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ABSTRACT

The ternary hydride phases, $DyFe_3H_x$ with x = 1.7, 2.5, and 4.2 all retain the $PuNi_3$ rhombohedral structure of $DyFe_3$ with a maximum volume expansion of 18% for $DyFe_3H_{4.2}$. All phases show a preferential expansion parallel to the c_o axis. From bulk magnetization measurements, the Dy-Fe spin compensation temperature is found to decrease linearly from 545 K for $DyFe_3$ to 150 K for $DyFe_3H_{4.2}$ with increasing volume of the hydride phases. The ^{161}Dy Mössbauer results for the two Dy sites in the structure indicate a slight reduction occurs in free-ion moment found for $DyFe_3$ in all hydride phases. In addition, the ^{57}Fe Mössbauer data show that the average Fe moment for the five inequivelent Fe sites increases with hydrogen concentration up to x = 2.5. These trends in the local moments indicate that variation in the compensation temperature, which is related to the Dy-Fe exchange, is associated with lattice expansion effects due to the presence of hydrogen.

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INTRODUCTION

The absorption of hydrogen by the RFe_3 intermetallic compounds where R is a rare-earth can result in changes in their magnetic and electronic properties [1,2]. In many cases, the ternary hydride phases are expanded versions of the parent intermetallic with hydrogen occupying interstitial sites in the structure [2-4]. As a result, modifications in the host's properties of the intermetallic compound can be thought of as originating from a volume expansion effect coupled with a direct perturbation by hydrogen of the electronic and magnetic interactions. In RFe_3 compounds where R is a heavy rare earth element, the Fe-Fe ferromagnetic coupling is stronger than the R-Fe antiferromagnetic coupling. As a result, the compound is ferrimagnetic [5]. In view of this, the extent to which the presence of hydrogen in the lattice affects the magnetic properties will depend on how it alters the magnitude of these local moments and their couplings.

In the present work, the results of an investigation of the ternary hydrides of $DyFe_3$ using X-ray diffraction, ^{161}Dy and ^{57}Fe Mössbauer effect and bulk magnetization techniques are presented. From the Mössbauer measurements, information concerning the local Dy and Fe magnetic moments can be extracted. The coupling of these moments gives rise to the bulk moment measured with the magnetization technique. The results obtained in the present study are compared to those from ^{166}Er and ^{57}Fe Mössbauer effect experiments in hydrides of $ErFe_3$[2] and magnetization measurements in $DyFe_3H_3$[1].

EXPERIMENTAL

Stoichiometric quantities of Fe (99.99%) and Dy (99.9%) were arc melted under high purity Argon gas (99.999%) passed through a hot Ti getter. The buttons were turned and remelted several times to insure a homogeneous mix

and were vacuum annealed at 1000°C for two weeks. The X-ray diffraction patterns taken with a Debye-Scherrer camera and Cu K_α radiation showed reflections characteristic of the $PuNi_3$ structure.

The hydrides were made by exposing the material to H_2 gas (99.999%) in a system of known volume. The hydride phases were then obtained by desorbing from the highest absorption point on the pressure-composition isotherm. In order to prevent further desorption of hydorgen, the samples were poisoned with SO_2 gas.

The Mössbauer experiments were carried out between 4.2 K and 300 K. A ^{57}Co in Rh source was used for the ^{57}Fe resonance (14.4 keV) and a $Gd_{0.5}Dy_{0.5}F_3$ source for the ^{161}Dy resonance (25.7 keV). Both sources were at ambient temperatures. Magnetization data were obtained between 4.2 K and 400 K using a Faraday-type balance.

RESULTS AND DISCUSSION

The pressure-composition isotherms for hydrogen desorption for $DyFe_3$ have been previously measured [4]. The data at 20°C are similar to those for the $ErFe_3H_x$ hydride [2] and show two plateaus in H_2 pressure followed by a monotonic increase of absorbed hydrogen with pressure up to the maximum composition x = 4.2. The first plateau terminates at approximately x = 1.7 and the second at x = 2.5.

The X-ray diffraction patterns for hydride phases with three compositions (x = 1.7, x = 2.5, and x = 4.2) showed reflections which were consistent with the rhombohedral $PuNi_3$ structure of the parent intermetallic $DyFe_3$. The lattice parameters relative to the hexagonal basis of the rhombohedral lattice are given in Table 1. As can be seen from the results, the unit cell volume increases with increasing hydrogen content. In addition, there is a

preferential expansion parallel to the c_o axis in all phases. These data are similar to those for $ErFe_3H_x$ [2] and indicate that the same sites may be filled by hydrogen in both intermetallics.

