MASTER

MAGNETIC PROPERTIES OF $DyFe_2H_2$ FROM ^{57}Fe, ^{161}Dy MÖSSBAUER EFFECT AND MAGNETIZATION MEASUREMENTS[a)]

by

P. J. Viccaro, J. M. Friedt, D. Niarchos, B. D. Dunlap,
G. K. Shenoy, A. T. Aldred and D. G. Westlake

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Prepared for

24th Annual Magnetism Conference

Cleveland, Ohio

November 14-17, 1978

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

U of C-AUA-USDOE

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Operated under Contract W-31-109-Eng-38 for the
U. S. DEPARTMENT OF ENERGY

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Department of Energy, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona
Carnegie-Mellon University
Case Western Reserve University
The University of Chicago
University of Cincinnati
Illinois Institute of Technology
University of Illinois
Indiana University
Iowa State University
The University of Iowa
Kansas State University
The University of Kansas
Loyola University
Marquette University
Michigan State University
The University of Michigan
University of Minnesota
University of Missouri
Northwestern University
University of Notre Dame
The Ohio State University
Ohio University
The Pennsylvania State University
Purdue University
Saint Louis University
Southern Illinois University
The University of Texas at Austin
Washington University
Wayne State University
The University of Wisconsin

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights. Mention of commercial products, their manufacturers, or their suppliers in this publication does not imply or connote approval or disapproval of the product by Argonne National Laboratory or the U. S. Department of Energy.

Magnetic Properties of $DyFe_2H_2$ from ^{57}Fe, ^{161}Dy Mössbauer Effect and Magnetization Measurements[a)]

P. J. Viccaro,[b)] J. M. Friedt,[c)] D. Niarchos,[d)] B. D. Dunlap,
G. K. Shenoy, A. T. Aldred and D. G. Westlake
Argonne National Laboratory
Argonne, Illionis 60439

ABSTRACT

A single phase stable hydride with nominal composition $DyFe_2H_2$ is shown to have the cubic C15 Laves structure with a 5% larger lattice constant. ^{57}Fe Mössbauer spectra show two sites with nearly equal population and with different isomer shifts and hyperfine fields. Based on the average hyperfine field at 4.2 K, an Fe moment of approximately 1.6 μ_B is estimated. From the ^{161}Dy data at 4.2 K, which show a single site, a nearly free-ion moment of 9.8 μ_B is determined. These results, combined with the total moment of 3.5 μ_B from bulk magnetization measurements, indicate that the Dy and Fe moments may not be strictly antiparallel in the hydride. Relaxation effects in the ^{161}Dy spectra above 77 K, combined with a sharp decrease in the moment with increasing temperature, imply a weakening of the Dy-Fe magnetic coupling induced by the presence of the hydrogen.

PACS numbers; 75.30.Cr, 75.50.Gg, 76.80.+y

INTRODUCTION

The Laves-phase intermetallic compound, $DyFe_2$ readily absorbs approximately 4 hydrogen atoms per formula unit at ambient temperature [1,2]. Previous investigations have considered hydrides of this material with hydrogen content presumably near this maximum. For these cases, multiple phases are usually encountered [1], making an unambiguous determination of the magnetic and electronic properties of these materials difficult. In the present study, a stable intermediate hydride with composition near $DyFe_2H_2$ is considered. This compound presents only one crystallographic phase and appears to be the most stable of the $DyFe_2H_x$ phases.

In an attempt to determine the influence of hydrogen on the magnetic and electronic structure of $DyFe_2$, ^{161}Dy and ^{57}Fe Mössbauer effect studies and magnetization measurements were carried out. Emphasis is given to the determination and correlation of microscopic and bulk properties in this system. The results are compared to those of $DyFe_2$.

