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MÖSSBAUER SPECTROSCOPY**

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ELECTRONIC AND STRUCTURAL STUDIES OF THE HYDRIDES OF ErFe_2 FROM ^{57}Fe AND ^{166}Er MÖSSBAUER SPECTROSCOPY[†]P.J. Viccaro[†], G.K. Shenoy, B.D. Dunlap, D.G. Westlake and J.F. Miller*Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.*

Résumé.- On étudie deux hydrures du composé intermétallique ErFe_2 qui présente une phase de Laves C15. Les analyses par rayons X de $\text{ErFe}_2\text{H}_{3.65}$ révèlent la présence d'une phase cubique C15 dilatée et d'une phase de symétrie inférieure. Le champ hyperfin moyen à saturation pour ^{57}Fe est 20% plus élevé que dans ErFe_2 tandis que le champ hyperfin de ^{166}Er est inférieur de 15%. Ces résultats, combinés aux mesures antérieures du moment total, impliquent que le couplage Er-Fe n'est pas antiparallèle dans l'hydrure. Dans $\text{ErFe}_2\text{H}_{4.12}$ on ne détecte qu'une phase qui est compatible avec une structure trigonale. Les résultats Mössbauer suggèrent une température de transition magnétique entre 1,7 et 4,2 K et une réduction importante du moment du fer dans cet hydrure.

Abstract.- Two different hydrides of the C15 Laves phase intermetallic ErFe_2 are considered. For $\text{ErFe}_2\text{H}_{3.65}$, X-ray analyses showed the presence of an expanded C15 cubic phase and a lower symmetry phase. The ^{57}Fe mean saturated hyperfine field is 20% larger than in ErFe_2 and the ^{166}Er hyperfine field is 15% smaller. These results coupled with previous measurements of the net moment imply that the Er-Fe coupling is not antiparallel in this hydride. For $\text{ErFe}_2\text{H}_{4.12}$, the only phase detected was rhombohedral. The Mössbauer results indicate a magnetic transition temperature between 1.7 K and 4.2 K and a drastic reduction of the Fe moment in this hydride.

1. Introduction.- Many rare-earth 3d transition metal intermetallic compounds readily absorb large quantities of hydrogen /1,2/. The hydrogen capacity of these systems is thought to be closely related to their structural and electronic properties. A favorable case where these properties are relatively well known is that of the Laves phase intermetallics of the type RM_2 where R is a rare-earth element and M a 3d transition metal. Presented here is an investigation of the hydrides of one such compound, ErFe_2 , using X-ray diffraction and ^{57}Fe and ^{166}Er Mössbauer spectroscopy.

2. Experimental.- The ^{166}Er 80.6 keV resonance experiments were done using a $\text{Y}_{0.61}\text{Ho}_{0.39}\text{H}_2$ source held at 10 K /3/. For the ^{57}Fe experiments, a source of ^{57}Co in Rh was utilized.

The ErFe_2 intermetallic compound was prepared by argon arc melting using ultra pure argon (99.999%) passed through a titanium getter. Ingots of Er(99.9%) and Fe(99.99%) were used as the starting materials. After melting, the samples were annealed at 750°C for 7 days in quartz capsules sealed under vacuum. Debye-Scherrer X-ray powder diffraction patterns showed only the C15 cubic Laves structure (Fd3m).

The hydrides were formed by exposing pieces

of ErFe_2 of known mass to H_2 gas (99.999%) above one atmosphere in a system of known volume at room temperature. The actual amount of retained hydrogen was subsequently determined by both volumetric and gravimetric analyses. In one case, the hydride of initial composition ErFe_2H_4 , as determined by monitoring the pressure change upon H_2 absorption, was removed from the apparatus after equilibrium had been reached. The equilibrium pressure for this hydride is less than 0.1 atm. /2/, and it is reported to be stable with respect to hydrogen desorption at room temperature. Subsequently, volumetric and gravimetric analysis showed the composition to be $\text{ErFe}_2\text{H}_{3.65 \pm 0.02}$. In a second case, the surface of the hydride of initial composition ErFe_2H_4 was "poisoned" with SO_2 gas. This procedure reportedly inhibits decomposition of the hydride /4/. In this case, the volumetric analysis gave the composition as $\text{ErFe}_2\text{H}_{4.12 \pm 0.02}$. All the hydrides were stored at 77 K to preclude any loss of hydrogen.

