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S. K. Malik,** A. M. Umarji, and G. K. Shenoy

Materials Science and Technology Division
Argonne National Laboratory, Argonne, Illinois 60439

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MAGNETIC AND MÖSSBAUER STUDIES ON $GdCo_3B_2$ AND $DyCo_3B_2$*

S. K. Malik,** A. M. Umarji, and G. K. Shenoy

Materials Science and Technology Division
Argonne National Laboratory, Argonne, Illinois 60439

ABSTRACT

Magnetization and Mössbauer studies have been carried out on $GdCo_3B_2$ and $DyCo_3B_2$. These compounds are magnetically ordered with Curie temperatures of 56 K and 21 K respectively. The Co atoms are either nonmagnetic or carry a small moment in these compounds. The saturation moment of $DyCo_3B_2$ at 5 K is smaller than the Dy^{3+} free-ion value. From ^{161}Dy Mössbauer studies, the measured hyperfine magnetic field at the Dy site is also observed to be smaller than the free-ion value. ^{155}Gd Mössbauer measurements in $GdCo_3B_2$ reveal the presence of large crystalline electric fields at the rare-earth site. This causes the moment and the hyperfine field at the Dy site in $DyCo_3B_2$ to be reduced from its free-ion value.

I. INTRODUCTION

The RCo_3B_2 (R=rare-earth) compounds crystallize in the hexagonal $CeCo_3B_2$ type structure [1] which is obtained from the well-known RCo_5 type structure by an ordered replacement of (2c) Co atoms by B atoms. These compounds belong to a homologous family represented by the general formula $R_{n+1}Co_{3n+5}B_{2n}$ which reduces to RCo_5 for n=0 and to RCo_3B_2 for $n\to\infty$ [2]. The magnetism of RCo_5 compounds has been very thoroughly investigated [3]. In the light of interest in rare-earth ternary borides, we have investigated the magnetic behavior of RCo_3B_2 compounds. In this paper we report the results of magnetization and Mössbauer studies on $GdCo_3B_2$ and $DyCo_3B_2$. The Mössbauer effect studies provide information on local properties of the system which can be profitably used to supplement the bulk magnetic behavior.

II. EXPERIMENTAL

The compounds $GdCo_3B_2$ and $DyCo_3B_2$ were prepared by arc melting of stoichiometric amounts of the constituent elements in purified Argon atmosphere. The alloy buttons were turned over and melted several times to ensure homogeneity. The weight loss during melting was negligible. The samples were subsequently wrapped in tantalum foil and annealed in vacuum at 800°C for 7 days. Powder X-ray diffraction patterns were obtained, using CuK_α radiation, on Rigaku X-ray diffractometer equipped with a monochromator. Magnetic ordering temperatures of the compounds were determined using an ac induction method. The magnetization of these compounds was measured in the temperature range of 5 to 300 K using a SQUID magnetometer. Magnetization versus field isotherms were recorded at 5 K. We have used the 86.5 keV Mössbauer resonance in ^{155}Gd and the 25.6 keV resonance in ^{161}Dy to probe $GdCo_3B_2$ and $DyCo_3B_2$. Mössbauer spectra of Gd and Dy were obtained at 4.2 K

using conventional Mössbauer spectrometer and cryostat and with the following sources: ^{155}Eu in $SmPd_3$ (held at 4.2 K) for the ^{155}Gd resonance, and ^{161}Tb in $Dy_{0.5}Gd_{0.5}F_3$ (held at 298 K) for ^{161}Dy resonance.

III. RESULTS AND DISCUSSION

(a) Crystal Structure:

Room temperature powder X-ray powder diffraction patterns revealed that within the X-ray detection limit these compounds are single phase materials crystallizing in the hexagonal $CeCo_3B_2$ type structure. The lattice parameters obtained from the least-squares fit of observed d values are given in Table 1 and are in good agreement with those reported earlier [1]. As mentioned above, the structure of RCo_3B_2 compounds can be obtained from that of RCo_5 by an ordered replacement of the (2c) Co sites by the B atoms. The rare-earth occupies the unique (1a) site and the Co occupies the (3g) and B the (2c) site. The site symmetry at the rare-earth site is axial (6/mmm).

