Mössbauer studies of hydrogen absorption in Dy, DyMn$_2$, DyFe$_2$, DyCo$_2$, and DyNi$_2$

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The Mössbauer effect has been used to study hydrogen absorption in Dy, DyNi$_2$, DyCo$_2$, DyMn$_2$, and DyFe$_2$. Isomer shifts in the hydrides of the intermetallics are similar to those found in the dysprosium hydrides. Measurements at 4.2 K for the hydrides of the intermetallics show the magnetic order to be quite different from that of dysprosium hydride. Both atomically ordered and amorphous hydrides were studied.

I. INTRODUCTION

There is a considerable interest in hydrogen absorption in intermetallic compounds.[1] Many of these compounds reversibly absorb large amounts of hydrogen at normal temperature and pressure. The present investigation uses results from Mössbauer studies at various temperatures between 297 and 4.2 K to determine the effects of hydrogen absorption on intermetallic compounds of the type DyT_2 where T represents the transition metals Ni, Co, Mn, or Fe. In this study we compare spectra of these cubic Laves-phase intermetallics with those of their hydrides. Mössbauer studies provide information complementary to that obtained by the more frequently used methods of x-ray diffraction and pressure-concentration isotherms. X-ray diffraction measures long-range atomic order whereas Mössbauer measurements sense the immediate environment of the absorbing nucleus.

The phase diagrams of the RT_2-H system (R a heavy rare earth) are more complex than that of LaNi$_5$-H and its analogs. Whereas LaNi$_5$ has only one stable saturated hydride, LaNi$_5$H$_x$ with $x \approx 6.7$, the RT_2 cubic Laves-phase materials have a number of stable phases, depending on the temperature, the hydrogen pressure, and the rare-earth and transition-metal components.[2-6] Typically, two hydride phases are found, at values of x (the number of hydrogens per rare earth) ≈ 2 and 3.4. Both these hydrides have the C-15 structure of the unhydrided RT_2 materials, with lattice constants increased by about 5% and 8%, respectively. Another phase, at $x \approx 4$, can be made at higher pressures and is rhombohedral.[4] In addition to these well-characterized phases, we have generated higher hydrides by treating with H$_2$ at 150 atm. These are either amorphous or microcrystalline, as indicated by the absence of diffraction peaks in their x-ray diagrams.

A number of Mössbauer studies of hydrides have been carried out, to study the hydriding process,[7,8] the effects on the rare-earth binding,[9] the effects of repetitive cycling,[10,11] and the effects of changes in electronic structure on the magnetic exchange between the rare-earth and transition-metal sublattices.[5,6] A more extended discussion of recent Mössbauer studies of intermetallic hydrides has recently been given.[11] In this work, we continue to explore a previous finding: that "Mössbauer parameters", especially the isomer shift, of the hydrided intermetallics are like those of the corresponding rare-earth hydrides.[8,9]

II. EXPERIMENTAL DETAILS

Samples of the intermetallics were prepared by arc melting, followed by vacuum annealing. X-ray diffraction patterns showed that they were of a single crystallographic phase with lattice constants shown in Table I. Hydriding of the intermetallics was carried out by exposing the compounds to various pressures up to ~150 atm for 1−24 h. In some cases, the intermetallics were activated by heating to 200 °C to ensure maximum absorption of hydrogen. Absorbers containing 50 mg per cm^2 of intermetallic were prepared from the hydride powder and epoxy. All absorbers were run immediately to prevent desorption of hydrogen. The amount of hydrogen absorbed was determined using apparatus and procedures described in Ref. 11. The hydrogen contents shown in Table I come primarily from the x-ray measurements on the Mössbauer absorbers (which allow us to identify our samples with those studied in Ref. 4) and to a lesser extent from direct volumetric determinations. We assume here that the phase relations established for YFe$_2$,[3] GdFe$_2$,[3] and ErFe$_2$[4] are valid for determining the hydrogen content of the other RT_2 Laves-phase materials we are studying here. Values of $x > 4$ are inferred in view of the high H$_2$ pressures during the charging process. Small amounts of second phase may have been present in some of the samples, but were not visible in the x-ray patterns.

The Dy hydrides were made by exposing small pieces of Dy metal to H$_2$ in a sealed tube. The amount of hydrogen absorbed was determined as a function of temperature by volumetric means, and results are shown in Fig. 1. The data are in reason-

TABLE I. Lattice constants, hydriding condition, and values of the H to RT_2 ratio x for samples studied here.

