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BY

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Superconductivity and Magnetism in the Series $R_2Fe_3Si_5$ by Mössbauer and Magnetization Measurements[a)]

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ABSTRACT

Members of the $R_2Fe_3Si_5$ series become either superconducting or magnetically ordered depending on whether the metal atom R (= rare earth, Y or Sc) is diamagnetic or paramagnetic respectively. We have taken Mössbauer effect and magnetization measurements to determine the magnetic state of the iron and the nature of the superconducting electrons.

^{57}Fe Mössbauer measurements on the Sc, Dy and Er compounds all showed two partially resolved, quadrupole split spectra at all temperatures from 300 K to 1.5 K, indicating that there is no resolvable magnetic interaction at the iron site. No major change in the spectrum of $Dy_2Fe_3Si_5$ was observed in passing through its antiferromagnetic ordering temperature of ~ 4 K. Measurements in an applied field of 5.6 T set an upper limit of 0.03 μ_B for the iron moment in $Sc_2Fe_3Si_5$. However, measurements at 4.2 K in fields up to 7 T for the Dy compound gave an internal field ~ 9% smaller than the applied field and linear with applied field. This corresponds to an induced moment at the iron site of ~ 0.07 μ_B at 7 T applied field.

The ^{161}Dy Mössbauer resonance clearly showed the onset of magnetic order around 4 K and the magnetic moment on Dy at 1.5 K was found to be 7.0 ± 0.2 μ_B consistent with the magnetization measurements. The nature of the superconducting electrons in the $R_2Fe_3Si_5$ series is discussed in the light of available measurements.

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INTRODUCTION

The series $R_2Fe_3Si_5$, discovered recently by Braun [1], contains an interesting mixture of magnetically ordered and superconducting compounds depending on whether the element R (= rare-earth, Y or Sc) has a local moment or not. Of particular interest is the role of the iron atoms in the series, since iron is not a common constituent of superconducting compounds.

In an earlier paper we reported the results of ^{57}Fe Mössbauer effect measurements on superconducting $Sc_2Fe_3Si_5$ [2]. In this we obtained an upper limit of 0.03 μ_B for the magnetic moment on the iron atoms occupying the two distinct crystallographic sites in this structure. In order to obtain further information on the magnetic interactions, we have carried out experiments on other members of the series $R_2Fe_3Si_5$ (R = rare-earth). In this paper we report in detail the results for $Dy_2Fe_3Si_5$ using the Mössbauer effect in ^{57}Fe and ^{161}Dy, and also magnetization measurements.

EXPERIMENTAL

The samples were prepared by arc melting stoichiometric amounts of the elements in an ultra pure Ar atmosphere, followed by vacuum annealing at 1000 °C for about 10 days. X-ray diffraction patterns gave excellent agreement with the lattice parameters of Braun [1] rather than the earlier results of Bodak et al. [3]. No trace of any second phase was observed.

The ^{57}Fe Mössbauer spectra were obtained using a ^{57}CoRh source and conventional drive electronics. Isomer shifts are reported relative to iron metal at room temperature. The ^{161}Dy Mössbauer spectra were measured using a neutron-irradiated $^{160}Gd_{0.5}{}^{162}Dy_{0.5}F_3$ source matrix held at room temperature. Both the resonances were utilized to collect data between 1.5 K and 300 K. The ^{57}Fe measurements were also performed in external magnetic fields up to 7 T at 4.2 K.

RESULTS AND DISCUSSION

The Mössbauer spectrum of $Dy_2Fe_3Si_5$ at 294 K using the ^{57}Fe resonance is shown in Fig. 1(a). This, as well as the spectrum at 77 K, is made up of two partially resolved quadrupole doublets. In analyzing the data, the area ratios for the two sites were constrained to the value 2:1 to represent the site populations dictated by the structure. Due to the small splittings and consequent poor resolution in the spectra, the data could be analyzed with more than one set of parameters (quadrupole splittings and isomer shifts for the two sites), with all the sets yielding fits of acceptable quality. The ambiguity could be resolved to obtain a unique set of parameters when the data obtained in external magnetic fields were also analyzed. The final set of parameters also showed a smooth gradation in quadrupole interaction as the rare-earth ionic size was reduced in the progression from Dy through Er and Lu to Sc.

The parameters obtained at room temperature for the 8h site were isomer shift (IS) = 0.16(3) mm s^{-1} and quadrupole splitting (QS) = 0.23(3) mm s^{-1}, where the quoted QS is 1/2 e^2qQ. For the 4d site the parameters were IS = 0.13(2) mm s^{-1} and QS = 0.56(2) mm s^{-1}. The figure in parentheses indicates the error in the last digit for each parameter.

