temperatures above and below  $T_c$  strongly suggest that all the hydrides discussed here order ferromagnetically like the parent compounds. This feature is confirmed by the Curie-Weiss behaviour of the reciprocal susceptibilities as a function of temperature (with positive  $T_c$ 's) as shown in figs: 3 and 4.

As has been pointed out previously, the (RE)Ru<sub>2</sub> compounds, with RE representing Gd, Tb, Dy, Ho and Er, were found to react with hydrogen to form new species, the ternary (RE)Ru<sub>2</sub>H<sub>3</sub> hydrides. Inspection of the data given in table 1 makes it clear that hydrogen uptake in



in the series  $(RE)Ru_2$  leads to a reduction in the magnetic transition temperature  $T_C$ . This remarkable behaviour may be understood by recalling that the main source of magnetic ordering in these systems is the indirect exchange interaction between RE ions, as discussed in the introductory section, since Ru is a nonmagnetic transition element. The exchange interaction given by the relation (1) polarizes the conduction electrons and this polarization propagates outward from the central RE ion in a damped oscillatory way. If, however, the conduction electrons polarization is non-vanishing in amplitude at the sites of adjacent rare earth ions, an exchange coupling between them results and, as a consequence, the system can order magnetically. Conduction electrons are then fundamental to understand the magnetic properties of rare earth systems since they mediate the RKKY interaction responsible for magnetic ordering. From the relations (1) and (2), and noting that  $\Gamma \approx J^2 N(E_F)$ , it follows that a reduction in  $T_C$  implies a weakening of the RE-RE exchange interaction in the hydrides, as compared with the hydrogen free compounds. Both protonic ( $H^+$ ) and anionic ( $H^-$ ) models have been proposed<sup>11</sup> to account for the several observed properties of metallic hydrides. In the protonic model electrons from the hydrogen sites are transferred to the band states in the hydride, whereas in the anionic model electrons are transferred from the band states to the hydrogen to form  $H^-$  anions. There are experimental evidences supporting both models. We believe that our results presented in table 1 are qualitatively consistent with the anionic model and that the weakening of the exchange coupling results from a decrease in the conduction electrons polarization due to a reduction of the conduction electrons concentration. <sup>155</sup>Gd and <sup>151</sup>Eu Mössbauer measurements on  $GdRu_2H_3$ ,  $GdRh_2H_3$ <sup>7</sup>,  $EuRh_2H_x$  and  $EuPdH_x$ <sup>12</sup> support this idea. Indeed, both the isomer shift and the absolute value of the hyperfine field were found to increase in all these hydrides relative to the corresponding parent compounds, consistent with the view that charge transfer takes place toward the hydrogen atoms.

It should be kept in mind however that much more experimental results are needed to ascertain whether the anionic concept is widely applicable in hydrides of intermetallic compounds just as it is in elemental rare earth hydrides or, on the other hand, if the  $(RE)B_2H_x$  discussed here are only marginal examples of its validity. Problems are

encountered for instance in application of the  $H^+$  and  $H^-$  models for  $(RE)_2B_xH_x$  hydrides when the B element carries a magnetic moment as usually occurs with Fe, Co and Ni compounds. Electron spin resonance and magnetization experiments are at the present in progress in our laboratory in an attempt to shed some more light on the interesting problem posed by the somewhat contrasting magnetic behaviour of the rare earth intermetallic hydrides.

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## Resumo

Resultados experimentais de susceptibilidade magnética AC e magnetização DC obtidos a baixas temperaturas entre 1.5 e 50K em alguns hidretos metálicos do tipo  $(RE)Ru_2H_3$  (RE=diversas terras raras) são apresentados e discutidos. Todos os compostos intermetálicos investigados da série  $(RE)Ru_2$ , não hidrogenados, ordenam-se ferromagneticamente. Após absorção de hidrogênio a ordem magnética é retida, porém, com ocorrência de uma significativa redução da temperatura de Curie nos hidretos correspondentes. Este efeito, induzido pela hidrogenação, é discutido em termos de um enfriamento da interação de troca RE-RE nos hidretos quando comparada àquela nos compostos metálicos não hidrogenados.