Material	Initial a_0 (Å)	Hydriding condition	Final a (Å)	a/a_0	x
DyMn$_2$	7.587	1 atm, 295 K	8.270	1.090	3.4
		1 atm, 295 K		~1.09	3.01
		150 atm, 295 K	Amorphous	$\cdots$	>4
DyFe$_2$	7.325	1 atm, 295 K	7.94	1.084	3.4
		150 atm, 295 K	Amorphous		>4
DyCo$_2$	7.175	1 atm, 295 K	7.721	1.076	3.4
		150 atm, 295 K	Amorphous		>4
DyNi$_2$	7.148	1 atm, 295 K	7.551	1.056	2.0
		4 atm, 295 K	7.56		~2.0
		13 atm, 295 K	7.60		~2.0
		150 atm, 295 K	Amorphous		>4
Dy		1 atm,			2.15
		1 atm,			3.15

able agreement with the results of Ref. 12.

The 26-keV γ ray from [161]Dy was used for absorption studies. The source was produced by neutron irradiation of Dy$_{0.5}$Gd$_{0.5}$F$_3$.[13] During experiments the absorber was stationary and the source, at room temperature, was driven by a constant acceleration drive.[14] Spectra were recorded with a multichannel analyzer driven in up-down multiscaler mode and data were analyzed by using a least-squares routine, fitting either one Lorentzian line or two lines as appropriate. For the doublet spectra, the isomer shift was taken as the average of the two line positions. The estimated accuracy of the isomer shift determinations is ±0.1 mm/sec, limited by statistics and the slightly non-Lorentzian line shapes. Isomer shifts are referred to that of DyF$_3$ at 298 K.

III. RESULTS

Figures 2 and 3 show some of the Mössbauer spectra obtained. Values for the room-temperature isomer shift of the starting materials and various hydrides are shown in Fig. 4. The trend in the data is clear—as hydrogen is added to the lattice of these intermetallics, the electron density at the Dy nucleus decreases, with the isomer shift eventually approaching that of the hydrides of dysprosium, ~0.5 mm/sec.[15] This extends results previously obtained

FIG. 1. Stoichiometry of the Dy-H system at 1 atm pressure. The absorption (desorption) of 1 atom of H per Dy (x) between DyH$_{\sim2}$ and DyH$_{\sim3}$ is reversible, but slow.
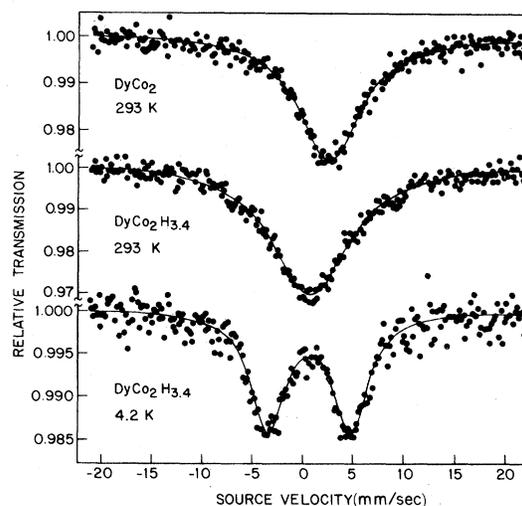
FIG. 2. [161]Dy Mössbauer spectra of DyCo$_2$ and its hydride at various temperatures. The Lorentzian least-squares fit line(s) to the data are shown.
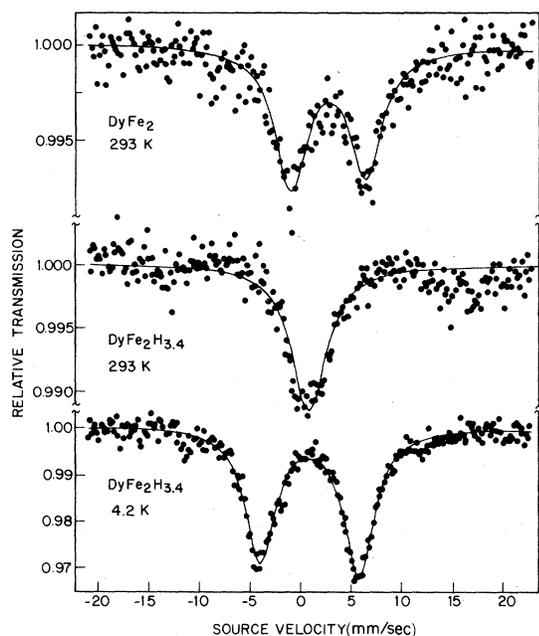
FIG. 3. ^{161}Dy Mössbauer spectra of $DyFe_2$ and its hydride. The doublet is the central part of a widely split magnetic hyperfine spectrum. After hydrogen is added, the magnetic interactions are decreased, and the hyperfine interaction is greatly reduced. The weak lines at $\sim \pm 15$ mm/sec are evidence of a weak residual hyperfine interaction. At low temperature, the magnetic interaction is dominant even in the hydride.
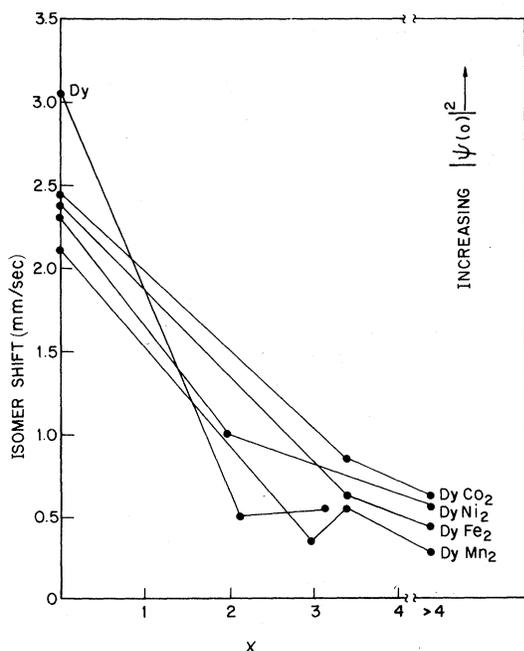
FIG. 4. Isomer shift data established in this work. As hydrogen is added to the lattice, the isomer shifts of the Dy intermetallics approach those of the pure Dy hydrides.

