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# Mössbauer Effect in $Dy^{161}$ in $DyCo_2$ and $DyNi_2$†

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The recoilless absorption spectra of the 26-keV $\gamma$ rays from $Dy^{161m}$ in $Dy^{161}$ situated in $DyNi_2$ and in $DyCo_2$ were measured at various temperatures. A value of $(-866\pm30)$ Mc/sec was found for the magnetic hyperfine constant $(g_0\mu_n H_{\rm eff})$ of the ground state of $Dy^{161}$ in $DyCo_2$ at 4°K. This value is about 4% higher than the free-ion value calculated for the $Dy^3{}_+$ ions in the fully magnetized state $(J_z=J)$ from data on electron spin resonance in dilute salts. For $Dy^{161}$ in $DyNi_2$, a value of $(-818\pm30)$ Mc/sec was found for $g_0\mu_n H_{\rm eff}$ at 4°K. This value corresponds to an ionic magnetic moment of $(9.8\pm0.3)\ \mu_B$, which is higher than that obtained by magnetic measurements ($7.1\ \mu_B$) and indicates probably that the Ni sublattice contributes to the total magnetization by an antiferromagnetic coupling. The isomeric shifts of Dy metal, $DyFe_2$, $DyNi_2$, and $DyCo_2$ absorbers were found to be the same within the experimental errors ($1.9\pm0.2$ mm/sec relative to $Dy_2O_3$).

## I. INTRODUCTION

In this work the recoilless absorption spectra of the 26-keV $\gamma$ rays from $Dy^{161m}$ in $Dy^{161}$, situated in $DyNi_2$ and $DyCo_2$ have been measured at various temperatures. These compounds belong to the family of the Laves compounds of the type $LnM_2$ which have cubic symmetry. Here Ln is a lanthanide ion (usually tripositive) and M can be one of several possible other ions. When M is an ion of the *3d* group, it may have a magnetic moment of its own. In a previous work,[1] $DyAl_2$ and $DyFe_2$ belonging to this family of compounds were investigated, using the Mössbauer effect technique. In that work, it was found that the values of $H_{\rm eff}$ at magnetic saturation are the same, within experimental errors, for $DyAl_2$ and Dy metal and that these values are in very good agreement with the free-ion value calculated for the $Dy^{3+}$ ions in the fully magnetized state $(J_z=J)$ from data on electron spin resonance in dilute salts.[2] The magnetic field acting on the Dy nucleus in $DyFe_2$ at magnetic saturation was found to be $(14\pm2)\%$ higher than in Dy metal.

Bulk magnetization measurements of $DyCo_2$ were carried out by Ross and Crangle.[3] They found that the Curie temperature of $DyCo_2$ is about 150°K and that the magnetic moment of $DyCo_2$ at saturation is about $6.7\ \mu_B$ (as compared to the free-ion value of $10\ \mu_B$). They explained the value obtained for the magnetic moment by assuming that the cobalt spins are aligned oppositely to the rare-earth moments, and equal to $1.7\ \mu_B$ per cobalt atom. The present experimental results support these assumptions.

Bulk magnetization measurements of $DyNi_2$ were carried out by Skrabek and Wallace.[4] They found that the Curie temperature of this compound is 32°K and that its magnetic moment at saturation is $7.1\ \mu_B$. Bleaney[5] explained the magnetic properties of $DyNi_2$ (and other $LnNi_2$ compounds) by assuming that the Ni is neutral and that the magnetic moment of the Dy ion in $DyNi_2$ is lower than the free-ion value because of crystalline field effects. One of the main purposes of the present work was to check the correctness of Bleaney's assumptions. The present measurements show that the value of $H_{\rm eff}$ acting on the Dy ion in $DyNi_2$ at 4°K is very close to the free-ion value and are therefore in disagreement with Bleaney's assumptions.

The isomer shifts between the various absorbers used and $Dy_2O_3$ were also determined. As the isomer shifts are expected to depend on the values of the wave functions of the *6s* conduction electrons at the Dy nucleus, it is possible to estimate from these measurements the relative values of $|\psi_{6s}(0)|^2$ in the various compounds used. Such an estimate contributes to the understanding of the nature of intermetallic bonding.

## II. EXPERIMENTAL DETAILS

The source used was $Tb^{161}$ in the form of $Tb_2O_3$ which emitted an unsplit line at room temperature. It was produced by neutron irradiation of $Gd_2O_3$ containing enriched $Gd^{160}$ of 90% isotopic abundance.