^{161}Dy Mössbauer effect spectra for $DyFe_3$ and its hydride phases all show well resolved magnetic hyperfine splittings at 4.2 K associated with the interaction of the ordered electronic moment on Dy with the $5/2^+$ ground and $5/2^+$ excited nuclear states of ^{161}Dy. For the situation where ordered magnetism exists, this interaction is equivalent to an effective magnetic hyperfine field (H_n) at the nucleus which is proportional to the local Dy magnetic moment [6]. When the magnetic exchange dominates the crystalline electric-field (CEF) interaction, the splitting of the J = 15/2 angular momentum manifold results in a $|J_z| = 15/2$ ground state. The Dy moment in this case has the free-ion value of 10 μ_B. If the CEF interaction is large enough, the mixing of the J_z states produces a moment less that the free-ion value.

In the $PuNi_3$ structure, Dy occupies two inequivalent crystallographic sites, both with axial symmetry and in a 2:1 population ratio. The spectra were fitted with a superposition of two spectra each characterized by different hyperfine parameters and constrained to the 2:1 intensity ratio. For the case of $DyFe_3$, the measured hyperfine field values of 6440 $\pm$ 50 kG and 6330 $\pm$ 50 kG are both larger than the free-ion value of 6200 kG expected for a $|J_z| = 15/2$ ground state [6]. The increase in H_n is associated with the polarization of the conduction electrons by the Fe moments [6] and is common in intermetallics where the transition metal carries a local moment. In addition, the quadrupole coupling constant e^2qQ for each site was 2800 $\pm$ 300 MHz and 2600 $\pm$ 300 MHz,

respectively. The values are again close to that expected for the free-ion (2520 MHz) [6]. From these results, we conclude that in $DyFe_3$ the magnetic exchange dominates over any CEF interaction that may be present.

The analyses of the ^{161}Dy Mössbauer data for the three hydride phases of $DyFe_3$ show a monotonic decrease in the values of H_n for each of the two Dy sites as the hydrogen content increases. From Fig. 1, we see that even for $DyFe_3H_{4.2}$ where the largest reduction occurs, the hyperfine fields are only slightly smaller than expected for a $|J_z| = 15/2$ ground state. From these results we deduce that the magnetic exchange still dominates the CEF interaction in all of the hydride phases. Supporting this is the absence of any large reductions in the e^2qQ values which are also close to the free-ion value in each hydride phase.

These results contrast those obtained for $ErFe_3H_x$ [2] in which the decrease in the Er moment in the higher order hydride phases was more drastic than observed here for $DyFe_3H_x$. It should be noted that the R-Fe magnetic exchange is more than a factor of two larger in $DyFe_3$ than in $ErFe_3$ [5]. The presence of a stronger magnetic exchange in $DyFe_3$ could account for the dominance of this interaction over the CEF interaction in the $DyFe_3H_x$ phases.

A second aspect of the ^{161}Dy data for the hydrides is the decrease observed in isomer shift relative to $DyFe_3$. Approximately the same relative shift of -2.0 ± 0.2 mm/s (averaged over the two Dy sites) is found in all three hydride phases. For ^{161}Dy, this decrease is equivalent to an overall decrease in the s electronic density at the nucleus. A likely source of this reduction is from the Dy 5d-6s shells which, in the case of $DyFe_3$, are part

of the conduction band for this intermetallic. In DyH_2 [7,8] where similar effects have been observed, an overall negative charge buildup around hydrogen is postulated. This occurs at the expense of the 5d-6s conduction band resulting in a net decrease of 6s density at the Dy site. Evidence of a decrease in the 6s density has been also observed in hydrides of the Laves phase intermetallic compounds DyT_2 (T = Ni, Co, Mn, Fe) [8], indicating that similar perturbations of the conduction band by hydrogen occur in these materials. The same mechanism would be consistent with our observations for $DyFe_3H_x$.

The ^{57}Fe Mössbauer spectra for $DyFe_3$ and the three ternary hydride phases at 4.2 K are shown in Fig. 2. In the parent intermetallic, Fe occupies three different crystallographic sites in the structure. In addition, the direction of the Fe moment is not parallel to the c_o axis, [9] which results in five magnetically inequivalent Fe sites. As can be seen, these five sites cannot be resolved in the spectrum for $DyFe_3$. An acceptable fit to the data can be achieved, however, by imposing constraints on the hyperfine parameters consistent with the symmetry requirements at each Fe site [9].

