CONF-780868--4

CRYSTAL FIELD AND MAGNETIC PROPERTIES OF $Dy(OH)_3$, $Ho(OH)_3$ AND $Er(OH)_3$

by

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Prepared for

International Conference on the
Applications of the Mossbauer Effect

Kyoto, Japan

August 28 - September 1, 1978

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

Crystal Field and Magnetic Properties of $Dy(OH)_3$, $Ho(OH)_3$ and $Er(OH)_3$*

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Résumé

Les interaction hyperfines quadrupolaire et magnétique déduites par spectroscopie Mössbauer de ^{161}Dy dans des cristaux de $Dy(OH)_3$ et de ^{166}Er dans $Ho(OH)_3$ et $Er(OH)_3$ sont interprétées à l'aide des modèles du champ cristallin et du champ d'échange moléculaire. Les paramètres de champ cristallin établis par spectroscopie optique permettent de rendre compte des paramètres d'interactions hyperfines. Les propriétés électroniques et magnétiques de ces composés isolants ferromagnétiques sont bien interprétées à l'aide de ce modèle.

Abstract

The electric quadrupole and magnetic hyperfine interactions measured from the ^{161}Dy Mössbauer resonance in crystalline $Dy(OH)_3$ and from the ^{166}Er resonance in crystalline $Ho(OH)_3$ and $Er(OH)_3$ are interpreted using the crystal field and molecular exchange field model. The crystal field parameters established from previous optical spectroscopy results account well for these hyperfine parameters. The crystal-field and magnetic properties of these ferromagnetic insulators are described well within the model.

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*Work performed under the auspices of the U. S. Department of Energy.

+On leave from Centre de Recherches Nucléaires, Strasbourg, France

1. INTRODUCTION

The crystalline heavy rare-earth hydroxides $RE(OH)_3$ provide an interesting opportunity for the interpretation of hyperfine interaction parameters in terms of the crystalline electric-field (CEF) and magnetic exchange field models. These compounds crystallize in a simple hexagonal structure with an axial symmetry at the RE site (C_{3h} point symmetry) [1]. Some of them exhibit a ferromagnetic order in the liquid helium temperature range [2,3] with the highly anisotropic moments along the crystal c axis. Detailed magnetization, specific heat and optical data have been reported [2,3]. From these results information about the CEF effects and the magnetic exchange mechanisms was inferred. We report here the measurements of the hyperfine interaction parameters at the Dy^{3+} and Er^{3+} rare earth sites in the ferromagnetic insulators $Dy(OH)_3$ and $Ho(OH)_3$ respectively and compare the results with those calculated from the crystal field wave functions computed on the basis of the optical spectroscopy results. Also the Er^{3+} ion is investigated in the paramagnetic $Er(OH)_3$ host.

2. EXPERIMENTAL

The crystalline rare-earth hydroxides were prepared by hydrothermal synthesis and checked from X-ray Debye-Scherrer and chemical analyses [4]. The 26 keV Mossbauer measurements of ^{161}Dy were performed using a source of $^{160}Gd_{0.5}\,^{162}Dy_{0.5}F_3$ at 300 K with the absorber at temperatures between 300 and 1.5 K. The 81 keV resonance of ^{166}Er was measured in $Er(OH)_3$ against the single-line source of Ho-Y-H_2 at 10 K. The ^{166}Er source experiments in $Ho(OH)_3$ were performed with a neutron activated sample of $Ho(OH)_3$ against a single-line absorber of ErH_2 at 4.2 K.

3. RESULTS

The ^{161}Dy resonance data in Dy(OH)$_3$ reveal a single line at 300 K and 77 K. At 4.2 K one observes a hyperfine magnetic spectrum with broadened lines due to paramagnetic relaxation effects. Below the Curie temperature of 3.5 K the magnetic pattern sharpens, with a width of 8 mm/s (Fig. 1). The hyperfine interaction parameters deduced at 1.7 K are (a) hyperfine field, H_{hf}, of 5500 ± 100 kOe and (b) quadrupole coupling constant, e^2q_zQ, of 2360 ± 60 MHz. H_{hf} is along the principal axis of the electric-field-gradient (EFG) tensor, i.e. parallel to the crystal c axis.

Ho(OH)$_3$ has been investigated by using the ^{166}Er impurity resonance fed by the radioactive decay of ^{166}Ho. The broad single emission line of 27 mm/s width measured in the paramagnetic region remains basically unaltered in the ferromagnetic state below T_c = 2.54 K.

For the paramagnetic Er(OH)$_3$ absorber a slightly broadened single resonance line of 11 mm/s width is observed at both 4.2 and 1.5 K.