The absorbers were: 100 mg/cm² $DyNi_2$ and 150 mg/cm² $DyCo_2$. The intermetallic compounds were prepared by melting stoichiometric amounts of nickel or cobalt and dysprosium (of natural abundance). This was done in an induction furnace using a quartz crucible and an argon atmosphere. The 26-keV $\gamma$ rays were detected, either by a 1 mm thick NaI(Tl) scintillation counter with a 0.001-in. aluminum window or by an argon-methane proportional counter. For the comparison of isomer shifts, measurements were also carried out with $DyFe_2$, $DyAl_2$, and Dy metal absorbers.

The absorption as a function of relative velocity between source and absorber was recorded automati-

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TABLE I. Results for the hyperfine interactions observed in $DyCo_2$ and $DyNi_2$.

| Absorber | Temperature °K | $g_0\mu_nH_{\rm eff}/h$ Mc/sec | $g_1\mu_nH_{\rm eff}/h$ Mc/sec | $eqQ_0/4h$ Mc/sec | $eqQ_1/4h$ Mc/sec | $g_1/g_0$ | $Q_1/Q_0$ |
|---|---|---|---|---|---|---|---|
| $DyCo_2$ | 77 | 765±50 | 895±50 | 460±70 | 520±70 | 1.17±0.10 | 1.13±0.15 |
| $DyCo_2$ | 20 | 860±50 | 1020±50 | 570±70 | 630±70 | 1.19±0.10 | 1.10±0.15 |
| $DyCo_2$ | 4 | 890±50 | 980±50 | 540±70 | 620±70 | 1.10±0.10 | 1.15±0.10 |
| $DyNi_2$ | 4 | 800±50 | 995±50 | 590±50 | 640±50 | 1.24±0.10 | 1.08±0.10 |

cally on a multichannel pulse-height analyzer as described previously.[6,7]

In all the measurements, the source was at room temperature. The absorbers were kept at 77, 20, or 4°K by placing them in liquid-nitrogen, liquid-hydrogen, or liquid-helium cryostats.

## III. EXPERIMENTAL RESULTS

### A. Hyperfine Fields

Absorption spectra of $DyCo_2$ were measured at 4, 20, 77, and 300°K. The absorption spectrum obtained at 20°K is shown in Fig. 1. The spectra obtained at 4 and 77°K were very similar in general shape to that obtained at 20°K and to those obtained previously with ferrimagnetic compounds of Dy as absorbers of the 26-keV $\gamma$ rays.[1,8] In the absorption spectrum of $DyCo_2$ at 300°K a single unsplit absorption line was obtained. With the $DyNi_2$ absorber, measurements were carried out at 4, 20, 77, and 300°K, but only the spectrum at 4°K showed resolved lines (Fig. 2), at 20°K, a relatively broad spectrum was obtained but no resolved lines could be identified. At 77 and 300°K single unsplit absorption lines were observed (Fig. 3). The identification of the lines and the methods of the analysis of the data were the same as those which had been used in the previous works. It was assumed that the energy of each sublevel is given by

$$W=\Delta E-mg\mu_nH_{\rm eff}+eqQ[3m^2-I(I+1)]/[4I(2I-1)],$$

where $g$ is the gyromagnetic ratio of the level and $Q$ its quadrupole moment. Table I shows the results of a least-squares analysis of the experimental peak positions giving $g\mu_nH_{\rm eff}$ and $eqQ/4h$ for both the ground state $(g_0,Q_0)$ and the first excited state $(g_1,Q_1)$. The problem of the determination of the signs of the hyperfine splitting parameters was discussed in Ref. 1. The values of $g_1/g_0$ and $Q_1/Q_0$ determined from the separate measurements are consistent with each other and with the values obtained from recoilless absorption measurements carried out with Dy metal, $DyFe_2$ and $DyAl_2$ absorbers.[1] The average value deduced for $g_1/g_0$ from the present measurements and from those described in Ref. 1 is $-1.18\pm0.03$. The value is consistent with a recent value of $-1.21\pm0.03$ given by Nowik and Wickman.[9] The average value of $Q_1/Q_0$ was determined to be 1.03 ±0.06. In column 3 of Table II, the experimental results for the over-all splittings $[(5|g_0|+5|g_1|)\mu_nH_{\rm eff}]$ are given. In addition the over-all splittings obtained previously for Dy metal,[1] $DyFe_2$,[1] $DyAl_2$,[1] $DyNi_5$,[10] and $DyCo_5$[10] are included in the table. For the various absorbers and temperatures the over-all splitting, which can be determined quite accurately, are proportional to the value of $H_{\rm eff}$. The values of $g_0\mu_nH_{\rm eff}/h$ given in the 4th column of Table II were deduced from the over-all splittings taking into account the measured value of $g_1/g_0$ $(-1.18\pm0.03)$. It was shown in Ref. 1 that the value of $H_{\rm eff}$ in Dy metal at magnetic saturation is very close to the free-ion value calculated from data on electron spin resonance in dilute salts. In the last column of Table II the ratios of the measured over-all splittings to that obtained previously for Dy metal at 20°K are given. These numbers represent therefore the ratios of the internal magnetic fields to the free-ion values.