For the hydride phases, the situation is more complex due to distribution of hyperfine parameters producing broader resonances in these materials. The fit to the data shown in Fig. 2, were achieved using a superposition of five spectra with amplitudes constrained to the ratios expected for the five Fe sites in the $DyFe_3$ structure. The spectrum for the hydride with the highest composition could not be fit in this way. In Fig. 3, the H_n values obtained from the fits for the five components spectra are plotted for $DyFe_3$ and the two hydride phases with x = 1.7 and x = 2.5. As can be seen, the average H_n at 4.2 K is largest in the phase with the larger hydrogen

content. The average H_n estimated for the phase $DyFe_3H_{4.2}$ would appear from Fig. 2 to be smaller than measured in the previous phases. As was the case for $ErFe_3H_x$ [2], we assume for $DyFe_3H_x$ an approximately linear scaling between the ^{57}Fe hyperfine field and Fe magnetic moment. The results then show an increase in the average low temperature Fe moment with increasing hydrogen content up to x = 2.5 followed by a small decrease in this moment in the x = 4.2 phase.

This correlation is similar to that obtained for the $ErFe_3H_x$ [2]. In both cases, the initial increase in H_n in the lower order hydride phase could be associated with either a localization of the 3d moment due to the expansion in the lattice or to actual perturbations of the 4s and/or 3d density in the conduction band. Which of the two effects are prevalent cannot be determined from these data, alone. Consistent with either effect, the fitting showed an overall increase in the average isomer shift relative to $DyFe_3$ as a function of hydrogen concentration. For ^{57}Fe this shift represents a decrease in the overall s electronic density, which could result from an increase in the 3d density and/or decrease in the 4s density.

Although a detailed temperature dependence of the ^{57}Fe spectra was not carried out, measurements at 77 K and 300 K for the hydrides with x = 1.7 and x = 2.5, showed only slight variation of the hyperfine field over this temperature interval. This would indicate that the magnetic transition temperatures are substantially higher than 300 K for both phases. For the highest order phase $DyFe_3H_{4.2}$, the spectrum at 300 K consisted of a broad resonance with unresolved structure. This measurement puts an upper limit on the average hyperfine field of approximately 50 kG at this temperature. This is smaller by nearly a factor of five than the average moments in either $DyFe_3$

or $DyFe_3H_x$ with x = 1.7 and x = 2.5 at 300 K. A much stronger temperature dependence of the hyperfine field in $DyFe_2H_{4.2}$ implied by this result indicates a significantly lower magnetic transition temperature in this phase.

The results for the magnetization measurements from 4.2 K to 400 K for the $DyFe_3H_x$ hydrides are shown in Fig. 4. The values of the magnetization are those obtained in a 14 kG external field and do not necessarily correspond to the actual saturated moment of the hydride in question due to the inherently high anisotropy in these systems. The maximum moment in all three hydride phases at 4.2 K is significantly smaller than that of the parent intermetallic $DyFe_3$ extrapolated to the same external field values.

In addition, the data for each of the hydride phases show a minimum in the magnetization curve as a function of temperature. This minimum, as can be seen, shifts to lower temperatures as the concentration of hydrogen increases. A similar shift has been observed for $DyFe_3H_3$ [4]. For $DyFe_3$, the minimum occurs at 545 K (not shown in Fig. 4), and corresponds to the temperature at which compensation between the Dy and Fe local magnetic moments occurs. As is known [5] these moments are coupled antiferromagnetically with the Dy moment dominating at temperatures below the compensation temperature (T_{comp}). In the molecular field approximation, T_{comp} is directly proportional to the product of Dy-Fe exchange parameter and the factor $g(g + 1)\ J(J + 1)$ where g is the Lande factor and J is the total spin of the R atom. If such an approximation is assumed for the hydride phases, then the data imply that the reduction in T_{comp} is due to a decrease in either or both of the above factors.