4. CRYSTAL FIELDS AND HYPERFINE INTERACTIONS

In the C_{3h} point symmetry of these materials, the ground J multiplet of the RE ion is split by the CEF and the magnetic exchange interactions according to the Hamiltonian:

$$\mathcal{H}=\mathcal{H}_{CEF}+\mathcal{H}_{exch} = B_2^0\,O_2^0 + B_4^0\,O_4^0 + B_6^0\,O_6^0 + B_6^6\,O_6^6 - g_J\mu_B\,\vec{J}\cdot\vec{H}_{mol} \qquad (1)$$

where the B_n^m are CEF parameters and the O_n^m are Stevens operators. H_{mol} is the molecular field in the magnetic state of the material. The electronic wave-functions (Γ_i) and energy splittings (E_i) can be calculated with the knowledge of the CEF parameters and H_{mol}. Thus, the electric field gradient

(q_{4f}) corresponding to each of the levels is given by:

$$q_{4f}(\Gamma_i) = -(1 - R) <J||\alpha||J><\Gamma_i|3J_z^2 - J(J + 1)|\Gamma_i><r^{-3}>_{4f} \qquad (2)$$

where $<J||\alpha||J>$ is the Stevens factor (equal to −0.00635 and 0.00254 for Dy^{3+} and Er^{3+} respectively) and R is the inner Sternheimer factor. The radial average $<r^{-3}>_{4f}$ over the 4f distribution is taken to be 9.619 and 11.24 a.u. for Dy^{3+} and Er^{3+} [5].

In addition to the ion's own contribution to the EFG one has to consider the contribution from the electrostatic charges spread through the lattice (q_{1at}). The EFG component along one of the axes is $q = q_{4f}(T) + q_{1at}$. In all the systems under investigation q_{1at} can be estimated from the EFG measured at the Gd^{3+} ion is in the isostructural compound $Gd(OH)_3$. This is so because the Gd^{3+} ion is in an orbital S state ion for which the 4f contribution (eq. 2) vanishes to zero. Therefore, the quadrupole coupling constant $e^2q_{1at}Q$ at the Dy^{3+} and Er^{3+} sites in the respective $RE(OH)_3$ is estimated simply by scaling the experimental value in $Gd(OH)_3$ (−221 MHz) [6] by the ratio of the quadrupole moments. This makes a common assumption that the lattice antishielding factor (γ_∞) is the same for all three RE ions. The lattice EFG can also be obtained from the second-order CEF component (B_2^0) [7]:

$$q_{1at} = (1 - \gamma_\infty)\, q'_{1at} = -\frac{(1 - \gamma_\infty)}{(1 - \sigma_2)} \; \frac{4B_2^0}{<J||\alpha||J><r^2>_{4f}} \; . \qquad (3)$$

where σ_2 is a shielding coefficient for the free-ion radial distribution

$\langle r^2 \rangle_{4f}$. However, lack of reliable knowledge of σ_2 makes this procedure less reliable.

The hyperfine field acting at the nucleus in an insulator for a CEF state Γ_i is expressed as a sum of an orbital term and of a core polarization term [5]. The core polarization term has been found to be negligibly small from spin-polarized atomic calculations [8]. The orbital contribution itself is proportional to $\langle \Gamma_i | J_z | \Gamma_i \rangle$ and hence to the magnetic moment of the CEF state in question. Thus,

$$H_{hf}(\Gamma_i) = 2\mu_B \langle r^{-3} \rangle_{4f} \langle J || N || J \rangle \langle \Gamma_i | J_z | \Gamma_i \rangle \qquad (4)$$

where the matrix element $\langle J || N || J \rangle$ is 0.71 and 0.78 for Dy^{3+} and Er^{3+} ions respectively.

If more than one Γ_i level is occupied at a given temperature a thermal average of the hyperfine parameters for the occupied levels is taken, provided a dynamical equilibrium is achieved in these states.

5. DISCUSSION

5.1 $Dy(OH)_3$

The CEF parameters for $Dy(OH)_3$ have been reported from optical spectroscopy work [2]. They are $B_2^0 = -1.91$ K, $B_4^0 = 6.43 \times 10^{-3}$ K, $B_6^0 = -5.97 \times 10^{-5}$ K, and $B_6^6 = 8.07 \times 10^{-4}$ K. These can be used in eq. 1 to deduce Γ_i and E_i provided the value of the molecular field is known. The knowledge of Γ_i and E_i then permits one to obtain $e^2 q_{4f} Q$ and H_{hf} using eqs. 2 and 4.

Since H_{mol} is not know a priori, we have made it a parameter in the calculations used to compute the hyperfine interactions. In Fig. 2 we show the variation in the value of the quadrupole interaction and magnetic hyperfine field (reduced by their free ion values) as a function of H_{mol} with the above CEF values. The best value of H_{mol} will then be that which reproduces the experimental data for H_{hf} and $e^2q_{4f}Q$. As pointed out earlier, $e^2q_{4f}Q$ is obtained by substracting the lattice contribution $e^2q_{1at}Q$ from the measured quadrupole interaction. The lattice contribution is found to be -327 MHz by scaling from the value in $Gd(OH)_3$ as described in the last section. A similar value of $e^2q_{1at}Q$ is obtained from eq. 3 provided we use $(1 - \gamma_\infty)/(1 - \sigma_2) = 112$. This value is somewhat smaller than that reported in the literature [9]. The arrows in Fig. 2 indicate the experimental vlaues of $H_{hf} = 5500$ kOe and $e^2q_{4f}Q = 2690$ MHz, or 0.85 and 0.87 respectively in terms of their free ion values. The best choice for H_{mol} is 4.5 ± 0.5 kOe (Fig. 2).

