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# METALLIC HYDRIDES.

## Magnetic properties of laves-phase rare earth hydrides

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**Résumé.** — La diffraction des neutrons montre que l'introduction d'hydrogène dans les composés  $RFe_2$  ( $R = Tm, Ho, et Er$ ) diminue sensiblement la température de Curie moyenne et résulte en une réduction du moment à 0 K sur le site de terre rare. Le moment de la terre rare se désordonne à une température inférieure à la température critique macroscopique dans  $ErFe_2H_{3,5}$ . Le moment à 0 K du sous-réseau de fer dans  $ErFe_2H_{3,5}$  est essentiellement le même que celui trouvé pour le composé non hydruré et reste sensiblement constant jusqu'à approximativement  $0,8 T_c$ .

**Abstract.** — Neutron scattering results show that the introduction of hydrogen into  $RFe_2$  compounds ( $R = Tm, Ho, and Er$ ) significantly lowers the overall Curie temperature and produces a reduced 0 K moment on the rare earth site. The rare earth spins disorder at a temperature lower than the bulk  $T_c$  in  $ErFe_2H_{3,5}$ . The 0 K iron sublattice moment in  $ErFe_2H_{3,5}$  is essentially the same as that found in the non-hydride compounds and remains nearly constant to approximately  $0.8 T_c$ .

1. **Introduction.** — Gualtieri, *et al.* [1] have shown that the  $RFe_2$  compounds readily absorb hydrogen and form a hydride phase with approximately 4 hydrogen atoms per formula unit. The hydride can be made stable against desorption of hydrogen at room temperature and ambient pressure by poisoning the surface with  $SO_2$ . X-ray diffraction has shown that the materials remain in the cubic Laves phase structure, but exhibit a significant increase in lattice parameter  $a_0$ . For example,  $a_0 = 7.28 \text{ \AA}$  for  $ErFe_2$  and  $a_0 = 7.83 \text{ \AA}$  for  $ErFe_2H_{3,9}$ . The theoretical maximum (but experimentally not attained) number of hydrogen atoms which can be introduced into the Laves phase structure is 7 per formula unit assuming complete occupation of 3 tetrahedral sites.

The heavy rare earth ( $RFe_2$ ) compounds (non-hydride) are ferrimagnetic with the R moment equal to the free ion moment (at 0 K) and aligned antiparallel to the two Fe moments each equal to approximately  $1.6 \mu_B$  [2, 3]. The Curie temperatures of the  $RFe_2$  compounds range from 535 K for  $YFe_2$  to 793 K for  $GdFe_2$  [1].

The introduction of hydrogen into the crystal lattice produces changes in the electronic density of states, lattice parameter, crystal field screening, etc., and as a result can strongly affect the magnetic interactions. After hydriding, bulk magnetization data [1] show the Curie temperatures to be significantly reduced from that of the pure compounds

and to be fairly sensitive to small changes in hydrogen concentration and/or preferential occupation of sites. Because of the large crystal field anisotropy (except for Gd) magnetic moment data on the compounds do not show saturation in normally available laboratory fields ( $\approx 100 \text{ kOe}$ ) and thus a definitive determination of the full moment is not possible by conventional methods. Therefore, we have used neutron scattering to study the effect of hydrogen on the sublattice magnetization and Curie temperature of  $HoFe_2$ ,  $ErFe_2$  [2] and  $TmFe_2$ .

2. **Magnetic neutron scattering.** — In the hydride compounds, due to the unknown site occupancy of the hydrogen, calculation of the nuclear contribution to the structure factor is not straightforward. As a result an absolute determination of the scattering intensity was made by normalization to a copper powder. The magnetic contribution [3] to the scattering below  $T_c$  was determined by subtraction of the high temperature (above  $T_c$ ) nuclear component from the total intensity. In the case of  $ErFe_2H_{3,5}$  data were taken both using total scattering and also with an analyzing crystal to reduce the inelastic incoherent component of the  $H$ , with substantially the same results. The  $HoFe_2D_{3,5}$  data were taken on a deuterated sample which further reduced the incoherent contribution. Results for the sublattice moment on the R site are shown in figures 1 and 2 for  $HoFe_2D_{3,5}$ ,  $HoFe_2$ ,  $TmFe_2H_{3,5}$ ,  $TmFe_2$ , and on both R and Fe sites for  $ErFe_2H_{3,5}$  and  $ErFe_2$ .