(b) Magnetization:

AC susceptibility measurements showed that the compounds $GdCo_3B_2$ and $DyCo_3B_2$ are magnetically ordered below 56 K and 20.6 K, respectively. Figure 1 shows the variation of magnetization of RCo_3B_2 (R=Gd, Dy) as a function of applied field at 5 K. The magnetization of $GdCo_3B_2$ shows tendency towards saturation even in a low field of 10 kOe. The magnetic moment per formula unit extrapolated to infinite field is 6.4 μ_B which may be compared with a moment of 7 μ_B for Gd^{3+} ion. It is well known that there is antiparallel coupling of rare-earth moment and 3d moment when rare-earth belongs to second half of the rare-earth series (including Gd). If the decrease in the moment

in $GdCo_3B_2$ from the value of Gd^{3+} free-ion is attributed to Co atoms then it appears that Co atoms have a low moment $\simeq 0.2\ \mu_B$ per Co. This is consistent with the low ordering temperature of the RCo_3B_2 compounds (Table 1) because the rare-earth moments are usually well-localized and interact indirectly via conduction electrons. However, Oesterreicher et al. [4] have obtained a value of 6.9 μ_B as the moment in $GdCo_3B_2$ in which case the moment on Co is nearly zero. The discrepency in the moments obtained by us and that in Ref. 4 may be due to small value of the field available in the present case. In $DyCo_3B_2$, the saturation moment is only 7.6 μ_B per formula unit. Even if 0.2 μ_B per Co is added to this, the net moment is lower than the moment of Dy^{3+} free-ion (10 μ_B). We do not expect Co moment to be substantially different in Dy compound compared to that in Gd compound. The Curie temperature of $DyCo_3B_2$ is also low. It may also be remarked that in both the compounds a small contribution to the moment may come from conduction electron polarization.

The temperature dependence of the magnetization of $GdCo_3B_2$ and $DyCo_3B_2$ in an applied field of 5 kOe is shown in Fig. 2. Magnetization shows a large drop around 56 K and 21 K for Gd and Dy compounds, respectively. These temperatures are in agreement with the ordering temperatures obtained from ac susceptibility measurements on these compounds. In the paramagnetic state the susceptibility follows Curie-Weiss behavior for $GdCo_3B_2$ with $\mu_{eff} = 8.05\ \mu_B$ and $\theta_p = 59$ K. However, for $DyCo_3B_2$, the susceptibility deviates from the Curie Weiss behavior. It is, as yet, not clear whether this is an intrinsic effect or is due to traces of impurity phases. The R-Co system has many intermetallics which order at high temperatures [3]. However, as mentioned above, no extra phases were detected in the powder X-ray patterns.

(c) Mössbauer Hyperfine Fields

Figure 3 shows the ^{155}Gd Mössbauer spectrum in $GdCo_3B_2$ at a temperature of 4.2 K. We observe a quadrupole split doublet but with no well resolved magnetic hyperfine pattern. The spectrum has been analyzed by assuming that the principal axes of electric field gradient and the hyperfine magnetic field are parallel. The least-squares fit to the Mössbauer spectrum from such an analysis is shown as the solid line in Fig. 3. The analysis yields a quadrupole interaction $e^2qQ = -1008 \pm 80$ MHz and a magnetic hyperfine field of 129 ± 20 kOe at 4.2 K. Since Gd is an S state ion, there is no contribution to electric field gradient (efg) from the aspherical 4f electrons. The efg arises from the lattice charges only. The B_2^0 term in the crystalline field Hamiltonian is related to efg and large efg implies a large B_2^0 term in the crystal fields acting on the rare-ion in RCo_3B_2 compounds. The analysis yields $B_2^0/k = -6.37$ K for Dy^{3+} in $DyCo_3B_2$, which is rather large compared to that in many other rare-earth ternary borides and sulphides [5,6].

The ^{161}Dy Mössbauer spectra in $DyCo_3B_2$ at 30 K and 4.2 K are shown in Figure 4. A well resolved hyperfine pattern is observed from which, by least square fit, a value of 4588 kOe is obtained as the field acting on Dy nuclear site. This may be compared with the free-ion value of about 5800 kOe. The reduction in the field is about the same as the reduction in the Dy moment. We attribute this reduction to the crystal field effects. Detailed calculations of crystal field effects are underway and the results will be presented elsewhere.