The Mössbauer results show, however, that no drastic reductions in the local moments in either of the metal atoms occur in any of the hydride

phases. From this, we deduce that the Dy-Fe exchange parameter decreases as a result of increasing hydrogen content in the lattice. More significant is the fact that the reduction in T_{comp} is linearly dependent on the volume of a given hydride phase (Fig. 5). (The volume change itself is, however, not linear with hydrogen concentration). This correlation is highly suggestive that the weakening of the Dy-Fe exchange is associated primarily with lattice expansion. Such an effect has been previously noted in a hydride of YFe_2 [10] for which both the change in magnetic transition temperature and Fe moment could be described from volume expansion considerations only. The data for $DyFe_3H_x$ presented here offer convincing evidence that the linear correlation between the volume and strength of the Dy-Fe exchange appears valid over a large hydrogen concentration interval.

TABLE 1. The lattice constants for the different hydride phases of $DyFe_3$. Errors are $\pm$ 0.05Å. V is the unit cell volume of a given phase and V_o is the volume of $DyFe_3$ unit cell.

x	0	1.7	2.5	4.2
a_o	5.12	5.25	5.34	5.36
c_o	24.48	25.54	25.79	26.40
c_o/a_o	4.77	4.86	4.83	4.93
V/V_o	1	1.096	1.146	1.18

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FIGURE CAPTIONS

1. Variation of the ^{161}Dy magnetic hyperfine fields vs hydrogen concentration for the rare earth sites in the R3m structure.
2. ^{57}Fe hyperfine spectra at 4.2K for the $DyFe_3H_x$. Solid lines are fits to the data assuming five magnetic sites.
3. Variation of the ^{57}Fe hyperfine fields for the five sites vs hydrogen concentration. The sites are identified as b, c, h_1, h_2, and h_3 according to the notation of Ref. 9.
4. Magnetization vs temperature at 14.5 kG. The data for $DyFe_3$ (21 kG) are from Ref. 1.
5. Variation of the spin compensation temperature T_{comp} vs volume expansion for the $DyFe_3H_x$.

