

CBPF-NF-002/90

^{89}Y NMR MEASUREMENTS IN $(\text{Dy}_x\text{Y}_{1-x})\text{Fe}_2$ COMPOUNDS*

by

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*To be published in J. Appl. Phys.

ABSTRACT

In a previous work, ^{89}Y measurements at 4.2 K in $(\text{R}_x\text{Y}_{1-x})\text{Fe}_2$ compounds, with R = Tb and Ho and $0.05 \leq x \leq 0.20$, have shown broad NMR spectra, due to transferred hyperfine interactions. ^{89}Y NMR signals could not be observed with R = Dy in the same composition range. In the present work, compounds were prepared with dysprosium substitution in the concentration range $0.005 \leq x \leq 0.02$ to investigate the origin of this anomaly. Compared to the pure YFe_2 compound, the observed NMR spectra are broadened and show a shift towards higher frequencies. With increasing Dy concentration, the NMR signals fall very rapidly. Measurement of relaxation times shows that the decrease in the signals cannot be attributed to a sharp increase in the nuclear relaxation rate due to the presence of Dy atoms in the matrix. Magnetization measurements at 4.2 K were performed in samples with Tb, Ho and Dy; the results indicate that the behavior of the Dy compounds is qualitatively different in the low magnetic field region of the curves, requiring a minimum applied field to start increasing the magnetization. The NMR data and the magnetization results of the Dy compounds can both be explained as arising from a much lower mobility of the domain walls.

Key-words: NMR; hf interactions; Rare earth; Intermetallic compounds.

PACS: 75.60.-d, 75.30.Hx, 75.50.-y, 75.60.Lz

Introduction.

RFe_2 intermetallic compounds have a C15 Laves phase structure where all R atoms occupy equivalent cubic crystallographic sites. YFe_2 is ferromagnetic, with a transition temperature of 542 K and a magnetic moment of $1,5 \mu_B$ per Fe atom at saturation; the magnetization prefers to align along an $[111]$ easy direction¹. In an earlier work², ^{89}Y -NMR measurements at 4.2 K were performed in $(R_x Y_{1-x})Fe_2$ compounds with $R = Tb$ and Ho in the composition range $0.05 \leq x \leq 0.20$, to study the transferred hyperfine (hf) interactions arising from the R impurities. Compared to the YFe_2 narrow single-line spectrum centered at 45.94 ± 0.02 MHz, the pseudo-binary spectra at 4.2 K were broadened and the line centers shifted towards higher frequencies as the R concentration increased. The spectra were interpreted within a model that restricted the R contributions to the Y hf field only to indirect transfers of interactions via the Fe sub-lattice. The model takes as effective on the Y site field every rare earth atom that shares at least one Fe common first neighbor with the Y atom. In this picture, R atoms in the first, second and third shells around the Y site contribute to the Y field, since they have 6, 2 and 1 common Fe first neighbors, respectively. On that same study, one could not measure Y NMR spectra of samples with $R = Dy$ in the composition range indicated above: the echo signals were very weak even for a sample with $x = 0.02$, and were not observed for higher values of Dy concentration.

Significant effects of reduction in the amplitude of NMR echo signals had also been observed in other systems containing Dy, like in the pure Dy metal and in the series $(Dy_x Y_{1-x})Al_2$, which were related to limitations upon the domain walls motion^{3,4}. Similar effects were also reported for ^{59}Co NMR in $(Y,Dy)Co_5$ compounds⁵.

In a magnetic medium the generation of detectable NMR signals is largely related to the value of the enhancement factor η , which measures the effect of amplification of the applied radio frequency field H_1 at the nuclear site⁶. The origin of this amplification is the appearance of a transverse component of the electronic magnetization under the rf field; this component oscillates with the frequency of the field H_1 . Considering that the hyperfine field H_{hf} is collinear with the electronic magnetization, a transverse component of the hf field that adds to the applied field H_1 is generated. The factor η_w in the domain walls can be considerably larger than the value of η_d in the domains of a specimen, since the motion of the walls produces larger turning angles of the electronic magnetization in their interior.

In order to understand the peculiar behavior of our series with Dy substitution, NMR measurements were performed at 4.2 K and 77 K in Dy-substituted compounds with $0 \leq x \leq 0.02$, and curves of magnetization versus applied field were taken in compounds with Ho, Tb and Dy substitution for $x \leq 0.20$.

Experimental.