REFERENCES

* Work supported by the U.S. Department..

** On leave from Tata Institute of Fundamental Research, Bombay 400 005, India.

(1) K. Niihara and S. Yajima, Bull. Chem. Soc. Japan 46, 770 (1973).

(2) Y. B. Kuz'ma and N. S. Bilonishko, Kristallografiya 18, 710 (1973).

(3) See, for instance, W. E. Wallace, "Rare-Earth Intermetallics", Academic Press, New York (1973) p. 112.

(4) H. Oesterreicher, F. T. Parker, and M. Misroch, Appl. Phys. 12, 287 (1977).

(5) G. K. Shenoy, D. R. Noakes, and D. G. Hinks, Solid State Commun. 42, 411 (1982).

(6) D. R. Noakes, G. K. Shenoy, and D. G. Hinks, Phys. Rev. (submitted).

FIGURE CAPTIONS

Fig. 1. Magnetic moment per formula unit for RCo_3B_2 (R=Gd, Dy) compounds versus applied field at 5 K.

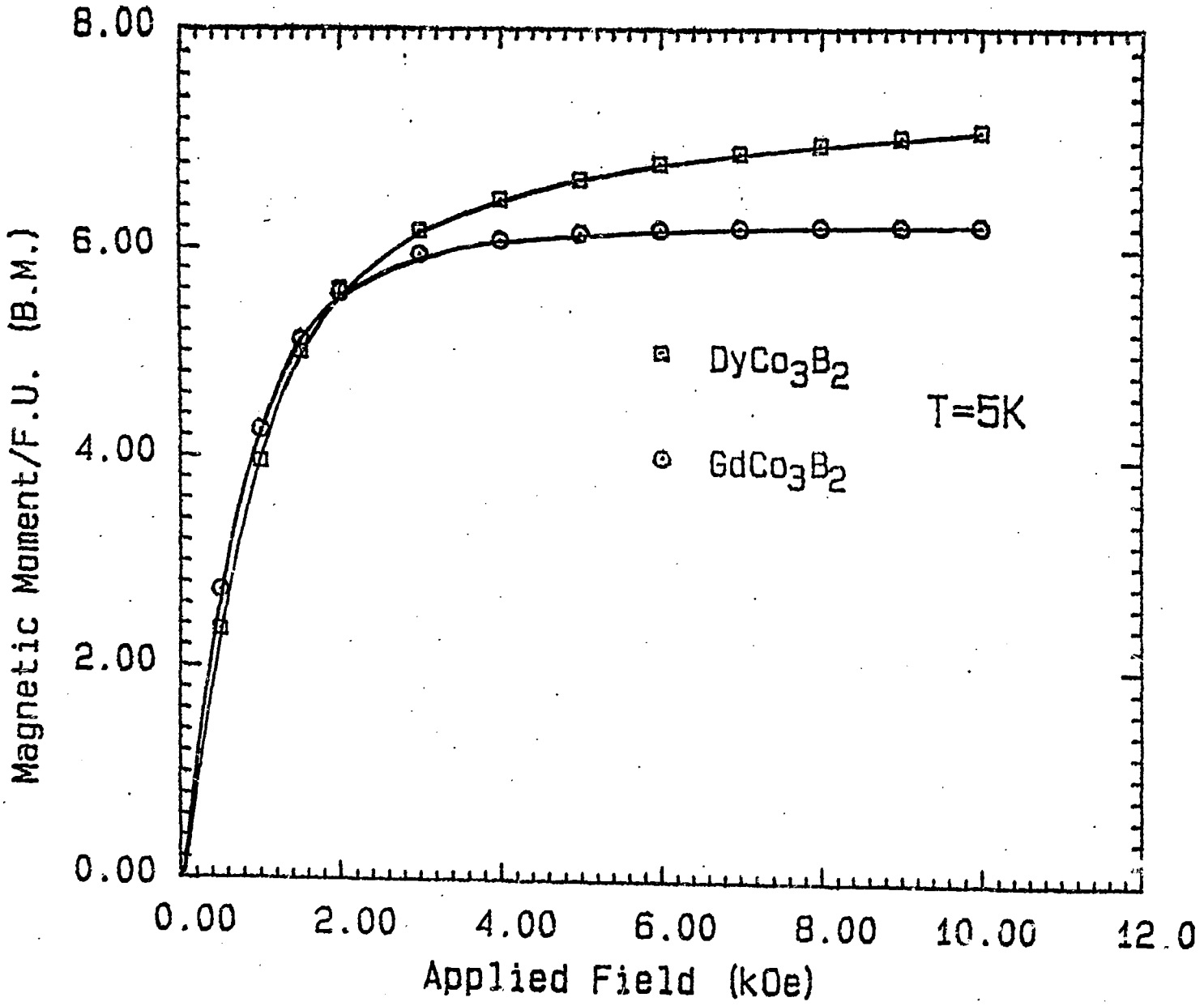
Fig. 2. Magnetic moment per formula unit for RCo_3B_2 (R=Gd, Dy) compounds versus temperature in 5 kOe applied field.