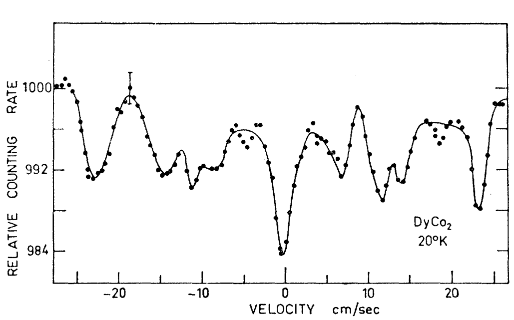

FIG. 1. The absorption by $DyCo_2$ at 20°K of the 26-keV $\gamma$ ray emitted in the decay of $Tb^{161}$, as a function of relative velocity between source and absorber.

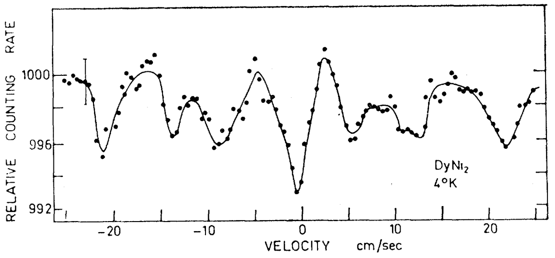

FIG. 2. The absorption by $DyNi_2$ at 4°K of the 26-keV $\gamma$ ray emitted in the decay of $Tb^{161}$, as a function of relative velocity between source and absorber.

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TABLE II. Results for over-all splittings of various ferrimagnetic compounds of dysprosium.

| Absorber | Temperature (°K) | Over-all splittings cm/sec | $g_0\mu_n H_{\mathrm{eff}}$ Mc/sec from over-all splittings | $H_{\mathrm{eff}}$ relative to the free-ion value |
|---|---|---|---|---|
| $DyCo_2$ | 77 | 40.4±0.6 | −767±30 | 0.94±0.02 |
| $DyCo_1$ | 20 | 45.5±0.6 | −864±35 | 1.04±0.02 |
| $DyCo_2$ | 4 | 45.6±0.6 | −866±30 | 1.04±0.02 |
| $DyNi_2$ | 4 | 43.1±0.6 | −818±30 | 0.98±0.02 |
| Dy metal | 20 | 43.7±0.5[a] | −830±30 | |
| $DyFe_2$ | 20 | 49.7±0.5[a] | −944±30 | 1.14±0.02 |
| $DyAl_2$ | 4 | 44.3±0.5[a] | 841±30 | 1.01±0.02 |
| $DyCo_5$ | | | | 1.04[b] |
| $DyNi_5$ | | | | 0.95[b] |

[a] Reference 1.
[b] Reference 10.

The magnetization measurements of $DyCo_2$ carried out by Ross and Crangle[3] indicated that the $Dy^{3+}$ ion in $DyCo_2$ is magnetically saturated at temperatures below 20°K. This is also proved from our measurements by the fact that the over-all splittings measured for $DyCo_2$ at 4 and at 20°K were identical (45.5 cm/sec). We may therefore conclude that the ratio of the value of $H_{\mathrm{eff}}$ acting on the Dy nucleus in $DyCo_2$ at magnetic saturation to the free-ion value is 1.04±0.02.

The Curie temperature of $DyNi_2$ is 32°K.[4] The present experimental results show that the ratio of the value of $H_{\mathrm{eff}}$ acting on the Dy nuclei in $DyNi_2$ at 4°K to the free-ion value is 0.98±0.02. As it is possible that at 4°K the Dy ion is not completely magnetically saturated, we may conclude that the value of this ratio at magnetic saturation of $DyNi_2$ is not lower than 0.98±0.02.