The resonance spectra measured at 4.2 and 1.5 K are qualitatively similar to the ones measured at 77 K. The quadrupole interaction at the 4d site, however, shows a 30% decrease. Braun [4] has found that $Dy_2Fe_3Si_5$ shows antiferromagnetic order below about 4 K. However, there is no evidence of any large magnetic hyperfine field down to 1.5 K at the Fe nucleus. The fit to the spectrum measured at 1.5 K can, however, be improved slightly by the inclusion of hyperfine magnetic fields of 0.5 ± 0.4 T at the 8h site and 0.8 ± 0.8 T at the 4d site. These results imply the following: The magnetic moment at the iron site in $Dy_2Fe_3Si_5$ is rather small, consistent with our study of $Sc_2Fe_3Si_5$ [2] and the polarization of electrons by the Dy moments produces a small spin density at the Fe nucleus in the antiferromagnetic state of the compound.

In order to gain further understanding of the magnetic interactions at the iron site, Mössbauer spectra were taken at 4.2 K in external magnetic fields up to 7 T which was applied parallel to the direction of the gamma-ray absorption. Data analysis was carried out by diagonalizing the ground and excited state Hamiltonians for the ^{57}Fe occupying both sites, with the magnetic interaction at various angles to the quadrupole tensor and then carrying out a powder average. The measured hyperfine field was less than the applied field by approximately 9% at both the sites for each of the spectra. This result should be contrasted with that on $Sc_2Fe_3Si_5$ where the measured fields and applied fields were identical [2].

Since the Mössbauer investigation is effectively a microscopic magnetization measurement, we find the induced moment at the iron sites in $Dy_2Fe_3Si_5$ at 4.2 K to be 0.009 μ_B T^{-1} and in the opposite direction to the applied field. The applied field measurements also showed the sign of the quadrupole interaction at the 4d site to be negative, as it was for $Sc_2Fe_3Si_5$. The resolution was inadequate to determine the asymmetry parameter at either site or the sign of the quadrupole splitting for the 8h site although this is probably positive from the gradation mentioned above.

The onset of antiferromagnetic ordering was seen more dramatically in the ^{161}Dy Mössbauer spectra. At 4.2 K [Fig. 2(a)], the spectrum is a broad singleline with a full-width at half-maximum of 40 mm s^{-1}. This is more than four times the usual width measured with this source. By 1.5 K [Fig. 2(b)], the spectrum has developed into a well resolved hyperfine magnetic pattern. The field at the Dy nucleus is 413 ± 5 T and the observed quadrupole interaction is e^2qQ = 1362 ± 40 MHz. These are considerably less than the respective free-ion values of 584 T and 3100 MHz. The proportionality between the hyperfine magnetic field and the magnetic moment on the atom in rare-earths [5] permits us to deduce the ordered moment on Dy to be 7.0 ± 0.2 μ_B.

We have also made magnetization measurements on a powdered sample of $Dy_2Fe_3Si_5$ in the temperature range 5-300 K and in magnetic fields up to 1.5 T. The observed moment was linear with field up to 1.5 T for all temperatures and far from reaching saturation values.

The effective moment on the Dy atoms as determined from a Curie-Weiss plot was 6.8 μ_B in the temperature range 20-40 K and rose to 7.6 μ_B in the range 200-300 K. These values were arrived at by assuming no contribution to the magnetization from the Fe atoms (as shown from Mössbauer studies) as well as from the conduction electrons. The low temperature moment value is in fairly good agreement with the ^{161}Dy Mössbauer results taken below the ordering temperature.

The measurements to date do not enable us to unambiguously answer the question "where are the superconducting electrons in the $R_2Fe_3Si_5$ series?" The large value of the superconducting transition temperatures suggests that d-electrons must participate in the superconductivity. If we further assume the criterion that the clustering of metal atoms in the structure is essential in realizing superconductivity [6], then the iron atoms at the 8h sites satisfy this requirement. Thus superconductivity could be assigned to the 3d electrons on Fe. The R atoms also form a cluster, but their separation is large. Certainly, if the Sc 3d electrons were the superconducting ones in $Sc_2Fe_3Si_5$, their replacement with magnetic rare-earth atoms should make them non-superconducting as is the case in $Dy_2Fe_3Si_5$, supporting the suggestion that Sc 3d electrons could also form superconducting pairs.