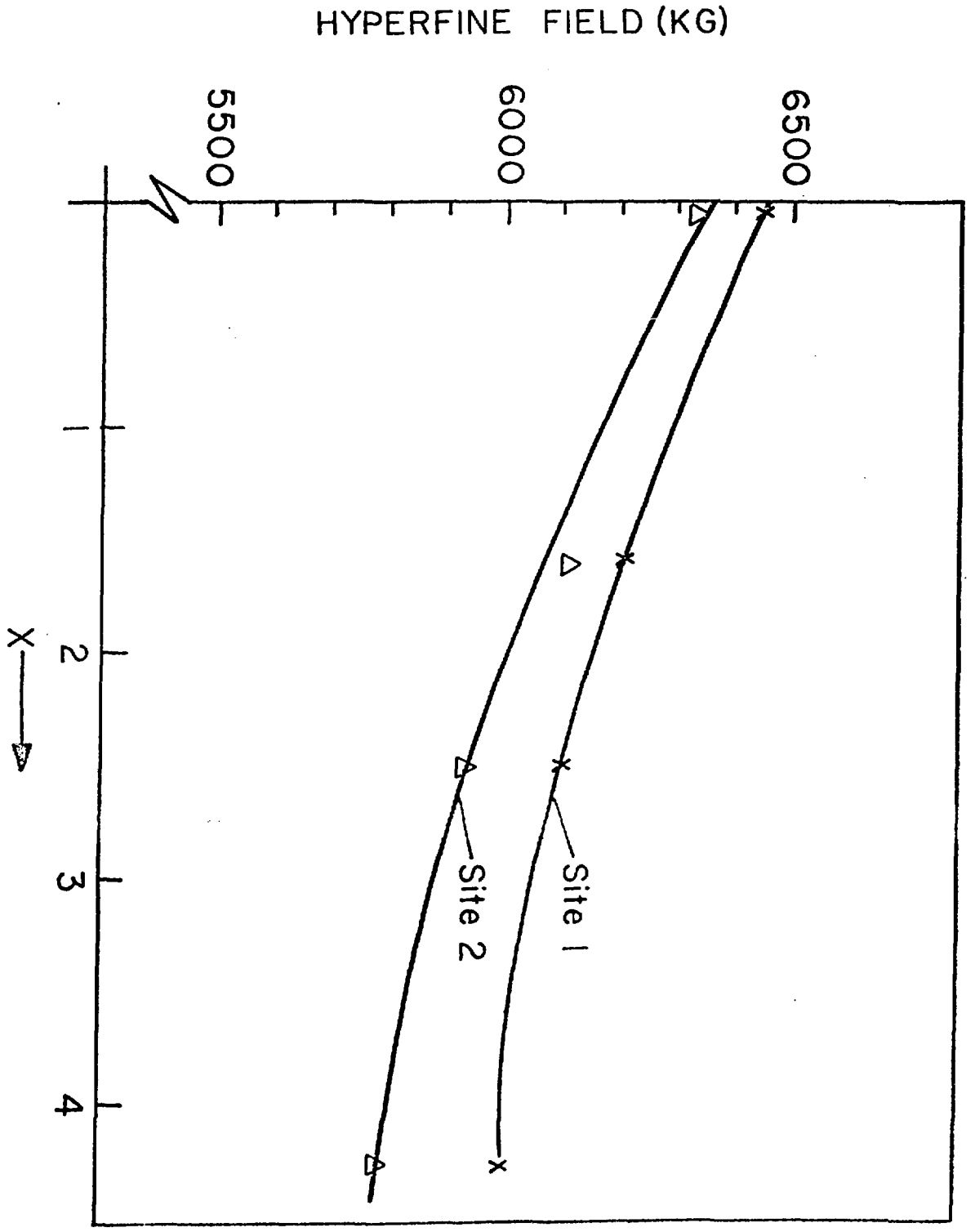
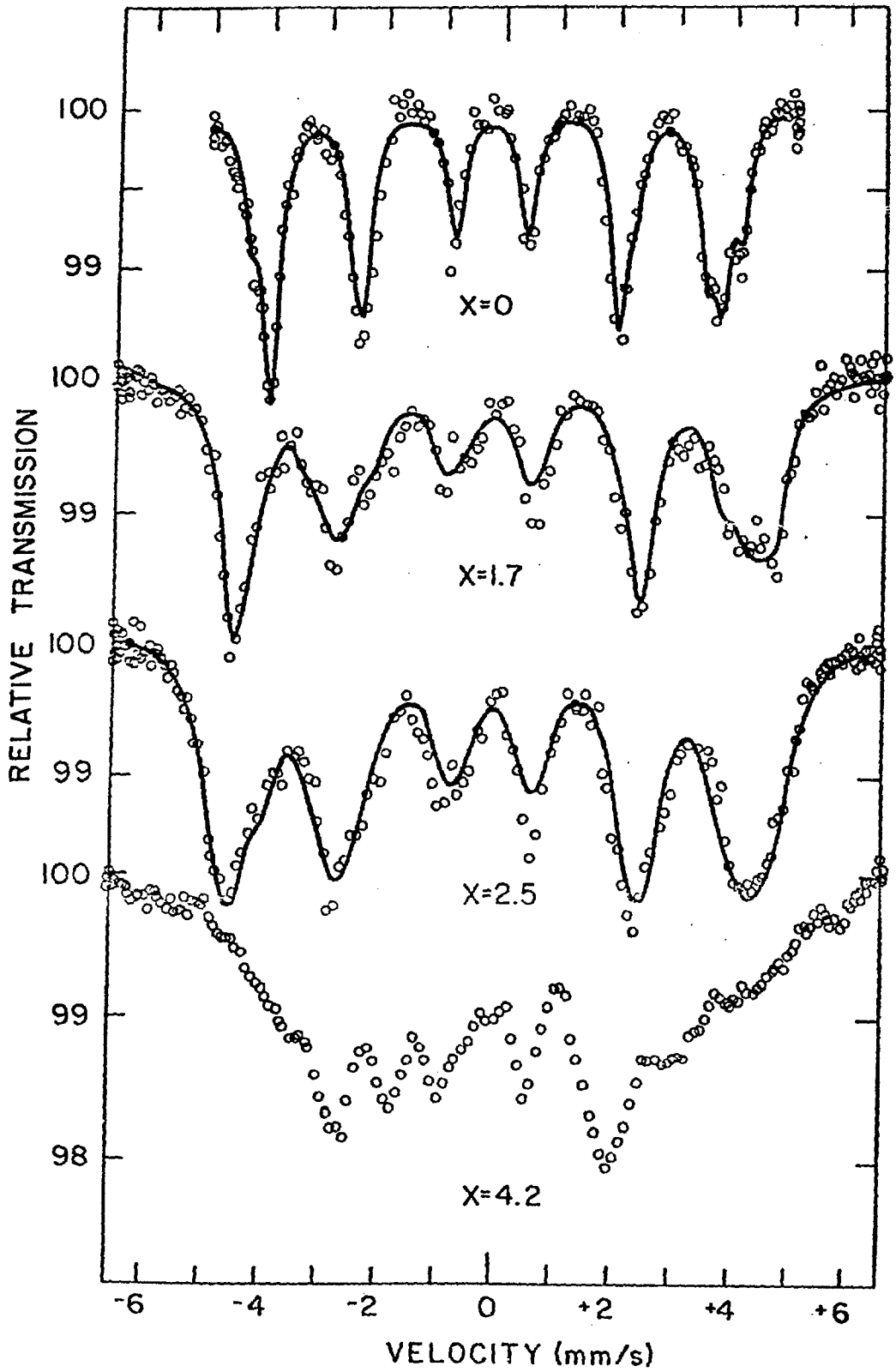