EXPERIMENTAL

$DyFe_2$ was prepared by argon arc-melting of Dy(99.9%) and Fe(99.99%) metals. The compound was then annealed at 750 °C for 7 days. Debye-Scherrer x-ray diffraction patterns taken with Cu Kα radiation showed only the C15 Laves structure. The hydride was formed by exposing $DyFe_2$ to an appropriate amount H_2 gas in a system of known volume to form $DyFe_2H_2$. A subsequent volumetric analysis of the hydrogen content of the material gave $DyFe_2H_x$ with $x = 1.92 \pm 0.02$. X-ray diffraction patterns of the hydride showed broader reflections than were obtained for $DyFe_2$. However, only the cubic C15 Laves structure was detected with a lattice constant approximately 5% larger than that of $DyFe_2$.

^{57}Fe Mössbauer measurements were made using a ^{57}Co in Rh source. For the ^{161}Dy experiments, a source of $Gd_{0.5}Dy_{0.5}F_3$ at ambient temperature was used. An apparatus based on a Faraday balance was employed for the magnetization measurements between 4.2 K and 300 K with a maximum field of 15 kOe.

RESULTS AND DISCUSSION

Representative ^{57}Fe Mössbauer spectra for $DyFe_2$ and $DyFe_2H_{1.92}$, both at 77 K are shown in Fig. 1a and 1b, respectively. $DyFe_2$ is ferromagnetic with an antiparallel arrangement of the Dy and Fe spins along the <100> direction [3,4]. Consequently, only one hyper-

fine field is observed corresponding to the single crystallographic (and magnetic) site in this material.

The spectrum for the hydride is more complex and shows resolved structure in spite of slightly broader resonances compared to $DyFe_2$. The fit to the data which best characterizes the spectra at this and other temperatures, consists of a superposition of two six-line magnetic hyperfine spectra of approximately equal total intensities and with different hyperfine field and isomer shifts. The different isomer shifts for the two spectra, indicates the presence of two crystallographically inequivalent Fe sites in the hydride. For $DyFe_2$, and the C15 Laves-phases in general, Fe occupies only one type of crystallographic site. Since the structure of $DyFe_2H_{1.92}$ is an expanded version of $DyFe_2$ relative to the metal atoms, then the different types of Fe sites in the former is associated with differences in the number and/or positions of surrounding hydrogen atoms. The two distinct sites for the Fe indicate that the hydrogen forms an ordered structure at this composition.

For the two sites A and B the measured hyperfine fields at 4.2 K are respectively 195 $\pm$ 4 kG and 242 $\pm$ 4 kG, compared to the value 225 $\pm$ 4 kG obtained for $DyFe_2$. The isomer shifts, on the other hand, are both positive relative to $DyFe_2$ by the amounts, 0.28 $\pm$ 0.02 mm/s and 0.08 $\pm$ 0.02 mm/s for the A and B sites, respectively at 295 K.

From the temperature variation of the average hyperfine field, the variation of the Fe moment was obtained (Fig. 2) assuming a simple scaling between these two quantities with Fe metal as the reference point. Such a procedure has been successfully applied to the analysis of the magnetic properties of $DyFe_2$ [5]. The magnetic transition temperature for the hydride was estimated to be above 500 K from these experiments. The actual value however, could not be deduced due to the desorption of hydrogen above this temperature.

The analysis of the ^{161}Dy data obtained at 4.2 K (shown in Fig. 1c) resulted in a single hyperfine field of 6050 $\pm$ 50 kG. This value is close to the free-ion value of 6200 kG measured in Dy metal but less than the value of 7080 kG for $DyFe_2$. [6]. Hence, the saturated Dy magnetic moment in the hydride, although somewhat reduced from the enhanced moment in $DyFe_2$ (due to conduction electron polarization), is still close to the free-ion value of $10\mu_B$.

For temperatures above 77 K, the ^{161}Dy data show broadening of the hyperfine lines of the magnetic pattern indicative of the presence of magnetic relaxation effects. As a first approximation adiabatic relaxation of a Kramers doublet [6] was assumed, and quite reason-

able fits to the data were obtained in this way. From the values of the hyperfine fields encountered in the above analysis, the temperature dependence of the Dy moment (presented in Fig. 2) was determined, assuming the moment to be proportional to the hyperfine field.