The pulsed NMR measurements were made on powdered polycrystalline samples of $(Dy_x Y_{1-x})Fe_2$ embedded in silicone oil, with $x = 0; 0.005; 0.0075; 0.01; 0.0125; 0.015$ and 0.02 . The compounds were melted in arc furnace under argon atmosphere from high purity metals; annealing of the as-cast buttons was done at $900^\circ C$ for periods of 100 hours. The formation of a C15 Laves phase structure in the compounds was confirmed by X-ray analysis of powdered samples at room temperature. The NMR spectra were obtained with a Bruker spectrometer and low temperatures were reached by dipping the samples into liquid helium and liquid nitrogen.

Optimization of the resonance conditions required typically pulses of $0.5 \mu\text{s}$ width; the Dy samples required higher power than the others. The spectra were made by plotting spin echo heights versus frequency, with pulses A and B separated by intervals of the order of $30 \mu\text{s}$.

The magnetization data were taken with a vibrating sample magnetometer, by using single pieces of the appropriate compound with masses of the order of 50 mg. The samples were cooled without an external applied field, and the measurements above 4.2 K were made by increasing continuously the temperatures.

Experimental Results.

Spectra at 4.2 K could be obtained with the power and sensitivity of the spectrometer for compositions with Dy up to $x = 0.015$. The relative intensity of the line decreases rapidly with Dy concentration by a factor of approximately 100 from 0 % to 1.5 %; for the sample with $x = 0.02$ the echoes were barely detectable at the frequency corresponding to the main peak in the other spectra. On the other hand, the spectra for $x \leq 0.02$ were easily obtained under normal conditions at $T = 77.4 \text{ K}$; for $x = 0.05$, however, the echoes were not observed. Figures 1a and 1b show some of the spectra at those temperatures. Measurements of nuclear relaxation times T_2 were also performed for some concentrations, at liquid helium and at liquid nitrogen temperatures; these relaxation times are of the order of milliseconds.

Apart from the echo intensity features mentioned above, the spectra of the pseudo-binaries at 4.2 K are characterized by a broadening of the line and a small increase in the center frequency compared to the pure YFe_2 case. In this respect the Dy spectra resemble the spectra obtained with other rare earth impurities.²

Since the signals are more intense at liquid nitrogen temperatures, resolved satellite lines could be observed at 77 K - Fig. 1b - with relative intensities that increase with the Dy concentration. It should be noted that the YFe_2 spectrum at this temperature is very narrow.

The magnetization curves at 4.2 K of several samples with Dy, Tb and Ho in the concentration range $0 \leq x \leq 0.20$ are presented in Fig. 2. Although measurements were made up to 13 kOe the figure draws attention to the initial part of the curves, corresponding to very low values of the applied magnetic field. Figure 3 shows a full cycle of magnetization for the sample with 20% Dy at 4.2 K. Figure 4 shows the values of critical fields for the Dy compounds versus concentration at 4.2 K and also the critical fields vs temperature for the 20% sample, obtained from the magnetization curves.

Discussion.

The anomalous behavior observed in the series $R Y_{1-x} Fe_x$ for $R = Dy$, leading to a reduction of the NMR signals, is not due to particularly shorter relaxation times T_2 , since the measured T_2 values are much longer than the typical interval of 30 μs between excitation pulses A and B. The anomaly in NMR behavior is paralleled by a large coercivity found in the same compounds, compared to those containing Tb and Ho (Fig. 2). One can observe that the Dy substitution for Y even in small percentages produces an immediate effect of reduction in the magnetic susceptibility $\chi = (\partial M / \partial H)_T$ of the compound. With the data plotted in Fig. 2 for small fields, it is found that in the compound with 2% of Dy χ is a factor of 10 smaller than the values observed in YFe_2 and in samples with $R = Ho$ and Tb. From 2% up to 20% of Dy, the low field susceptibility suffers a reduction by another factor of 10.

Besides this strong effect on χ values, the increase in Dy concentration introduces higher values of critical fields in the magnetization curves (defined as the point in the H axis where there is a turn in the magnetization). Fig. 4.b illustrates the behavior found for H_c at 4.2 K; the value of H_c for 20% of Dy (7.5 kOe) is 10 times larger than the maximum H_c observed^a across the system (Dy,Y)Al₂, indicating the possibility of larger fields for higher Dy concentrations in our system.