Fig. 3. ^{155}Gd Mössbauer spectrum in $GdCo_3B_2$ at 4.2 K. The solid line is a fit to the spectrum.

Fig. 4. ^{161}Dy Mössbauer spectrum in $DyCo_3B_2$ at (a) 30 K and at (b) 4.2 K. The solid lines are fit to the spectra.

Table I

	$GdCo_3B_2$	$DyCo_3B_2$
a(Å)	5.065	3.005
c(Å)	5.060	3.023
T_c(K)	56	20.6
Moment/f.u. (μ_B)	6.4	7.6
e^2qQ (MHz)	-1008 ± 80	727 ± 80
H(R) (kOe)	129 ± 20	4588 ± 100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GdCo3B2
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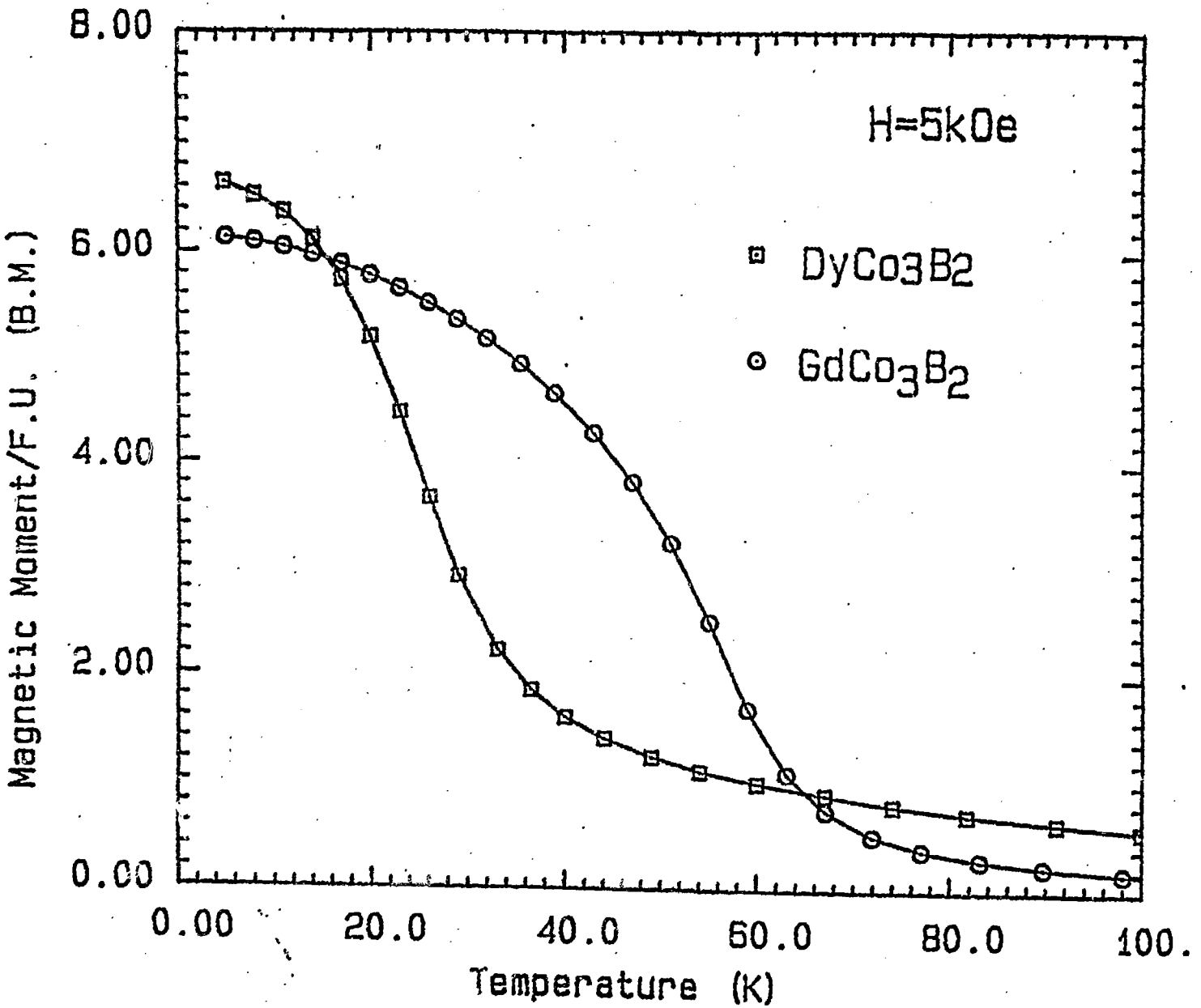
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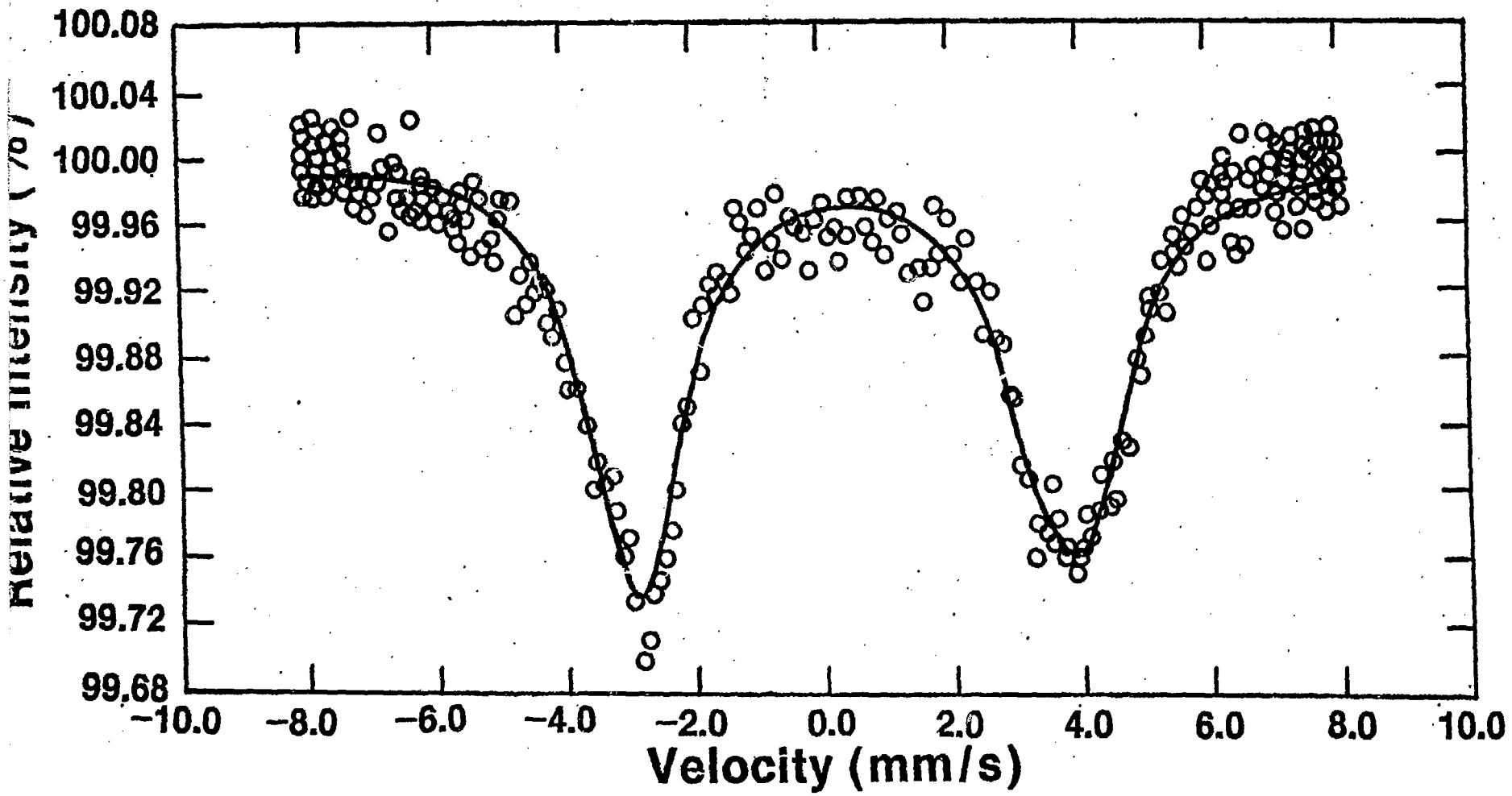
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