### B. Isomer Shifts

The present isomer-shift measurements, except that of $DyFe_2$, were carried out at temperatures above the Curie points of the absorbers, as more accurate values for the isomer shifts may be obtained from unsplit lines than from complex spectra. We have also repeated the previous isomer-shift measurements[1] in Dy metal, $DyAl_2$, and $DyFe_2$ with higher accuracy than done before. In Fig. 3 the unsplit absorption spectra obtained with Dy metal, $DyNi_2$, $DyCo_2$, and $DyAl_2$ absorbers are shown. The isomer shifts were determined by calculating the positions of the centroids of the absorption lines. The results obtained for the isomer shifts are given in Table III. The new results obtained with the $DyFe_2$ absorber showed that those quoted in Ref. 1 for the isomer shift in $DyFe_2$ were wrong. The measurements described in Ref. 1 were carried out at 730°K and we now conclude that at that temperature the $DyFe_2$ sample, which was heated in an oven, was oxidized.

TABLE III. Isomer shifts for various dysprosium absorbers.

| Absorber | Temperature (°K) | $\Delta E$ mm/sec |
|---|---|---|
| Dy metal | 300 | 1.9±0.2 |
| Dy metal | 500 | 1.8±0.4 |
| $DyCo_2$ | 300 | 1.7±0.2 |
| $DyNi_2$ | 300 | 1.7±0.2 |
| $DyNi_2$ | 77 | 2.1±0.2 |
| $DyAl_2$ | 300 | 0.6±0.2 |
| $DyAl_2$ | 77 | 0.5±0.2 |

The present measurement of the isomer shift in $DyFe_2$ was carried out at 300°K. At that temperature the material is ferrimagnetic and the absorption spectrum extends to velocities of about[11] 15 cm/sec in each direction. In the measurement shown in Fig. 4, the velocity range was −1 to +1 cm/sec. This means that in Fig. 4 only the central peak of the total split spectrum is seen. This central peak is composed of two sub-lines (as is also seen from Fig. 4), corresponding to the transitions $-\frac{1}{2}\rightarrow+\frac{1}{2}$, $+\frac{1}{2}\rightarrow-\frac{1}{2}$.

The positions $W_1$ and $W_2$ of the two sub-lines can be expressed in terms of the splitting parameters of the ground level and the 25.6-keV level and of $\Delta E$, in the form

$$W_1=\Delta E+1/2g_1-1/2g_0+\tfrac{1}{5}eq(Q_1-Q_0)$$

and

$$W_2=\Delta E+1/2g_0-1/2g_1+\tfrac{1}{5}eq(Q_1-Q_0).$$

The position of the centroid of the two sub-lines is therefore given by

$$\Delta E+\tfrac{1}{5}eq(Q_1-Q_0)=\Delta E+\tfrac{1}{5}eqQ_0(Q_1/Q_0-1).$$

The centroid of the central absorption line of $DyFe_2$ at

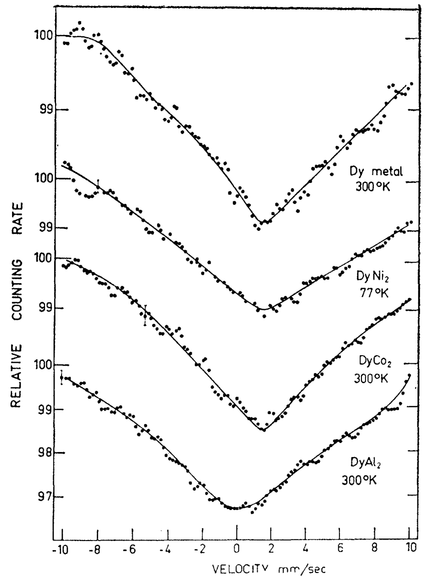

FIG. 3. The absorption of $DyAl_2$, $DyCo_2$, and Dy metal at 300°K and of $DyNi_2$ at 77°K, as a function of relative velocity between source and absorber.