3. Results and Discussion.- 3.1. Structure.- For the hydride $\text{ErFe}_2\text{H}_{3.65}$, the X-ray diffraction pattern shows evidence of two phases. One has a C15 Laves structure with lattice constant $a_0 = 7.838 \pm 0.005 \text{ \AA}$, which is 8% larger than that of ErFe_2 . The other phase is of lower symmetry. However, because of the limited number of observable reflections, a unique determination of the structure of this phase was not possible.

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For the compound $\text{ErFe}_2\text{H}_{4.12}$ the pattern was consistent with a rhombohedral lattice with $a_0 = 7.82 \pm 0.01 \text{ \AA}$ and $\alpha = 93.5 \pm 0.3^\circ$. No C15 structure reflections were detectable. Some of the reflections observed for this sample do coincide with those associated with the lower symmetry phase in $\text{ErFe}_2\text{H}_{3.65}$. Thus, it seems reasonable to assume that the second phase in $\text{ErFe}_2\text{H}_{3.65}$ may have the same structure as $\text{ErFe}_2\text{H}_{4.12}$.

These results are to be compared with previous ones /5/ reported for the hydride $\text{ErFe}_2\text{H}_{3.9}$ for which only an expanded C15 lattice was observed with $a_0 = 7.828 \text{ \AA}$.

3.2. Magnetic and Electronic Properties.— The ^{57}Fe Mössbauer spectra of $\text{ErFe}_2\text{H}_{3.65}$ are shown in figure 1 for three temperatures. At 300 K, the spectrum consists of an asymmetric doublet with an isomer shift of $0.45 \pm 0.02 \text{ mm/s}$ relative to ErFe_2 .

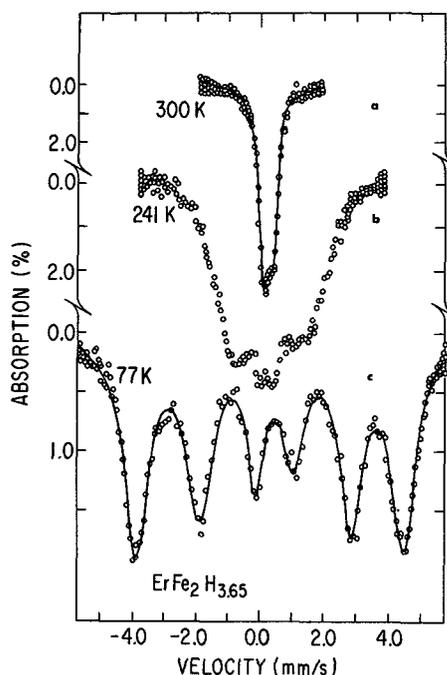


Fig. 1 : ^{57}Fe Mössbauer spectra of $\text{ErFe}_2\text{H}_{3.65}$ at (a) 300 K, (b) 241 K and (c) 77 K.

At 241 K, magnetic hyperfine splittings become apparent and the spectrum shows the existence of a distribution of hyperfine fields at the iron site. The temperature dependence of magnetic hyperfine splitting indicates the transition temperature to be slightly below 270 K. Previous measurements give the values of 280 K /5/ and 265 K /6/ for hydrides of ErFe_2 with similar compositions. A more precise determination of the transition temperature from the Mössbauer data was not possible because of the distribution of hyperfine fields encountered.

At lower temperatures (Fig. 1c) the distribution becomes less severe and the mean hyperfine field at the iron nucleus determined at 4.2 K was $265 \pm 5 \text{ kOe}$. This value is approximately 20% higher than that reported for ErFe_2 /7/. The increase encountered here may not necessarily imply a corresponding increase in the Fe magnetic moment in the hydride since the 3d electrons are expected to be delocalized to some degree. However, studies of the hydride of YFe_2 /9/, where the rare earth moment is absent, have shown that both the Fe saturated hyperfine field and moment increase when compared to YFe_2 . Based on this result, it can be concluded that the Fe moment in $\text{ErFe}_2\text{H}_{3.65}$ is larger than in ErFe_2 .