It must also be recognized that in an external magnetic field, a spin density at the Fe nucleus is induced via the Dy moments, and there is a negligible direct effect of the field on the Fe electrons. The coupling between the 4f moment and the conduction electrons is antiferromagnetic and is in turn adequate to destroy superconductivity of the Fe 3d electrons. From these arguments there is a strong bias to assume that the 3d electrons on Fe form Cooper pairs.

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a) Work supported by the U.S. Department of Energy.
b) On leave from Department of Physics, Monash University, Victoria, Australia.

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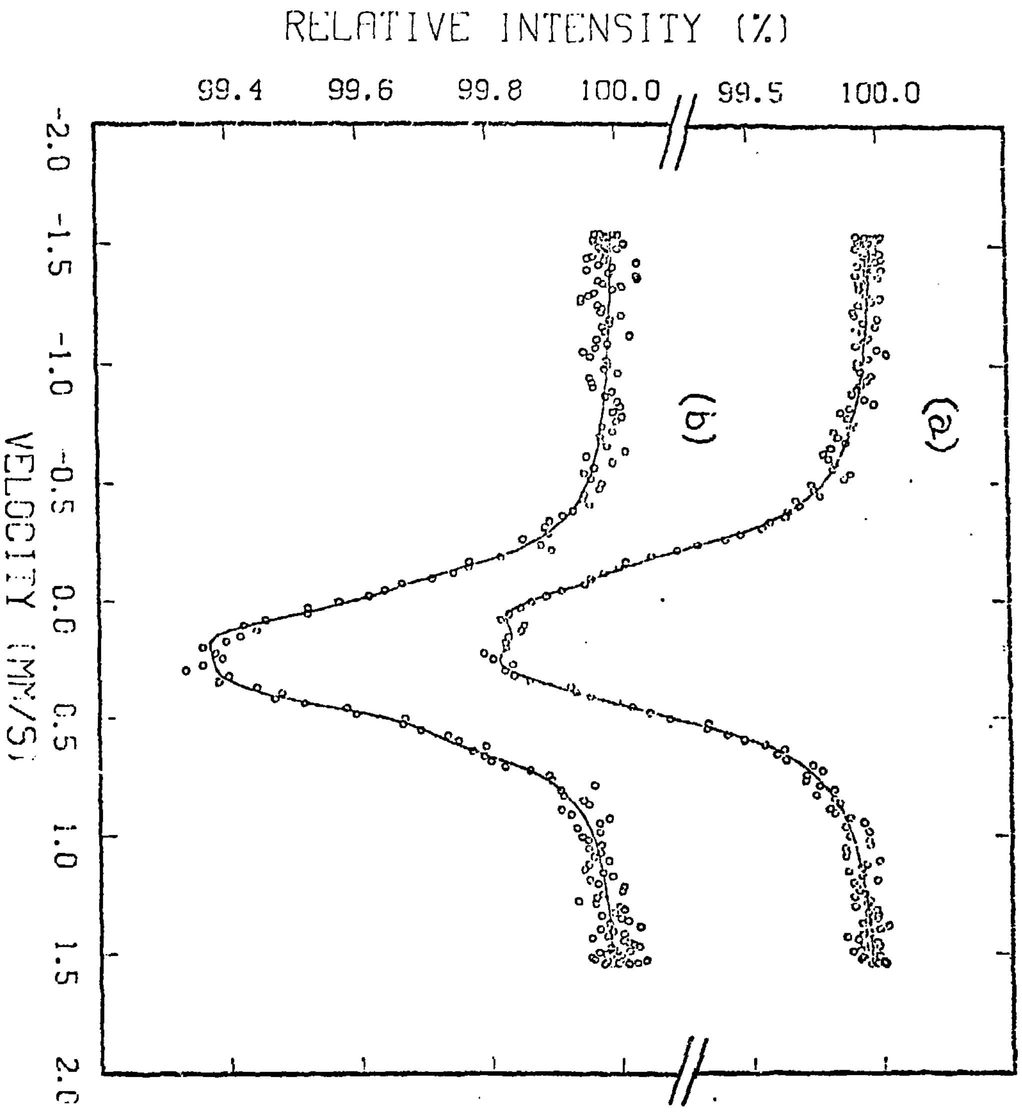
FIGURE CAPTIONS

Fig. 1 Mössbauer spectra of $Dy_2Fe_3Si_5$ measured using the 14.4 keV resonance gamma ray in ^{57}Fe at (a) 294 K and (b) 1.5 K. The solid curve through the data is a least squares fit as discussed in the text.