Also in Fig. 2, are the results for the magnetic moment of the hydride per formula unit as a function of temperature obtained from bulk magnetization measurements with a 15 kG field. However, it should be noted that magnetic saturation was not obtained at this field. Attempts to curve fit the magnetization field dependence indicates that the measured values are roughly 60% of saturation. A comparison of the three curves in Fig. 2 at low temperatures suggests the possibility that the Dy and Fe spins are not strictly antiparallel in the hydride, in contrast with $DyFe_2$. The difference between the measured moment ($3.5\mu_B$) and the value expected for simple antiparallel coupling ($6.7\mu_B$) is too large to be explained by a failure in the assumption of strict linearity between the Fe hyperfine field and magnetic moment. However the fact that full saturation was not reached in the magnetization measurements leaves the question of the spin structure in doubt at present.

From Fig. 2 one sees that the variation in the total moment is associated only with that of the Dy moment, since the Fe moment shows little variation with temperature up to 300 K. The temperature dependence of the Dy moment itself can be described by a molecular field calculation assuming a constant exchange field, presumably arising from the Fe sublattice, over the entire temperature region (solid line, Fig. 2). We do not observe a well-defined spin compensation between the Dy and Fe moments. However, based on the relative values of the two moments at 300 K, compensation could occur at higher temperatures provided that is indeed consistent with the magnetic structure of the hydride. One should also consider the possibility of a distribution in the direction of the Dy moments due to a distribution of near-neighbor hydrogen coordinations in this slightly non-stochiometric hydride.

The perturbation by hydrogen of the strength of the Dy-Fe magnetic coupling, on the other hand, cannot be deduced solely from these data. However, the sharper decrease of the Dy hyperfine field with increasing temperature in the hydride compared to $DyFe_2$ [5] would be consistent with a smaller exchange field in the former. Furthermore the presence of relaxation in the ^{161}Dy spectra above 77 K in the hydride and its absence in $DyFe_2$ also indicates a weakening of the Dy-Fe coupling induced by the presence of hydrogen. However detailed conclusions concerning this aspect require further investigation.

a) Work supported by the U. S. Department of Energy.
b) On leave from Instituto de Fisica, UFRGS, Porto Alegre Brasil.
c) Present Address: Centre de Recherches Nucleaires, Stasbourg, France.
d) IAEA fellow from Nuclear Research Center Demokritos, Athens, Greece.

REFERENCES

1. K. H. J. Buschow, Physica 86-88B, 79 (1977).
2. K. H. J. Buschow and R. C. Sherwood, J. Appl. Phys. 49, 1480 (1978).
3. G. J. Bowden, D. St. P. Bunbury, A. P. Guimaraes and R. E. Snyder, J. Appl. Phys. 39, 1323 (1968).
4. K. H. J. Buschow and R. P. van Stapele, J. Appl. Phys. 41, 4066 (1970).
5. E. Burzo, Solid State Commun. 14, 1295 (1974).
6. S. Ofer, I. Nowik and S. G. Cohen in Chemical Applications of Mössbauer Spectroscopy ed. by V. I. Goldanskii and R. H. Herber (Academic Press, New York) 1968, Chapter 8.

