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^{57}Fe Mössbauer effect in $ScFe_2$ and $ScFe_2H_2$

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The intermetallic compound $ScFe_2$ is able to absorb large quantities of hydrogen gas without a change in crystal structure. The ternary hydride has the composition $ScFe_2H_2$. Its lattice constants are $a = 5.279$ Å and $c = 8.507$ Å ($C14$ type). By means of magnetic measurements we found that the moment per Fe atom changes from $1.4\mu_B$ to $2.2\mu_B$. Using ^{57}Fe Mössbauer-effect spectroscopy we observed that an increase of the same magnitude (about 60%) also occurs in the hyperfine splitting. On the other hand, only a rather small change in isomer shift was observed to accompany the hydrogen absorption. Arguments are presented that it is difficult to explain the moment change in terms of a simple $3d$-band picture and charge-transfer effects.

I. INTRODUCTION

The changes in magnetic properties observed when H_2 gas is absorbed into $3d$-intermetallic compounds have been the subject of several previous investigations.[1] In the Co compounds H_2 absorption gives rise to a decrease in transition-metal moment. A contrasting behavior is found in the Fe compounds, where H_2 up take is accompanied by an increase in transition-metal moment. Attempts have been made to explain the difference in behavior between the Co and Fe compounds in terms of differences in charge transfer, Co and Fe having electronegativities slightly higher and lower than that of H, respectively.[1] In this investigation we report on the hydrogen absorption in $ScFe_2$ and the resulting changes observed by means of magnetic measurements and Mössbauer spectroscopy. It will be shown that the results obtained in $ScFe_2$ and its hydride can quite suitably be used to test the hypothesis that charge-transfer effects are important in producing the change in $3d$ moment. The reason for this is the following: In $ScFe_2$ as well as in its hydride well-resolved ^{57}Fe Mössbauer-effect spectra are observed from which important quantities such as the changes in isomer shift and in hyperfine splitting can be obtained with sufficient accuracy. Well-resolved Mössbauer spectra in ternary hydrides were reported before in the hydrides $ErFe_2H_{3.65}$ and $DyFe_2H_{1.92}$.[2,3] In these cases, however, the changes in Fe moment are only minor. Considerably larger changes in Fe moment were observed to occur in the hydride of $CeFe_2$ (Ref. 4) and in $Th_7Fe_3H_{30}$,[5] but in these cases conclusive information could not be obtained from Mössbauer spectroscopy. In the hydride of $CeFe_2$ the exact value of the H content has not been determined and extreme line broadening hampered detailed analysis of the spectrum in the magnetically ordered region while the data above the Curie temperature were not quite reliable, owing to H_2 desorption during the measurements. In the case of $Th_7Fe_3H_x$, Mössbauer spectra, reliable in this respect could be obtained in an only partly hydrogenated sample, not showing a change in Fe moment.[6]

II. EXPERIMENTAL

The compound $ScFe_2$ was prepared by arc melting followed by vacuum annealing at 900 °C for several weeks. After this treatment the sample was quenched in water to avoid polymorphic transformation. X-ray diffraction showed the sample to be single phase. The x-ray diagram has been indexed on the basis of the $MgZn_2$ ($C14$) structure type. The lattice constants are given in Table I. The charging of the sample with hydrogen gas and the determination of the hydrogen content were done by the same procedure as described earlier.[7] After charging, the composition of the hydride was found to correspond to approximately 1.92 atoms of H per formula unit. This hydride will be referred to in this paper as $ScFe_2H_2$. The x-ray diagram obtained from this sample is isotypic with that of the uncharged compounds $ScFe_2$, although a substantial expansion of the lattice had occurred. The lattice constants of the hydride are included in Table I. No change in lattice constant and in Mössbauer spectrum was observed after keeping the hydride in air at room temperature for several weeks. This indicates that the hydride $ScFe_2H_2$ is stable against desorption at atmospheric pressures. The study of the sorption isotherms of the system $ScFe_2H_x$ is in progress.

Magnetic measurements on $ScFe_2H_2$ were performed in the range 4.2–300 K by means of an adaptation of the Faraday method. Higher temperatures were avoided since desorption of hydrogen was suspected to occur. From the magnetic isotherm at 4.2 K it could be derived that saturation of the magnetization was reached nearly completely in 18 kOe, the highest field strength applied in this investigation. The corresponding moment per Fe atom equals 2.23 μ_B. This is almost one Bohr magneton higher than in the uncharged compound.