On the other hand, the critical field H_c shows a rapid decrease with temperature, as expressed in Fig. 4.a for 20% Dy, in spite of the fact that the magnetization intensity does not vary appreciably in this range of temperature, since the compound has a much higher T_c . Considering that H_c has a similar behavior with T in the sample with 2% of Dy, the coercive field eventually present at 77 K would be smaller than the RF applied field. Thus, the temperature dependence of the end point of this flat region in the beginning of the M vs H curve (Fig. 4a) points to a larger mobility of the domain walls at higher temperatures, and the recovery of the NMR signals at 77 K goes in the same direction. These facts can be understood if one accepts that most, if not all the signals measured in the pseudo-binaries originate from nuclei in domain walls. The smaller mobility of these walls at helium temperatures lowers the enhancement factor, and consequently eliminates the signals from this region of the samples; the amplification factor of the domains is not sufficient to allow a proper excitation of the nuclear spins system. In magnetic compounds with a large ratio between anisotropy and exchange energies, the domain pattern is characterized by particularly narrow domain walls; a further occurrence of crystal imperfections or pinning effects can generate a blocking of wall motion to fields below a critical value H_c . In these systems^a, the enhancement factor η_v can be related to the critical field

through $\eta_v \propto 1/H_c$. Applying this model to our case, the observed values of H_c indicate a reduction in η_v by a factor of 10^2 between the compounds with 2% and 20% of Dy. The attribution of the NMR signals to domain walls in these pseudo-binary compounds is also confirmed by the significant changes produced in the echoes by external magnetic fields.

The recovery of signals at 77.4 K for $x \leq 0.02$ has permitted the observation of spectra that broaden considerably with Dy concentration, following the pattern presented at 4.2 K and in compounds with other R. Furthermore, at this low range of composition, one has found satellite lines with relative intensities that increase with Dy concentration; these extra lines were not visible at 4.2 K, possibly due to the weakness of the signals.

Conclusions.

In the present work we have searched for the cause of the rapid decrease² in ^{89}Y NMR signals observed in the series of $\text{R}_x\text{Y}_{1-x}\text{Fe}_2$ pseudo-binary intermetallic compounds, for $\text{R}=\text{Dy}$, compared to the behavior with Ho and Tb. From the small value of the derivative of the curve of $M \times H$ obtained for the $\text{Dy}_x\text{Y}_{1-x}\text{Fe}_2$ series, we conclude that the observed anomaly in the NMR behavior is due to a lower mobility of the domain walls at 4.2 K in these compounds. These walls are very narrow, probably a few interatomic spaces thick, as in other Dy intermetallic compounds⁶. The cause of this blocking could be the Kersten mechanism as in $\text{Dy}_x\text{Y}_{1-x}\text{Al}_2$, or intrinsic pinning⁶. The study of the spectroscopy of the Dy series is under way, making use of the recovery of the NMR signals at higher temperatures.

Acknowledgements.

The authors are indebted to Dr. X.A. da Silva for several comments and discussions.