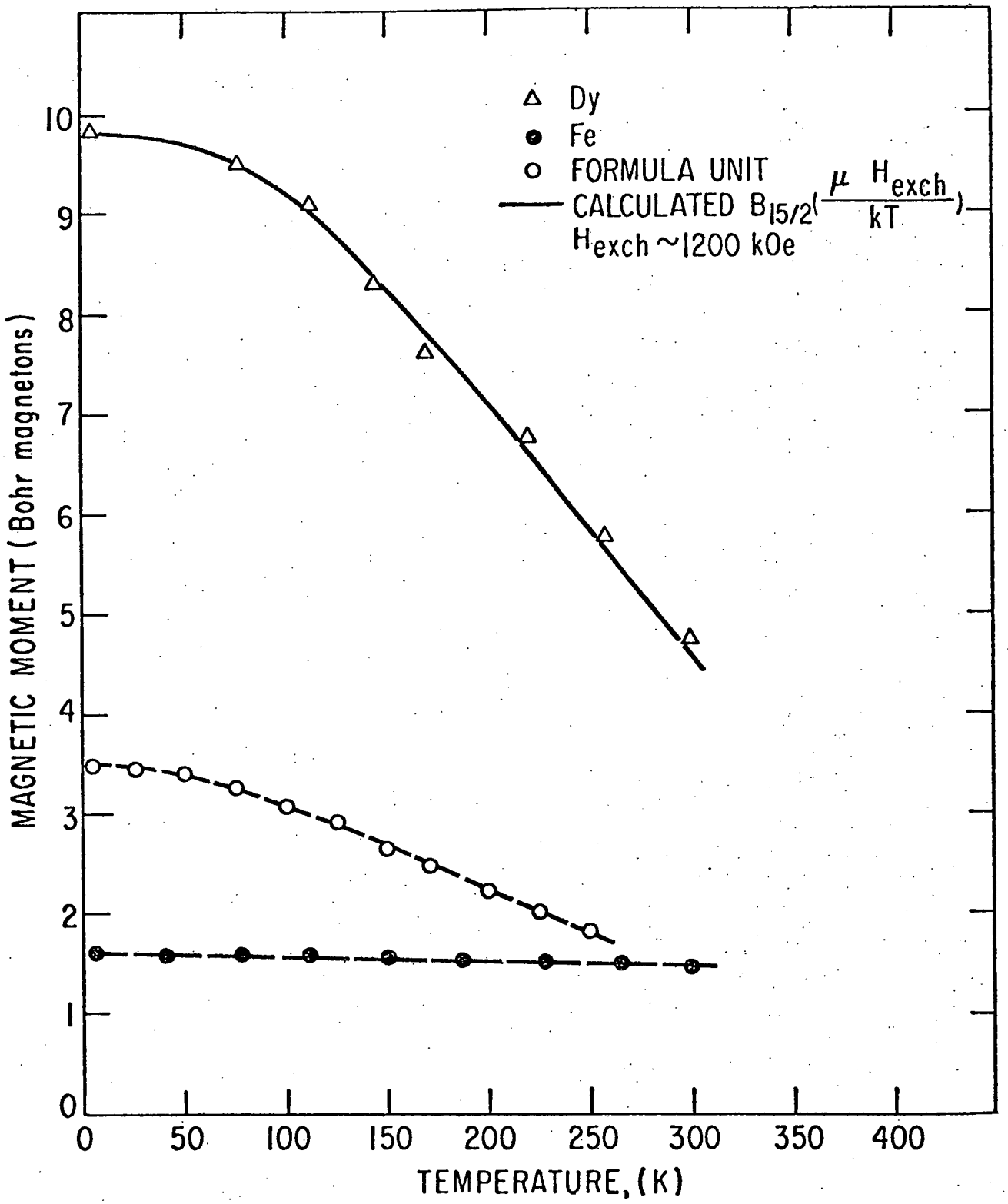

Fig. 2. Temperature dependence of the magnetization for $DyFe_2H_{1.92}$. Solid Circles give the Fe sublattice magnetization by averaging the two observed hyperfine fields and assuming linearity between the ^{57}Fe hyperfine field and the Fe magnetic moment. Open triangles give the Dy sublattice magnetization determined from the ^{161}Dy hyperfine field. Open circles give the bulk magnetization at 15 kOe (not in saturation, see text).