The ^{57}Fe Mössbauer spectra were recorded on a conventional constant-acceleration spectrometer with a ^{57}Co-in-Pd source that was moved with respect to the absorber. Spectra of the uncharged compound and the hydride can be compared in Fig. 1. The spectrum of $ScFe_2$ was fitted with curves of Lorentzian shape by superposing two six-line subspectra occurring with an intensity ratio of 3:1. The effective hyperfine field (H_{hf}), the isomer shift (IS), and the quadrupole splitting (QS) pertaining to these subspectra are listed in Table I. There are two crystallographic nonequivalent Fe sites ($6h$ and $2a$ in Wyckoff notation) in $C14$-type $ScFe_2$ occurring in the ratio 3:1. Dissimilar electron change distribution at these two sites may give rise to two subspectra. Moreover, if the preferred direction of magnetization is along the hexagonal (c) axis these two Fe sites become also magnetically inequivalent. The Fe nuclei of these two sites then experience different dipolar fields from the surrounding moments[8] and there is also a difference in the angle between the axis of the axially symmetric electric field gradient (EFG) tensor and the hyperfine field, leading to different quadrupolar splittings. From the experimental spectrum of $ScFe_2H_2$ in Fig. 1 it can readily be seen that in the hydride at least three subspectra are present. In or-

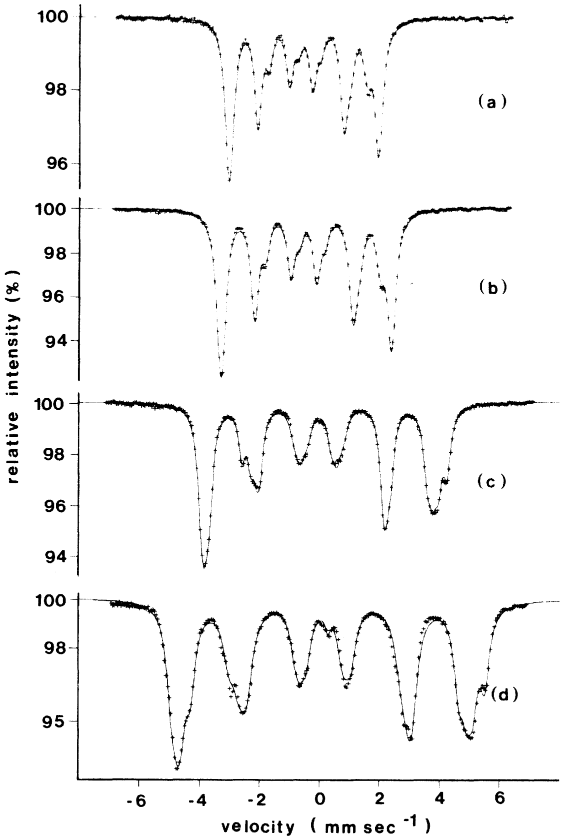

FIG. 1. ^{57}Fe Mössbauer spectra of $ScFe_2$ at (a) 300 K and (b) 78 K and $ScFe_2H_2$ at (c) 300 K and (d) 78 K. The experimental values are denoted by the symbol + and the drawn lines give the least-squares-fitted results, described in text.

TABLE I. Lattice constants, magnetization, hyperfine field (H_{hf}), isomer shift [IS, with respect to Co(Pd)], and quadrupole splitting (QS) or quadrupole coupling constant ($\frac{1}{2}e^2qQ$) of ^{57}Fe in $ScFe_2$ and $ScFe_2H_2$. The standard deviations in the values quoted are at most two points in the least significant digit, except for H_{hf} in $ScFe_2H_2$ where they may be larger.