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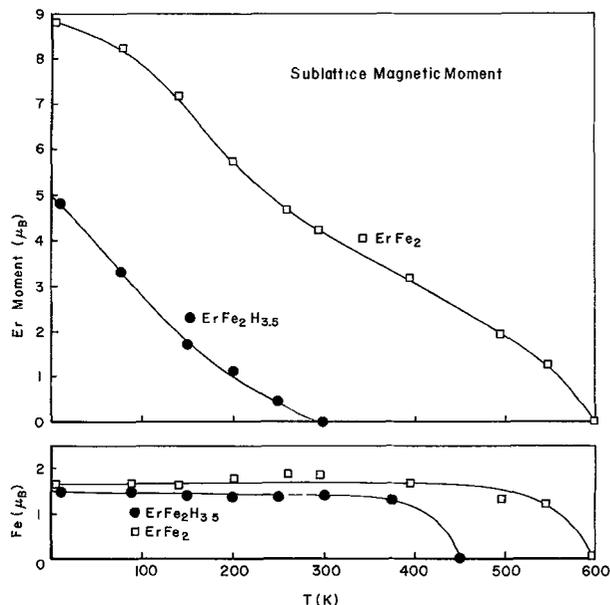


Fig. 1. — Sublattice magnetic moments as a function of temperature for Er and Fe in  $\text{ErFe}_2$  and  $\text{ErFe}_2\text{H}_{3.5}$ . The uncertainty in the moment shown is approximately  $\pm 0.3 \mu_B$  largely due to the effect of the incoherent scattering of  $H$ .

As is evident from the figures, the overall Curie temperature is reduced by more than 20% on hydriding. This reflects a reduction in Fe-Fe exchange due to the increased lattice parameter and Fe-Fe interatomic spacing. The magnitude of the iron sublattice moment and its relatively flat temperature dependence remain essentially unchanged. The effect on the rare earth is much more dramatic. First the 0 K moment in the hydride is sharply reduced from its free ion value. In addition the moment rapidly decreases with elevated temperature, reaching zero below the overall Curie temperature in  $\text{ErFe}_2\text{H}_{3.5}$ . This is in contrast to the behavior in  $\text{RFe}_2$  compounds for which both sublattice moments disorder at the same temperature. These features suggest a severe weakening of the R-Fe (and R-R) exchange interactions.

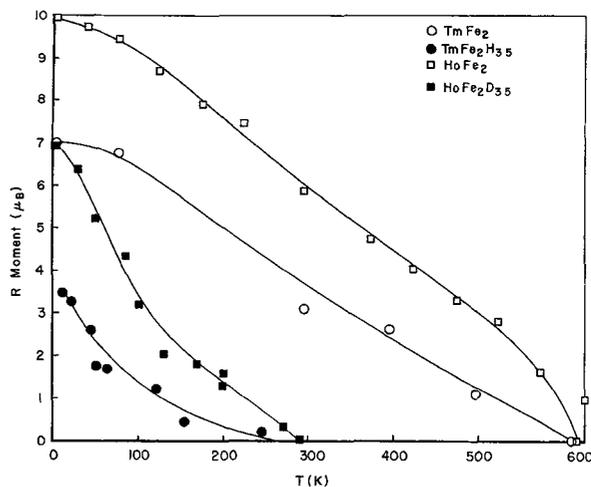


Fig. 2. — Tm and Ho sublattice moment versus temperature for  $\text{TmFe}_2$ ,  $\text{HoFe}_2$ , and for  $\text{TmFe}_2\text{H}_{3.5}$  and  $\text{HoFe}_2\text{D}_{3.5}$ . The overall Curie temperature of the Tm hydride is approximately 295 K and of the Ho deuteride 305 K.

The addition of hydrogen would be expected to perturb the electronic density of states, and thus affect the indirect exchange coupling involving the rare earth ions. The Fe-Fe coupling may proceed by nearest-neighbor direct overlap exchange which would not be strongly influenced.

The weaker rare-earth exchange in the hydride compound suggests that the crystal field interactions may perturb the energy levels away from pure  $J_2$  states, effectively reducing the observed sublattice moment. Inelastic neutron scattering studies are in progress to examine the magnetic excitations. Alternatively the loosely-coupled rare earth moments may be *fanning* about the direction of the net iron exchange field. The random occupation of the hydrogen sites can significantly distort the local anisotropy field in a manner similar to that found in amorphous rare earth alloys [4] leading to a reduction in spatially averaged moment as measured by the neutrons.

## References

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