The ^{166}Er spectrum for this hydride at 4.2 K (Fig. 2a) shows a magnetic splitting. The single hyperfine field fit to the data does reveal slight discrepancies related to deviations from the equal intensity ratios expected for the various hyperfine components of a $2 \rightarrow 0$ magnetic pattern. These deviations may be related to the presence of a slight distribution of hyperfine fields as was the case for ^{57}Fe , or relaxation of the Er moment.

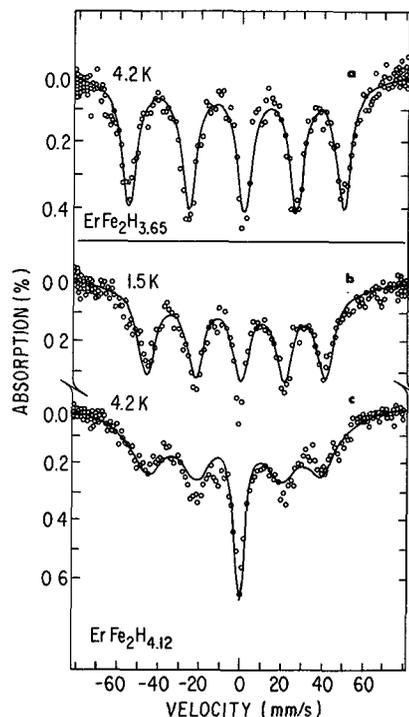


Fig. 2 : ^{166}Er Mössbauer spectra of a) $\text{ErFe}_2\text{H}_{3.65}$ at 4.2 K and $\text{ErFe}_2\text{H}_{4.12}$ at b) 1.5 K and c) 4.2 K. Detail of the least squares fits to the data indicated by the solid lines are discussed in the text.

Aside from these details, an acceptable fit is obtained with a hyperfine field of $7075 \pm 50 \text{ kOe}$ and a quadrupole coupling e^2qQ of $-8.4 \pm 0.8 \text{ mm/s}$. Both

these values are somewhat lower than the free ion hyperfine field of 7750 kOe and the free-ion quadrupole interaction of -14 mm/s. In ErFe_2 the field at the Er nucleus is 8400 kOe, the increase from the free-ion value reflecting a conduction electron polarization by the 3d spins. The quadrupole interaction in ErFe_2 is nearly the free-ion value. The results on the hydride in question point to two facts: a) There is a lower symmetry crystalline electric field (CEF) and/or a weaker exchange field acting on the Er^{3+} ion (inferred through a decrease in the quadrupole interaction). b) There is decrease (or absence) of conduction electron contribution to the hyperfine magnetic field (compared to ErFe_2), in addition to a decrease in the Er moments due to the CEF mentioned above. The observed hyperfine field then sets an upper limit of $8.2 \mu_B$ on the Er moment.

The change in the total moment of the hydride relative to ErFe_2 will of course be related to the changes in the individual Er and Fe moments and can be determined once the nature of coupling between these moments is known. In relation to this coupling, it has been proposed /1,6/ that the antiparallel alignment for the Er and Fe spins observed in ErFe_2 is retained in the hydride. If this is the case, then the observed decrease in the Er moment and increase in the Fe moment would imply a net decrease in the total moment for the hydride relative to ErFe_2 , since the Er moment dominates. However, the actual moment in hydrides of ErFe_2 is known from magnetization measurements /5,6/ to be substantially larger, not smaller, than in ErFe_2 . This comparison strongly suggests that the Er-Fe coupling does not result in a simple antiparallel arrangement of the spins. This conclusion is, in fact, consistent with recent neutron diffraction results reported in Reference /2/ for $\text{ErFe}_2\text{H}_{3.9}$ which show that the Er-Fe coupling is reduced to the extent that the two spins are almost decoupled. This being the case, the net increase in the moment for the $\text{ErFe}_2\text{H}_{3.65}$ hydride may be related to a more complicated arrangement of the rare earth-3d spins.