Compound	Temperature (K)	Lattice constants (Å)	M (μ_B/Fe)	H_{hf} (kOe)	IS (mm sec^{-1})	QS (mm sec^{-1})	$\frac{1}{2}e^2qQ$ (mm sec^{-1})
$ScFe_2$	300	$a = 4.965$		153 } 151	−0.37 } −0.37	· · ·	0.38
		$c = 8.125$		145	−0.35		
	78			174 } 172	−0.26 } −0.24	· · ·	0.26
				167	−0.19		
	4		1.37[a]–1.45[b]				
$ScFe_2H_2$	300	$a = 5.279$		254 } 239	0.0 } 0.0	0.0	· · ·
		$c = 8.507$		243	0.0	0.0	· · ·
				234	0.1	−0.1	· · ·
				225	0.0	0.0	· · ·
	78			323 } 300	0.2 } 0.2	0.1	· · ·
				301	0.3	0.0	· · ·
				291	0.0	0.0	· · ·
				285	0.3	0.0	· · ·
	4		2.23				

[a] Reference 11.

[b] Reference 12.

der to interpret the $ScFe_2H_2$ spectra we tried several refinement schemes based on sextets composed of Lorentzians. These included refinements with a single parameter for IS or two parameters for QS. None of these proved to be satisfactory. It was found that the best results were arrived at by assuming four independent sextets of equal intensity. In addition, the fit comprised the presence of a small doublet, having 1.5% of the total intensity. The presence of this small doublet shows that a tiny fraction of the iron atoms does not experience a magnetic hyperfine field while the quadrupolar splitting of 1 mm/sec shows that they no longer occupy sites of cubic symmetry. Presumably this is the result of a deterioration of part (1.5%) of the material during hydrogenation. In order to obtain meaningful values of the sextet variables it was found necessary to refine on the hyperfine parameters IS, QS, and H_{hf}, obtained by means of a linear transformation of the peak centroids, rather than on the peak positions themselves. The suggestion to refine on the hyperfine parameters in this way is due to Flinn,[9] and the necessary transformations were implemented in von Meerwall's least-squares program.[10] The results are shown in Fig. 1. The corresponding sextet parameters are listed in Table I. In order to make a comparison between the results obtained on $ScFe_2$ and $ScFe_2H_2$ more feasible we have included in Table I the weighted mean of the values of H_{hf} and IS.

III. DISCUSSION

Reducing the temperature from room temperature to 78 K in $ScFe_2$ leads to an increase in H_{hf} of 14% and a decrease in IS and QS. The peaks hardly broaden (0.32 $mm\,sec^{-1}$ at 78 K vs 0.30 $mm\,sec^{-1}$ at 300 K). No new subspectra appear implying an unaltered site occupancy. This indicates that the preferred direction of magnetization does not change with temperature. Lowering the temperature from 78 to 8 K yields the same hyperfine parameter values within the least-squares estimated standard deviations, compared with those at 78 K. This is to be expected in a ferromagnet having a high Curie temperature ($T_C = 542$ K).[11] For $ScFe_2H_2$ an increase in H_{hf} of 25% is found upon cooling from room temperature to 78 K. It is accompanied by an increase in IS, whereas QS remains practically constant. At 8 K the spectrum parameter values are again not different from those at 78 K, except for slightly (2%) larger values of H_{hf}. At room temperature the lines in $ScFe_2H_2$ have the same width as in $ScFe_2$ [full width at half maximum (FWHM) ≈ 0.30 $mm\,sec^{-1}$], but at 78 and 8 K the lines in $ScFe_2H_2$ are slightly broadened (FWHM ≈ 0.42 $mm\,sec^{-1}$).

The relatively larger increase in H_{hf} upon cooling from room temperature to 78 K observed in the hydride when compared to uncharged $ScFe_2$ can be regarded as an indication that the Curie temperature in the former is lower than in the latter. Such a decrease in Curie temperature upon H_2 up take has also been observed in, for instance, YFe_2.[1]