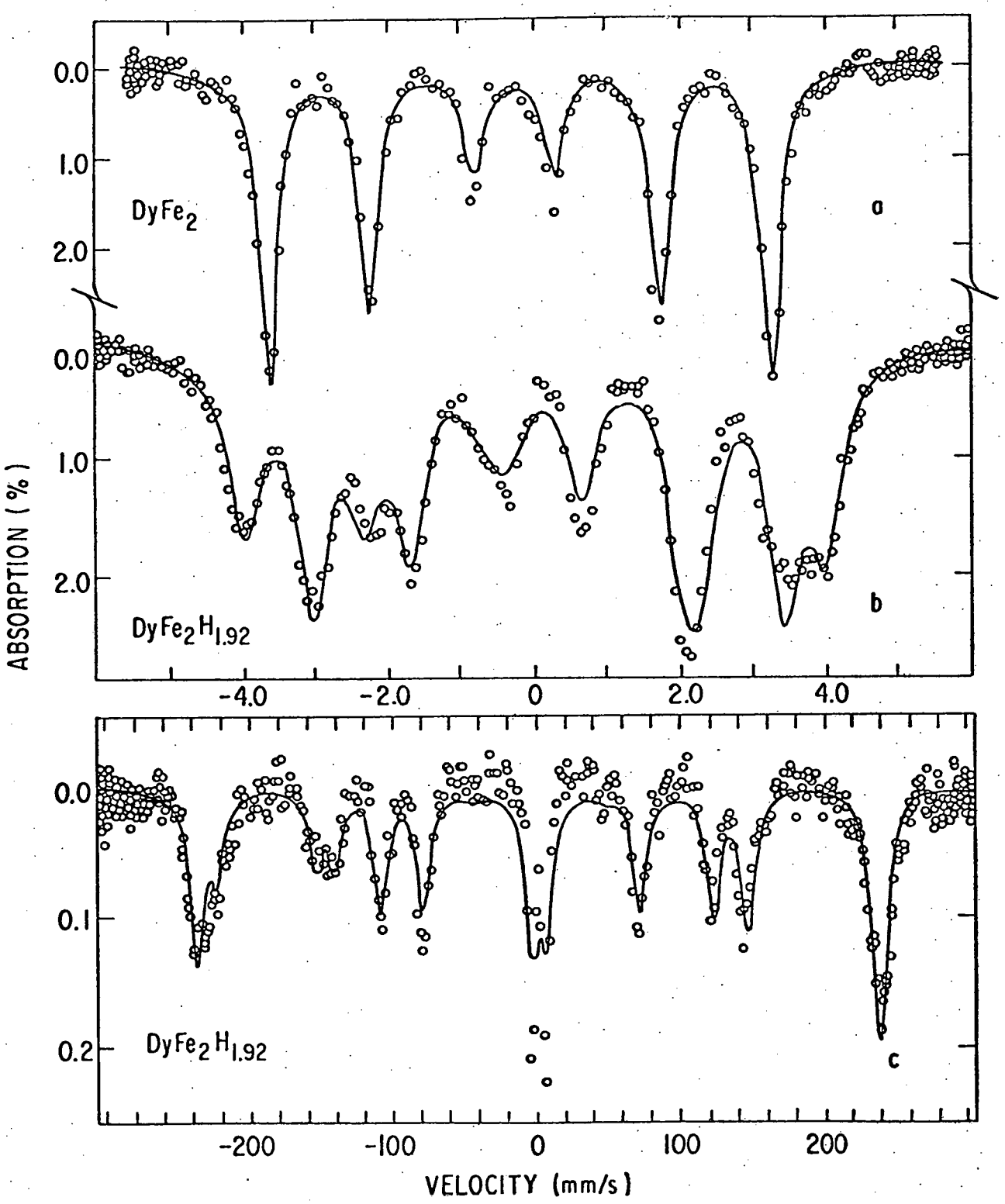

Fig. 1. Mossbauer spectra obtained at 77 K for (a) ^{57}Fe in $DyFe_2$. (b) ^{57}Fe in $DyFe_2H_{1.92}$ and (c) ^{161}Dy in $DyFe_2H_{1.92}$.