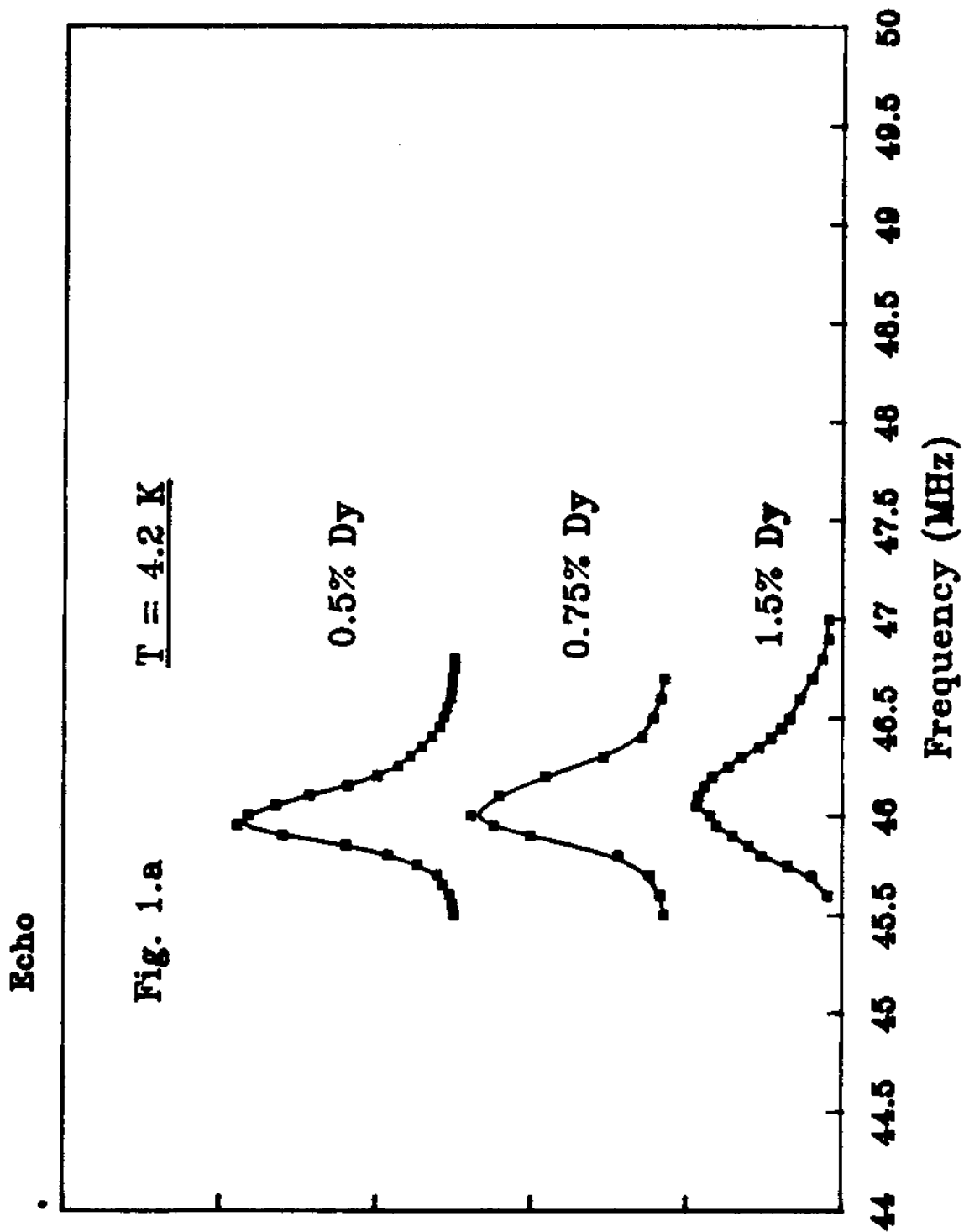
FIGURE CAPTIONS.

Fig. 1 (a) ^{89}Y spin echo NMR spectra of $\text{Dy}_x\text{Y}_{1-x}\text{Fe}_2$ at 4.2 K and (b) NMR spectra at 77.4 K; the area of the curves are normalized.

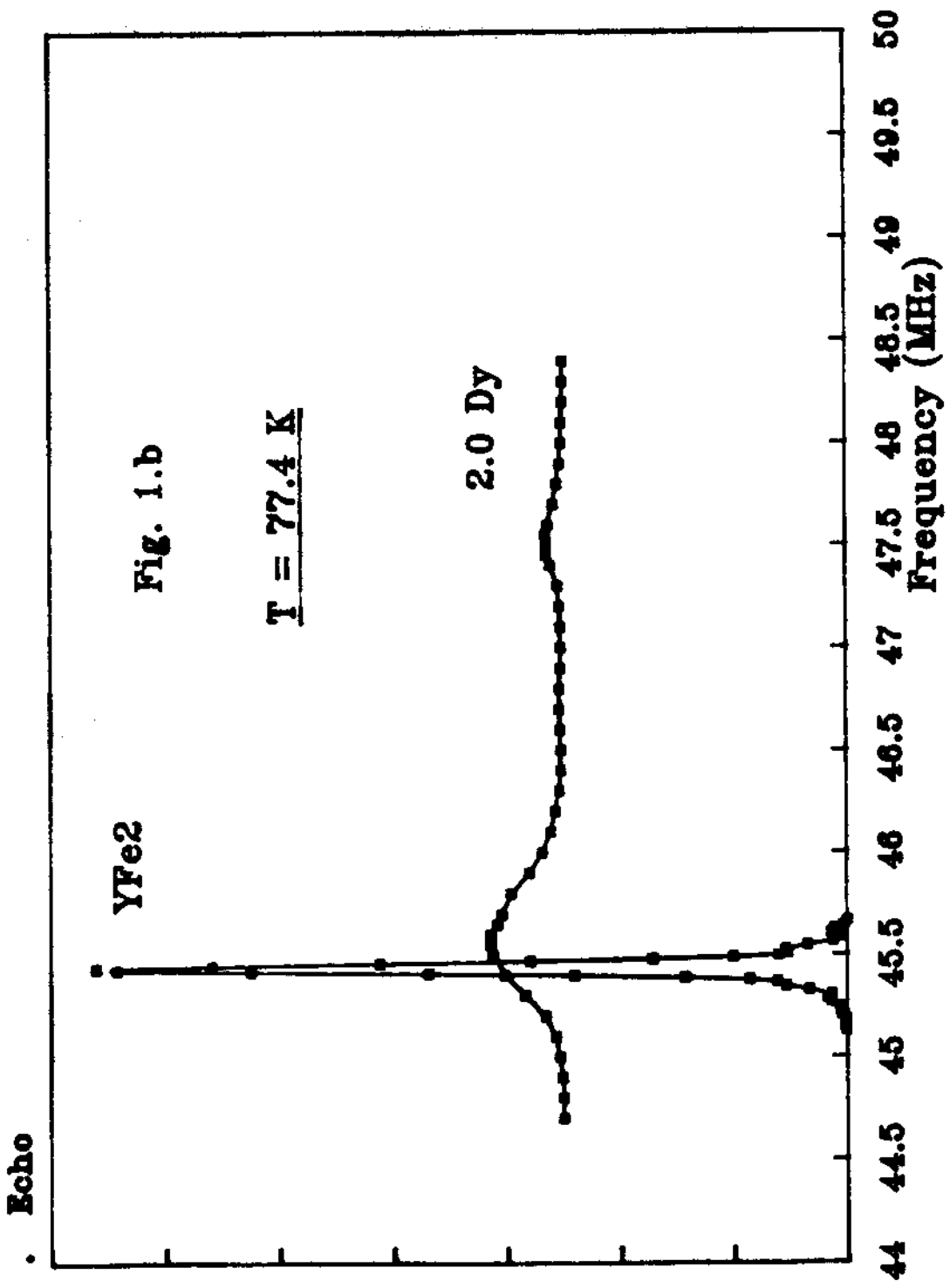
Fig. 2 Magnetization of $\text{R}_x\text{Y}_{1-x}\text{Fe}_2$ intermetallic compounds at 4.2 K versus external magnetic field. The experimental points for the different samples had the origins displaced by 1, 3, 5, 7, 9 and 11 emu/g to avoid superposition.