For $\text{ErFe}_2\text{H}_{4.12}$, the ^{57}Fe data (Fig.3) show that the magnetic hyperfine field on Fe has been dramatically reduced from that found for $\text{ErFe}_2\text{H}_{3.65}$. In fact, the data from 300 K to 4.2 K shows no magnetic interaction at Fe and consist only of a symmetric doublet with an isomer shift at 300 K of 0.60 ± 0.02 mm/s. The increase in the splitting of the doublet from 0.35 ± 0.02 mm/s to 0.45 ± 0.02 mm/s at 4.2 K cannot be associated with the presence of a

magnetic hyperfine interaction. The only evidence of a magnetic transition is the broadening of the resonances at 1.7 K (Fig. 3c). If a magnetic interaction is assumed responsible for this broadening, then the associated hyperfine field determined from the fit is 10 ± 3 kOe. In an attempt to determine the moment on Fe at 4.2 K, an external magnetic field of 75 kOe was applied. Analysis of the resulting data yields a field of 12 ± 3 kOe at the ^{57}Fe after subtracting the external field.

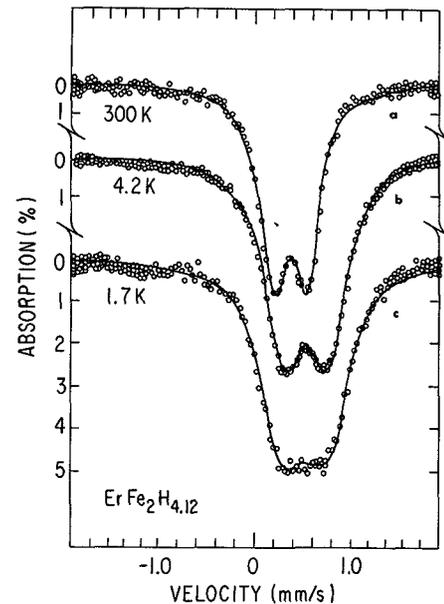


Fig. 3 : ^{57}Fe Mössbauer spectra of $\text{ErFe}_2\text{H}_{4.12}$ at (a) 300 K, (b) 77 K and (c) 4.2 K.

The ^{166}Er spectra measured at 4.2 K (Fig. 2c) and 1.5 K (Fig. 2b) gives a stronger indication of the presence of a magnetic transition in this temperature interval. The 4.2 K data show a complex spectrum in which the differences in relative intensities and widths cannot be described in terms of a single hyperfine field or a distribution of hyperfine fields. Rather, the data indicate slow relaxation of the hyperfine field. Since the detailed nature of the relaxation is not known, the data were fit as a first attempt with a model in which adiabatic relaxation of an electronic Kramer's doublet is assumed. Under these conditions a reasonable fit shown in figure 2c is achieved with a relaxation frequency of 410 ± 30 MHz, a hyperfine field of 5640 ± 100 kG and a quadrupole coupling of -5.1 ± 1.0 mm/s. However, at the lower temperature of 1.5 K, the relaxation lineshape sharpens into a simple magnetic spectrum (Fig. 2b) such as is commonly observed in the spin ordered situation. From these data, a hyperfine

field which is 15% lower than that of $\text{ErFe}_2\text{H}_{3.65}$ was determined.

In comparing the results for the two hydrides, it does not seem likely that the reduction in transition temperature is associated with volume effects as is supposedly the case for $\text{ErFe}_2\text{H}_{3.65}$ /10/. That is, although the structures are different for the two hydrides, the unit cell volumes are not much different. In both ErFe_2 and $\text{ErFe}_2\text{H}_{3.65}$, the magnetic transition is dominated by Fe exchange. On the other hand, if the external magnetic field results are a good indication of the decreased moment on Fe in the hydride with higher hydrogen concentration, then the Fe exchange would be severely reduced in this compound. In fact, it is probable that the magnetic transition may be driven by a dipole coupling of the Er moments rather than direct Fe exchange. Whether or not this is the case will be determined with further experimentation.

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