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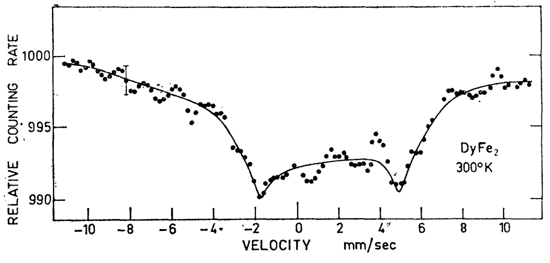

FIG. 4. The central part of the absorption spectrum of $DyFe_2$ at room temperature as a function of relative velocity between source and absorber. (Range of velocities $-1$ to $+1$ cm/sec.)

room temperature was found in the present measurements to be at $(1.6\pm0.2)$ cm/sec. Relying on the values of $eqQ_0$ and $eqQ_1$ obtained by Bauminger *et al.*, for $DyFe_2$ at room temperature ($\frac{1}{4}eqQ_0\sim\frac{1}{4}eqQ_1\sim300$ Mc/sec)[11] and on the known ratio of $Q_1/Q_0$ $(0.98\pm0.03)$,[10] one gets for $\Delta E$ the value $(1.8\pm0.6)$ mm/sec.

## IV. CONCLUSIONS

### A. Hyperfine Interaction in $DyCo_2$ and $DyNi_2$

The saturation value of the magnetic hyperfine interaction in $DyCo_2$ is higher by about 4% than the free-ion value. This is consistent with the idea that in rare-earth intermetallic compounds with $3d$ transition metals having high magnetic moments there is an additional contribution to $H_{\text{eff}}$. Similar effects were observed in $DyFe_2$,[1] $TmFe_2$,[12] $ErFe_2$,[13] and $DyCo_5$.[10] These effects are probably a result of a supplementary contribution to the magnetic field of the $4f$ electrons caused by core and conduction electrons of the rare-earth ions polarized by the $d$ electrons of the iron or cobalt ions.

According to bulk magnetization measurements the magnetic moment of $DyCo_2$ at magnetic saturation is 6.7 $\mu_B$,[3] whereas, the theoretical saturation moment of Dy is 10 $\mu_B$. Relying on these measurements and assuming that the dysprosium sublattice is coupled antiferromagnetically to the cobalt sublattice, a value of about 1.6 $\mu_B$ is obtained for the magnetic moment of the Co ion in $DyCo_2$. This is consistent with the value deduced from the magnetization measurements of $ACo_2$[3] and[14] $ACo_5$ compounds containing the heavier rare earths (whose quantum number $J=L+S$).

The observed effective magnetic field acting on Dy nuclei in $DyNi_2$ at 4°K is 98% of the free-ion value. This corresponds to a magnetic moment of 9.8 $\mu_B$. The value of the magnetic moment of $DyNi_2$ derived from bulk magnetization measurements is 7.1 $\mu_B$.[4] It is possible that with the magnetic fields used in the magnetization measurements, the orientation of the domains was not completely achieved and that the value of the magnetic moment of $DyNi_2$ is larger than that quoted. However, if we assume that saturation was reached during the bulk magnetization measurements, the present results show that the nickel sites in $DyNi_2$ carry a moment above 2.5 $\mu_B$, in disagreement with the assumption that the Ni is neutral in this compound. Bleaney's theoretical calculations of the magnetic properties of $DyNi_2$ were based on the assumptions that the Ni is neutral and that the magnetic moment of the Dy ion in $DyNi_2$ is lower than the free-ion value.[5] The present experimental results are not consistent with these assumptions and suggest that crystalline field effects are not important in Dy metal and in the intermetallic compounds investigated.

### B. Isomer Shifts

The isomer shift between the intermetallic compounds of Dy and $Dy_2O_3$ is probably caused by the $6s$ conduction electrons of the intermetallic compounds. The isomer shift is given approximately by the expression[15]

$$\Delta E=\tfrac{1}{5}(4\pi Ze^2r^2)S'(Z)(\Delta r/r)\{\Delta[\psi^2(0)]\}.$$

Here $r$ is the nuclear radius, $S'(Z)$ is the relativistic factor equal to about 4 for dysprosium and $\Delta r/r$ is the relative difference in charge radii of the nuclear excited and ground states. In our case, $\Delta[\psi^2(0)]$ is equal to $|\psi_{6s}(0)|^2$ in the metallic compound. The present results indicate that $|\psi_{6s}(0)|^2$ is, within the experimental errors, the same for Dy metal, $DyNi_2$, $DyCo_2$, and $DyFe_2$. The isomeric-shift measurement with the $DyAl_2$ show that for this compound the value of $|\psi_{6s}(0)|^2$ is smaller by at least a factor of 2 than its value for Dy metal, $DyNi_2$, $DyCo_2$, and $DyFe_2$. Estimates for $\Delta r/r$ derived from the isomer-shift measurements were given in Ref. 1.

## ACKNOWLEDGMENT

We would like to thank A. Mustachi for synthesizing the $DyNi_2$ and $DyCo_2$ samples used in the present work.

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