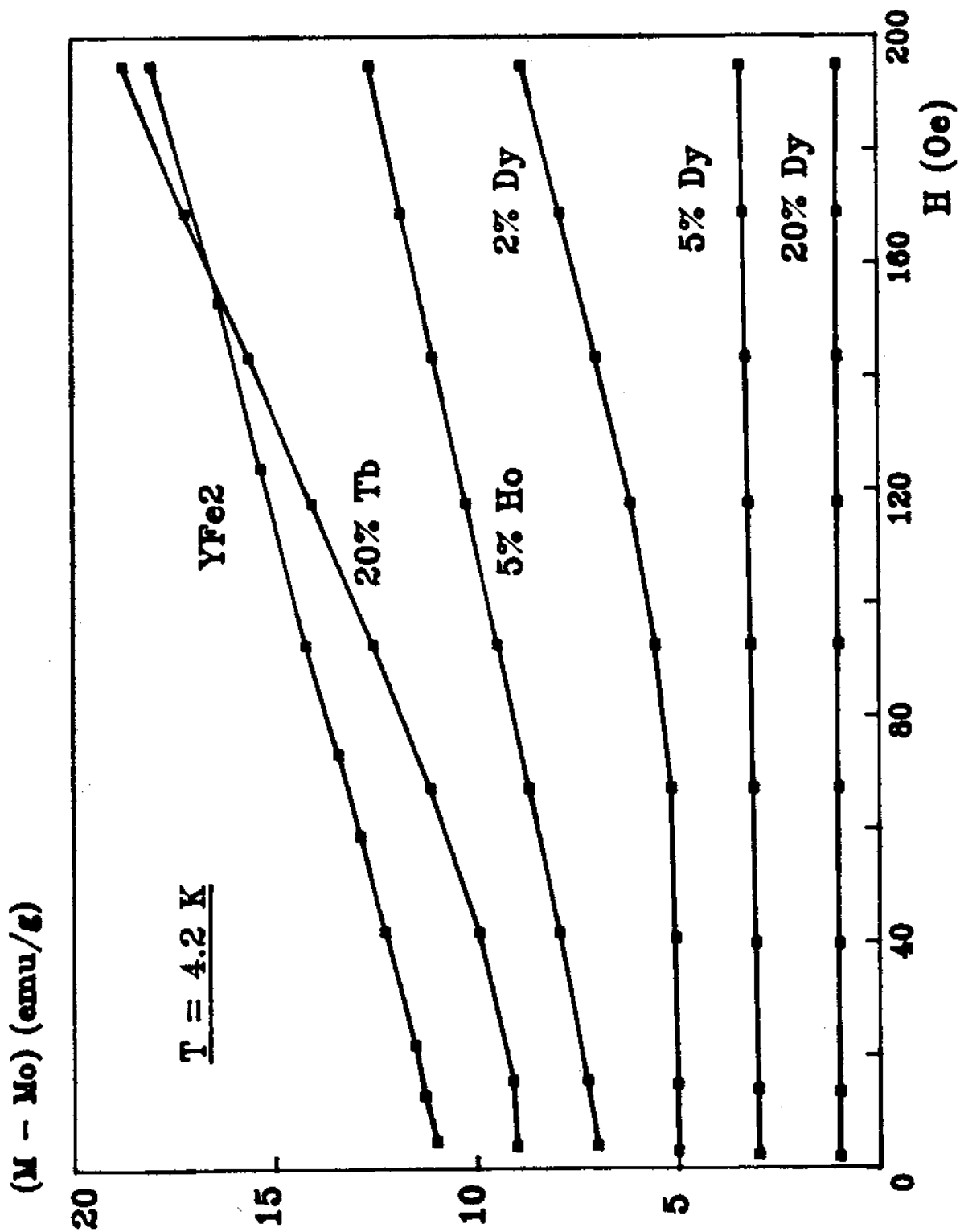
Fig. 3 Magnetization cycle for $\text{Dy}_x\text{Y}_{1-x}\text{Fe}_2$ ($x = 0.20$) at 4.2 K showing the large coercive field of this compound.