From the fact that the absorption of hydrogen in $ScFe_2$ is not accompanied by line broadening it can be inferred that the majority of H atoms occupy highly ordered positions in the hydride on a time scale much longer or shorter than the mean life time of the excited state of the ^{57}Fe nucleus (1.4×10^{-7} sec). In the *C*14 crystal structure there are a number of different interstitial positions available to the H atoms.[13] If the interstitial positions are occupied with different occupancy numbers, as is the case in the isotypic compound $ZrMn_2$, the equivalence of the 6*h* Fe sites will be destroyed.[13] For these reasons the spectrum of the hydride will be composed of at least four subspectra. This is in agreement with our analysis in terms of four subspectra. Since it is well known that the hydrogen occupancy numbers change with temperature (see for instance various contributions in Ref. 14) an irregular temperature dependence of IS and QS is expected. No substantial broadening of the spectra was reported by Viccaro *et al.*,[2,3] also in the hydrides of $ErFe_2$ and $DyFe_2$. The change in isomer shift by about 0.4 $mm\,sec^{-1}$ towards more positive direction observed by us in the hydride $ScFe_2H_2$ agrees well with their results. A novel feature of the present result is the rather large increase in hyperfine splitting (about 60%) upon hydrogen absorption. In general, the hyperfine field can be decomposed into core polarization (H_C), a contribution due to self-polarization of the conduction electrons (H_S) and the transferred hyperfine field (H_N). Since there may be large cancellations of the various contributions, a straightforward comparison between the magnitude of the hyperfine field and the Fe moment is difficult. It can be inferred from the data listed in Table I that the observed increase of H_{hf} is of the same magnitude as the increase in Fe moment (also about 60%). This result suggests that the relative magnitude (and sign) of the various contributions to H_{hf} mentioned above remain almost unchanged in going from $ScFe_2$ to $ScFe_2H_2$.

It has already been mentioned that increases in Fe moment upon H_2 absorption in intermetallic compounds were currently interpreted in terms of a decrease in occupancy of 3*d* band states due to electron transfer to the absorbed H atoms.[1,5] Since in the present investigation we have been able to observe in the same compound an appreciable change in moment and hyperfine field splitting together with a change in isomer shift, we expect both changes to reflect any alterations in 3*d* band occupation in a consistent way.

It is reasonable to assume that the ferromagnetism in $ScFe_2$ and $ScFe_2H_2$ is of the same kind as in Fe metal. In this so-called weak ferromagnetism the majority spin subband as well as the minority spin subband are partially depleted.[15] Schematically such a situation could be represented as in Fig. 2. Since the part above the minimum in the density of states $N(E)$ in each subband is usually considered to contain about 2.5 $3d$ electrons,[15] a likely position of the Fermi level in $ScFe_2$ would be as indicated by the full vertical line in Fig. 2, leaving a difference in occupation between the two subbands equal to $1.4/\mu_B$, which corresponds to the moment observed. It will be clear that an explanation of the increase in Fe moment ($\Delta M = 0.8/\mu_B/\mathrm{Fe}$) based on a further depletion of the $3d$ band would require about 0.8 electrons if only one subband would be partially occupied by presumably much more than one $3d$ electron per Fe if both subbands were partially occupied. This latter case could schematically be represented by shifting E_F downwards in Fig. 2. Such a decrease in $3d$ band occupation should be easily observable by means of a corresponding change in ^{57}Fe isomer shift. For electron acceptance one expects a change of IS of about -1 mm sec^{-1} per Fe per added s electron, whereas a change in opposite (positive) direction of about the same size is expected per added $3d$ electron.[16] It can be inferred from the data listed in Table I that the change δIS observed upon H_2 absorption is about $+0.4$ mm sec^{-1}. This shift, taken at face value, would correspond to an increase rather than a decrease in $3d$ electron character.

Since the H_2 absorption is accompanied by a strong volume increase, one might ask whether it is necessary to correct IS for this volume effect. Using $\delta \mathrm{IS}/\delta \ln V \approx -1$ mm sec^{-1}, given in the review of Kalvius *et al.*[17] together with the volume increase observed, this volume correction term would be equal to -0.3 mm sec^{-1}. This has to be regarded as an upper limit since a major portion of the extra volume is needed to accommodate the added H atoms. The change in IS observed ($+0.4$ mm sec^{-1}), taken with or without volume correction, is too small to account for a decrease in $3d$ character corresponding to more than one $3d$ electron and still has the wrong sign.