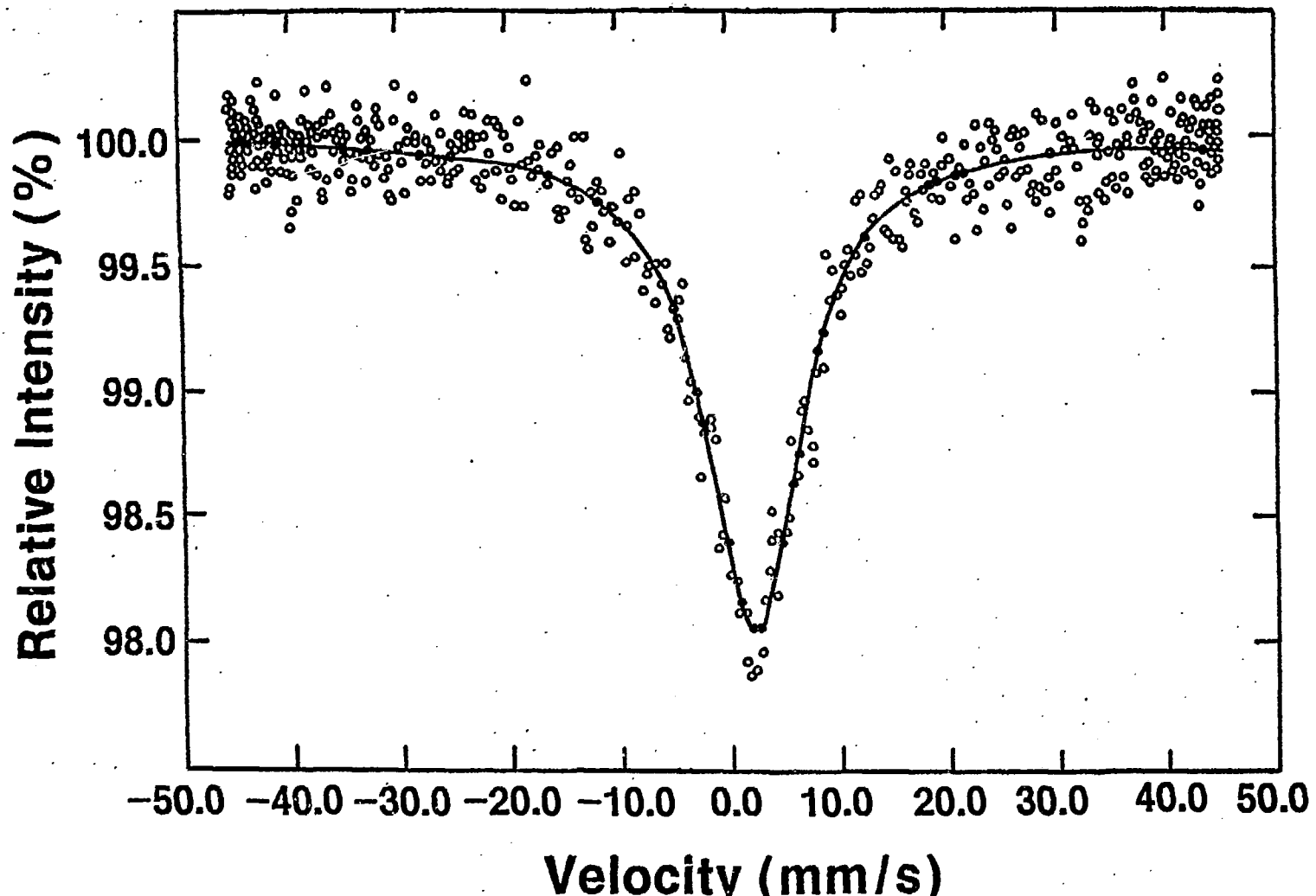
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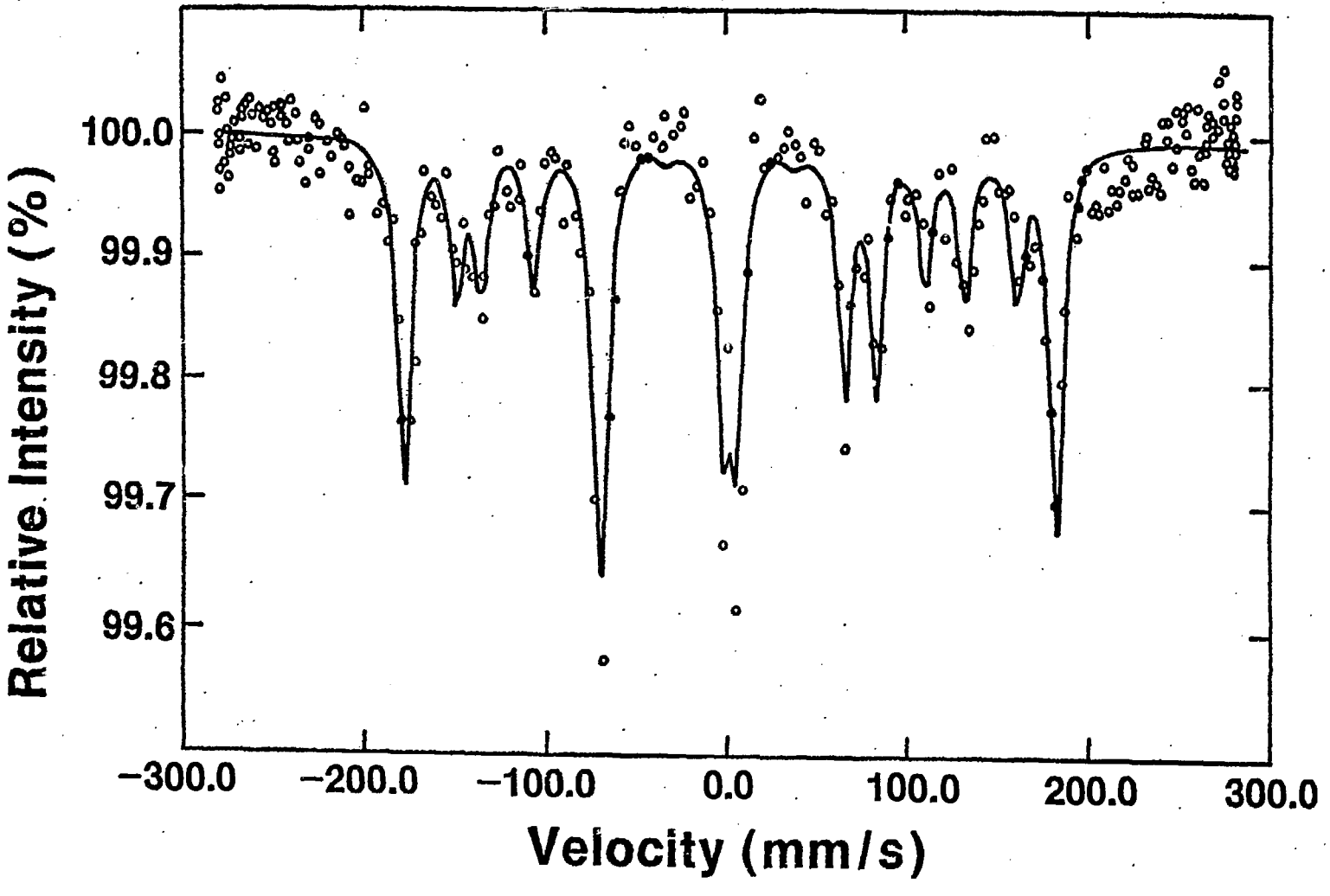
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300.0
Velocity (mm/s)