Fig. 4 (a) Logarithm of the magnetic critical field (see text) of the $\text{Dy}_x\text{Y}_{1-x}\text{Fe}_2$ ($x = 0.20$) pseudo-binary compound versus temperature and (b) Logarithm of the magnetic critical field at 4.2 K versus percentage of Dy in the $\text{Dy}_x\text{Y}_{1-x}\text{Fe}_2$ compounds. The curve is intended to guide the eyes.

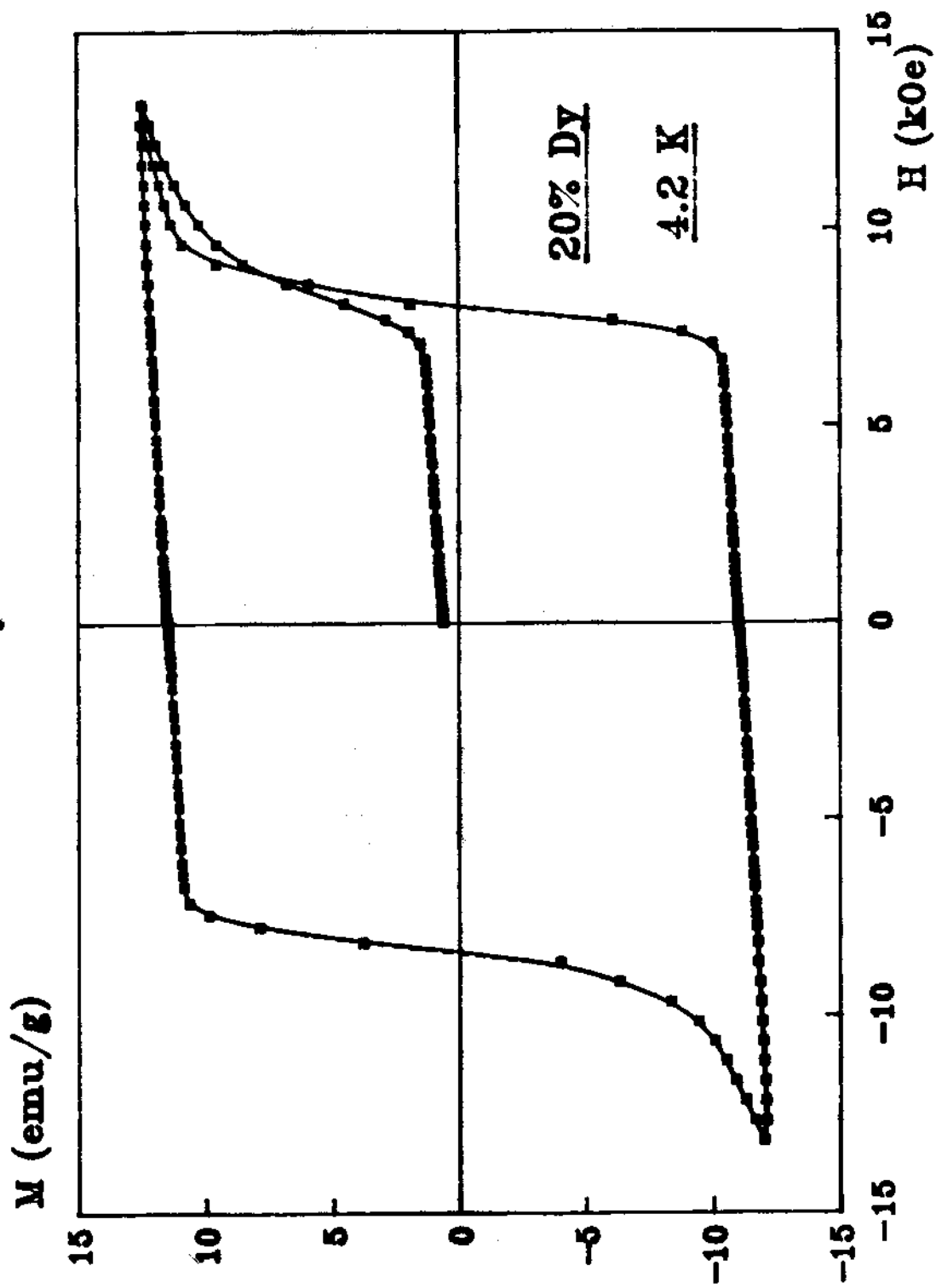


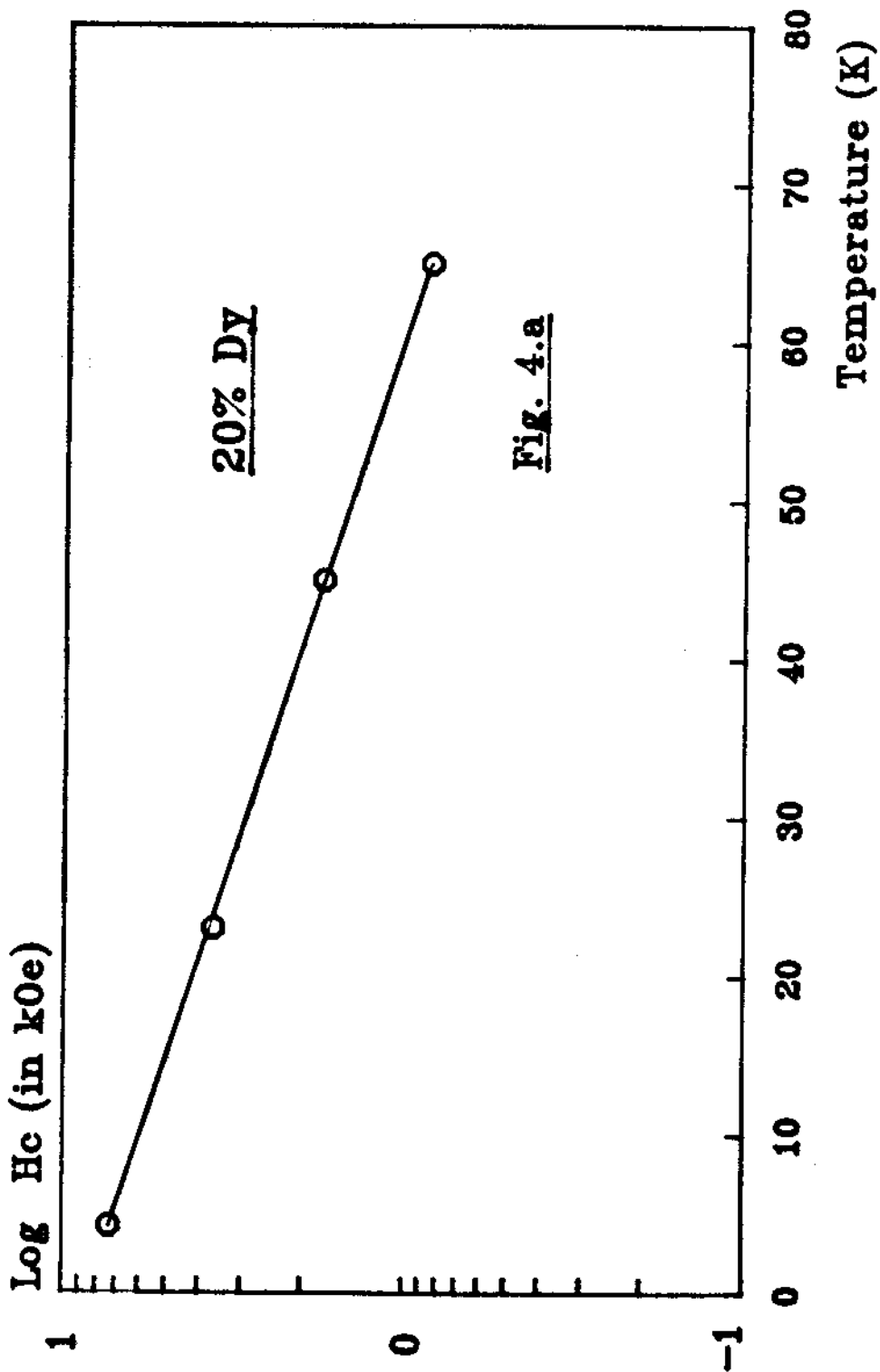
(Dy,Y)Fe₂ - 77.4 K



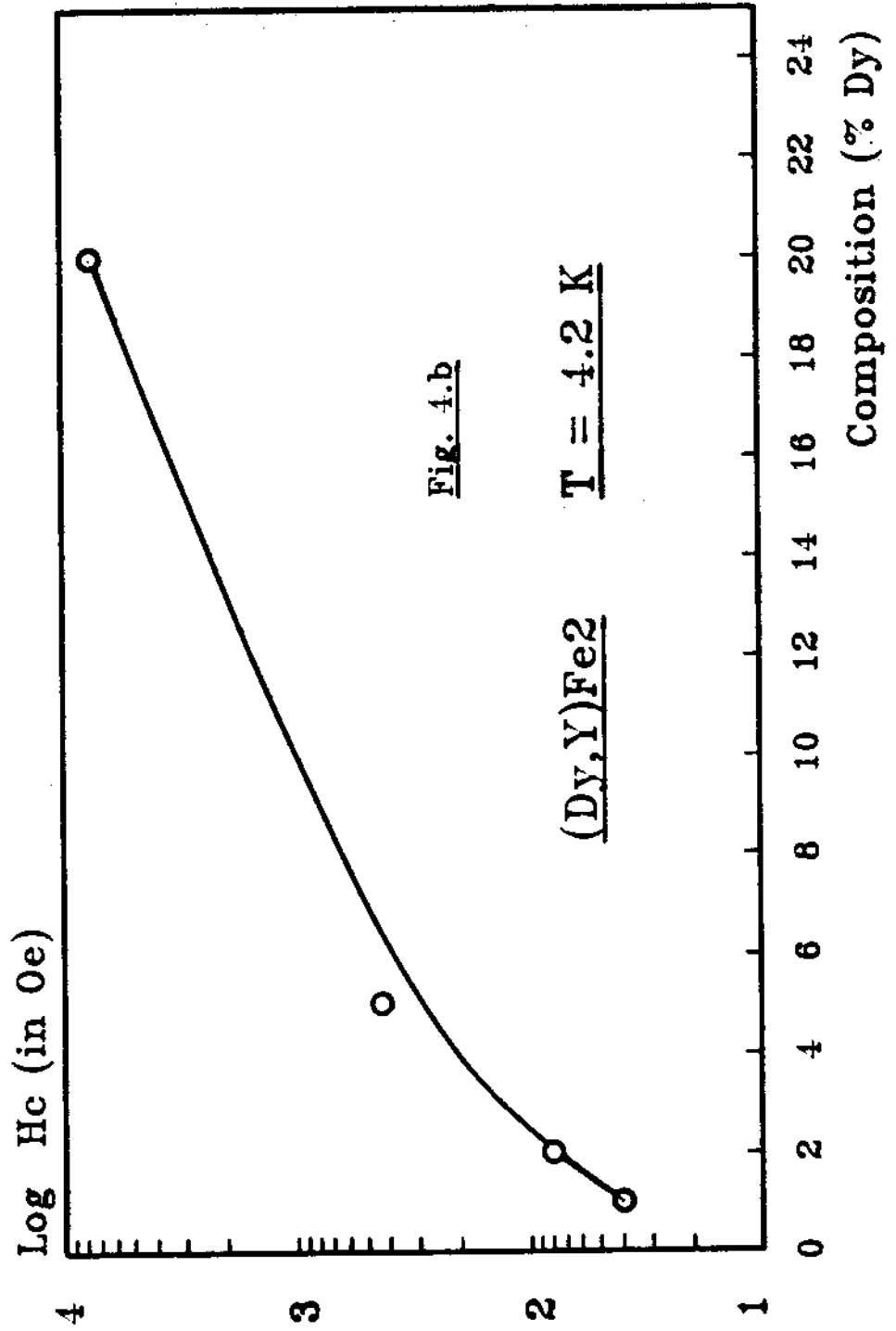


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