Fig 1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100
99
X=1.7
100
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X=2.5
100
99
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-4
-2
0
+2
+4
+6
VELOCITY (mm/s)

Fig. 2

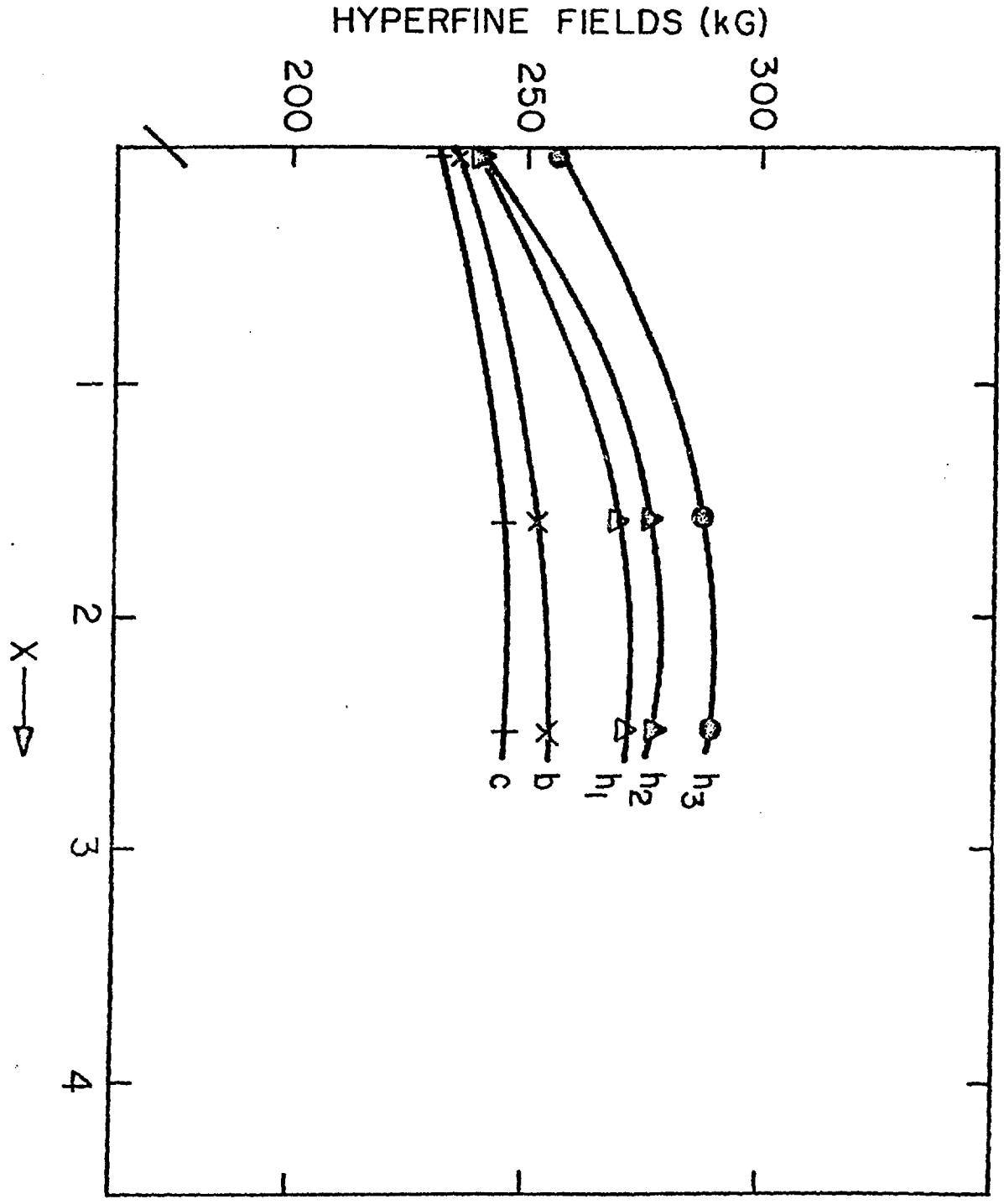
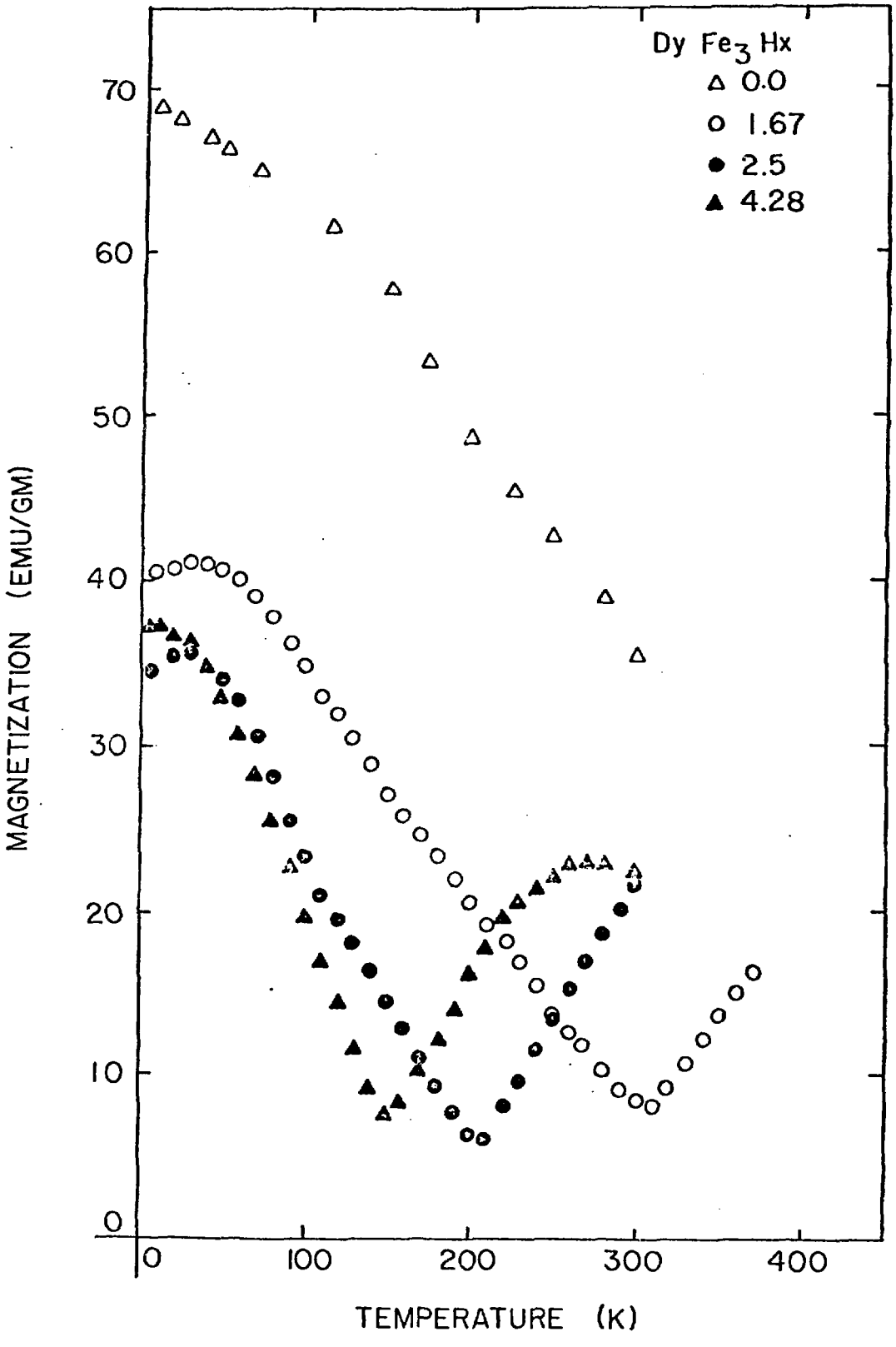