with a number of europium compounds[8-10] and with Gd-doped $LaNi_5$ and $LaCo_5$.[7] The isomer shifts of the saturated hydrides of the Dy intermetallics are not identical, but reflect the isomer shifts of the starting RT_2 compounds. This shows that the hydrides still retain some aspects of their original composition; i.e., we have not simply produced pure DyH_2 or DyH_3 by the hydriding process.

Except for the $DyFe_2$, all of the intermetallics showed spectra consisting of a single line at room temperature. For $DyFe_2$, the previously established magnetic hyperfine splitting is large[5] (~ 50 cm/sec overall) and we show only the central two lines in the spectrum (Fig. 3). In $DyFe_2$, the magnetic hyperfine splitting arises primarily from the polarization of the Dy ion moment by the exchange field from the iron sublattice. At 4 K, spectra of all the intermetallics and hydrided intermetallics were split by the magnetic hyperfine interaction. When $DyFe_2$ is hydrided, the spectrum no longer shows the magnetic hyperfine splitting at room temperature or 78 K. Either a decrease in the iron sublattice magnetization, or a decrease in the effectiveness of the exchange coupling between the iron and Dy sublattices could account for the observed elimination of hyperfine splitting after hydriding. Other experiments[3,5] have shown that the iron sublattice still has most of the magnetization of the unhydrided material. Thus, the coupling between the iron and Dy sublattices must be disrupted by the hydrogen absorption, as was proposed in Ref. 5. The isomer shift data give some hint about the underlying mechanisms. Using the scale of Fig. 4, Dy^{3+} in an ionic material should have an isomer shift near zero[15] (i.e., close to that of the DyF_3 reference standard). Dy metal and other metallic compounds have increased electronic density due to the presence of conduction electrons, especially $6s$ electrons. The unhydrided intermetallics are seen to have electron densities near those of the metal. When the samples absorb hydrogen, however, the $6s$ component of electron density is mostly removed (shown by the decreasing isomer shifts). Thus, there is a decrease in the number of electrons whose polarization carries the exchange, and the exchange should be reduced. This great decrease in conduction-electron density suggests that the band structure is completely changed by the hydriding. Similar arguments were made in Ref. 7. The hyperfine splitting is observed at 4 K even in the hydride because a weak exchange is adequate to produce polarization of the Dy moments at this low temperature. The result we find here is intermediate between those observed in $DyFe_2H_2$,[5] where the exchange is only slightly reduced, and $ErFe_2H_{4.12}$, where the iron sublattice magnetization is eliminated[6] when hydrogen is absorbed.

The spectra of the Dy hydrides were sharp single lines at room temperature. At 4 K the $DyH_{2.15}$ spectrum was similar to that shown in Ref. 16: a sharp

central line, plus side wings arising from super-paramagnetic hyperfine structure. The $DyH_{3.15}$ spectrum at 4 K was a complex line shape more than 10 mm/sec wide, with the broadening probably arising from paramagnetic hyperfine structure. All these results are in full agreement with the recent more detailed report of Friedt et al.[17]

IV. SUMMARY AND CONCLUSIONS

These studies of the isomer shifts of hydrided Laves-phase Dy intermetallics have shown that the addition of hydrogen to the material reduces the electron density. Saturated ternary hydrides show isomer shifts close to those of pure Dy hydrides. These findings have extended the validity of similar results observed for several hydrided Eu intermetallics.

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