Fig. 2 Mössbauer spectra of $Dy_2Fe_3Si_5$ measured using the 25.6 keV resonance in ^{161}Dy at (a) 4.2 K and (b) 1.5 K.



RELATIVE INTENSITY (%)
99.4
99.6
99.8
100.0
99.5
100.0
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
VELOCITY (MM/S)
(a)
(b)

Fig. 1.

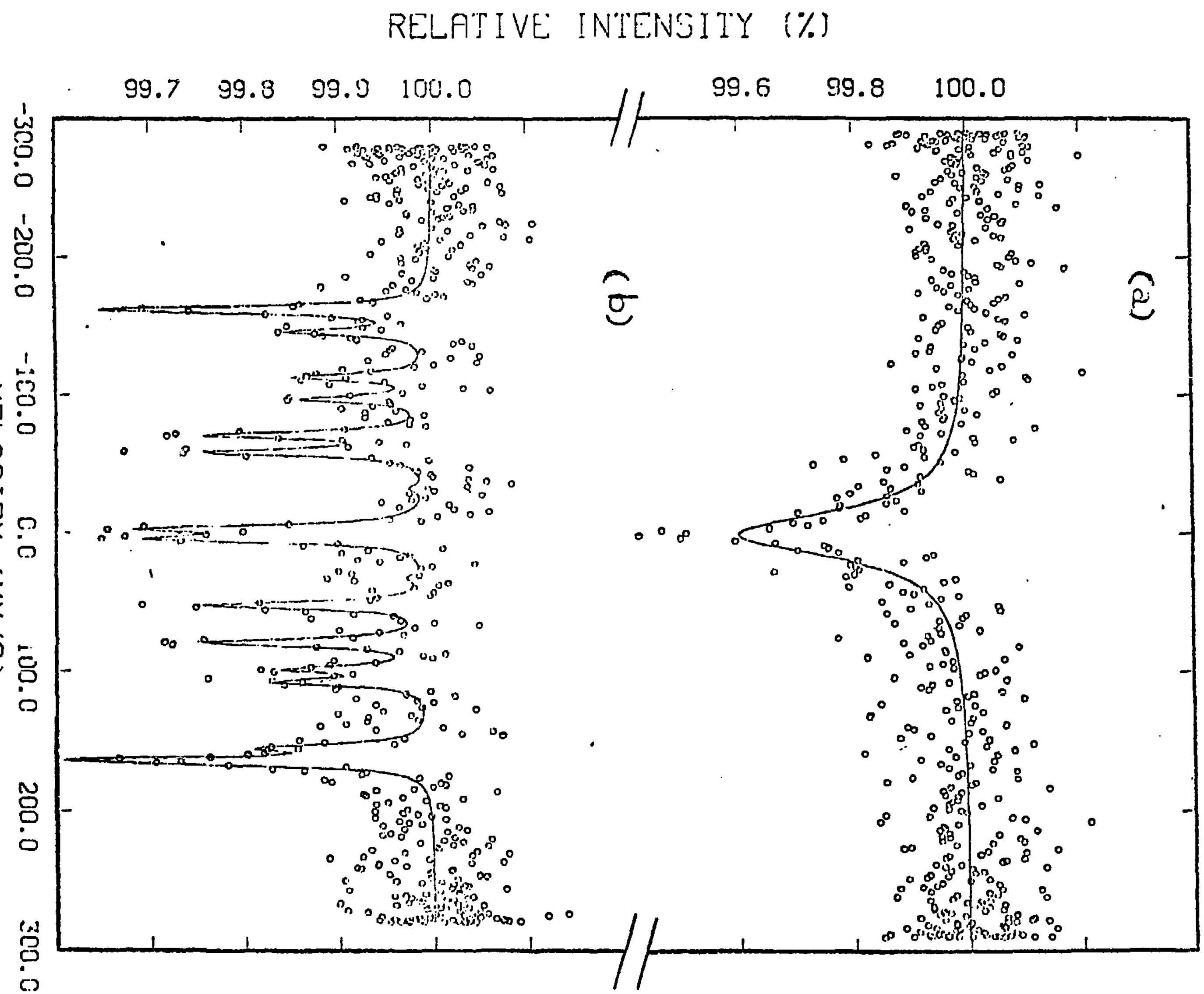

RELATIVE INTENSITY (%)
99.7
99.8
99.9
100.0
99.6
99.8
100.0
(b)
(a)
VELOCITY (MM/S)
-300.0
-200.0
-100.0
0.0
100.0
200.0
300.0

Fig. 2.