Fig 3


Dy Fe3 Hx
Δ 0.0
o 1.67
● 2.5
▲ 4.28
MAGNETIZATION (EMU/GM)
TEMPERATURE (K)
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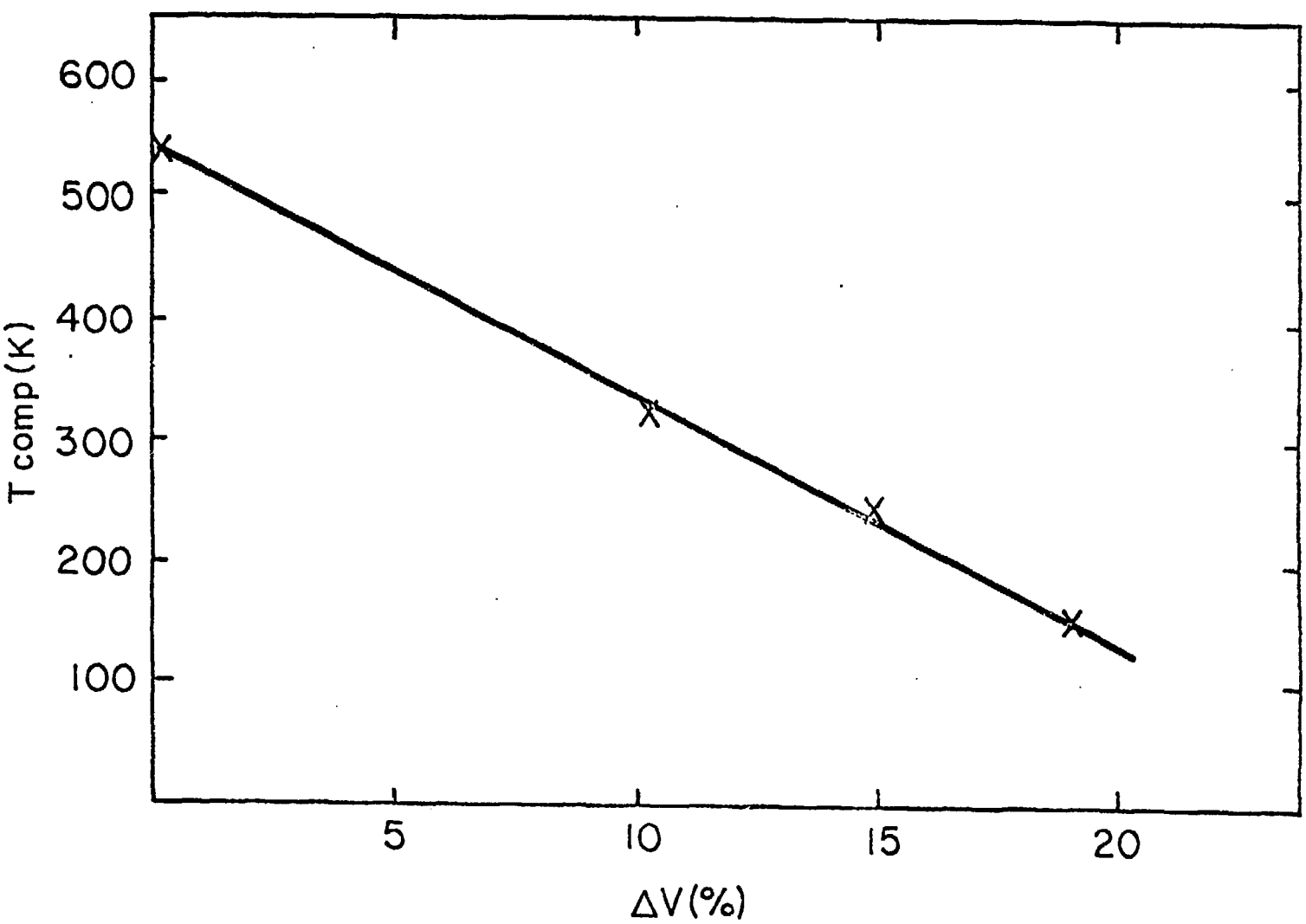
10
20
30
40
50
60
70
0
100
200
300
400

Fig 4


600
500
400
300
200
100
T comp (K)
5
10
15
20
ΔV (%)