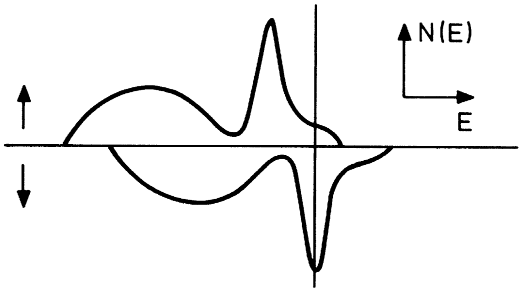

FIG. 2. Schematic representation of the density of $3d$ band states $N(E)$ in Fe compounds as a function of energy. The Fermi level is represented by a vertical line (see text).

The smallness of δIS in fact suggests that electron transfer is either very small or is composed of about equal amounts of $3d$ and s electrons. (The same net effect would of course be reached by an interatomic transfer of only s electrons followed by an intra-atomic $s \rightarrow d$ transfer.) Keeping in mind that a decrease of more than one $3d$ electron is required to account for the moment change this means that the total number of s and $3d$ electrons transferred is more than two per Fe atom (or per H atom in $ScFe_2H_2$). This is an unreasonably high value and by far surpasses estimates of the redistribution of charge due to the introduction of H atoms based on electronegativity differences between the three composing elements in $ScFe_2H_2$.[18] It can be concluded therefore that the observed change in isomer shift upon H_2 absorption in $ScFe_2$ is inconsistent with an explanation of the Fe moment increase in terms of charge transfer. The smallness of the change in IS furthermore indicates that there is no major shift in energy of the relative positions of the s and d bands that would lead to intra-atomic s-d transfer.

Alternatively one might try to understand the changes in Fe moment in terms of changes of the $3d$ band exchange splitting.[19,20] When Sc is combined with Fe the d and s,p electrons of the Sc atoms will hybridize with the $3d$ electrons of the Fe atoms. This hybridization leads to a reduction in the effective intra-atomic Coulomb repulsion between the $3d$ electrons and hence, to a reduction in $3d$ band exchange splitting in $ScFe_2$ compared to that in Fe metal. The introduction of H atoms, which in $ScFe_2H_2$ are expected to tend to be located as close to the hydrogen attracting Sc atoms as possible, leads to a substantial loss in contact between the Sc atoms and the Fe atoms. This can more or less undo the reduction in exchange splitting. In $ScFe_2H_2$ the situation is particularly favorable since the Fe moments in this hydride ($2.23/\mu_B/\mathrm{Fe}$) take virtually the same magnitude as in pure Fe metal ($2.22/\mu_B/\mathrm{Fe}$). A similar observation was made before in $CeFe_2$ ($1.24/\mu_B/\mathrm{Fe}$) where the Fe moment after charging with H_2 also became as high as in pure Fe.[4] However, this evidence was considered to be somewhat less convincing in view of the microstructural changes that accompanied the H_2 absorption in $CeFe_2$. In other Fe compounds charged with H_2 the moment increase is less drastic.[1-3] Possibly the favorable effect of the reduction in contact between the rare-earth (R) and Fe atoms is overshadowed in these hydrides by the unfavorable effect of hybridization of the Fe $3d$ electrons with the hydrogen s electrons.[19]

The question might be raised why intermetallic compounds of Co invariably[19] suffer a decrease in transition-metal moment upon hydrogen absorption. Here one has to consider the experimental evidence available for the uncharged compounds which shows that the presence of a moment on the Co atoms depends rather critically on the amount of contact with other Co atoms. For instance, when Co atoms are incorporated into the Pauli paramagnetic host $ThNi_5$ they develop a moment only after at least 65 at.% of the Ni have been replaced by Co.[21] Only a few at.% are needed in the case of replacement of Ni by Fe.[22] Further evidence that the Fe atoms can sustain a magnetic moment without the need to have nearest-neighbor Fe atom contacts comes from studies of the ^{57}Fe Mössbauer effect in Fe-doped nonmagnetic compounds like YIr_2 and YCo_2.[23] One may state therefore that the Fe moments apparently are more localized than the Co moments in this class of intermetallics. The Fe moments are therefore capable to benefit from the reduced R-$3d$ contacts without being much affected by the loss in mutual contact between the $3d$ atoms upon H_2 up take, whereas this loss leads to a moment reduction in the case of the Co compounds. Additional support for this explanation is offered by the results of a study of the magnetic properties of Mn compounds and their hydrides. These results show that the tendency of the Mn moments to be localized is even more pronounced than in the Fe compounds.[1]

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