In a ferromagnet one can estimate the molecular field from the knowledge of the transition temperature and the ground state magnetic moment [10]. This is found to be 6 kOe, in fair agreement with the value deduced from the experiments. $Dy(OH)_3$ orders primarily due to the dipolar interaction between the Dy^{3+} spins. The molecular field based on a dipolar sum calculation [2] also agrees with our deduction.

5.2 $Ho(OH)_3$ and $Er(OH)_3$

The primary result of our study in $Ho(OH)_3$ in its ferromagnetic state (with the Ho^{3+} moments parallel to the c-axis) is the absence of measureable hyperfine interactions at the Er^{3+} impurity ion. In order to seek an explanation for this we have performed CEF calculations in the same fashion as discussed above for $Dy(OH)_3$.

We shall assume that the CEF parameters at the Er^{3+} ion in $Ho(OH)_3$ are the same as those measured from optical spectroscopy [3] in $Er(OH)_3$.

In the absence of a molecular field this leads to the following ground doublet for the Er^{3+} ion: $|\Gamma_0\rangle = \pm 0.6796|\mp 5/2\rangle \mp 0.7336|\pm 7/2\rangle$, which gives g values of $g_{||} = 1.69$ and $g_{\perp} = 8.76$. The first excited CEF level is at 96 K. As has been shown in the last section the molecular field can be estimated from the value of the transition temperature, (2.54 K for $Ho(OH)_3$). Such an estimate gives $H_{mol} \simeq 4$ kOe. This field will act on the Er^{3+} ion along the c-axis of the host $Ho(OH)_3$ in its ferromagnetic state along with the crystal field, and has been included in Eq. (1) for a calculation of the CEF levels. At 1.7 K this calculation yields a hyperfine magnetic field of 190 kOe, which is only about 2% of the free-ion value. The value of $e^2q_{4f}Q$ using Eq. (2) is found to be -325 MHz which is about 35% of the free-ion value. As in the case of $Dy(OH)_3$, the lattice contribution to the quadrupole coupling at the ^{166}Er site can be deduced by scaling the value measured in $Gd(OH)_3$. This is found to be + 221 MHz. The use in Eq. 3 of $B_2^0 = 0.74$ K obtained from the optical study of $Er(OH)_3$ will produce the same lattice quadrupole interaction provided we use $(1 - \gamma_\infty)/(1 - \sigma_2) = 106$. A similar value was obtained above for this quantity in $Dy(OH)_3$. The net quadrupole interaction then will be only -104 MHz. Both the calculated magnetic hyperfine field and the quadrupole interaction will only produce a very slight broadening of the Mössbauer resonance line (of 420 MHz linewidth in the paramagnetic range). Our measurements are in excellent agreement with these expectations.

From our Mössbauer measurements we infer that $Er(OH)_3$ does not show magnetic ordering down to 1.5 K. The reason behind this lies in the fact that a dipolar coupling predominately determines the ordering of these hydroxides. With a small moment along the c-axis it is unlikely that a spin ordering will be realized along the c-axis, although it may be possible for spins to order in a direction perpendicular to the c-axis at lower temperatures. In a paramagnet the magnetic interaction can be observed through Mössbauer experiments if the spin relaxation times are larger than the characteristic time associated with a Larmor precesion of the nuclear moment. This being not the case here we anticipate only quadrupole interaction. As discussed above, we have estimated this to be too small to be observable.

CONCLUSION

The magnetic and quadrupole hyperfine interactions measured in $Dy(OH)_3$, $Er(OH)_3$ and $Er:Ho(OH)_3$ are interpreted successfully using crystal field and molecular field models. The CEF parameters obtained from optical spectroscopy can account for the hyperfine interactions. The molecular fields are in satisfactory agreement with the values estimated from molecular field theory. Thus, the hyperfine interaction parameters along with the magnetic susceptibility, the specific heat and the optical data [2,3] of this class of insulators can be well described with a single model in a self consistent fashion.

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FIGURE CATPIONS

Fig. 1. ^{161}Dy Mossbauer resonance in Dy(OH)$_3$ at 300 and 1.6 K. The solid line represents the best computer fit to the experimental data points.

Fig. 2. Calculated quadrupole coupling constant and magnetic hyperfine field reduced to the free ion value for Dy^{3+} in Dy(OH)$_3$ as a function of the magnetic exchange field H_{mol}. The free-ion values are H_{hf}(FI) = 6320 kOe and $e^2q_{4f}Q$(FI) = 3090 MHz.

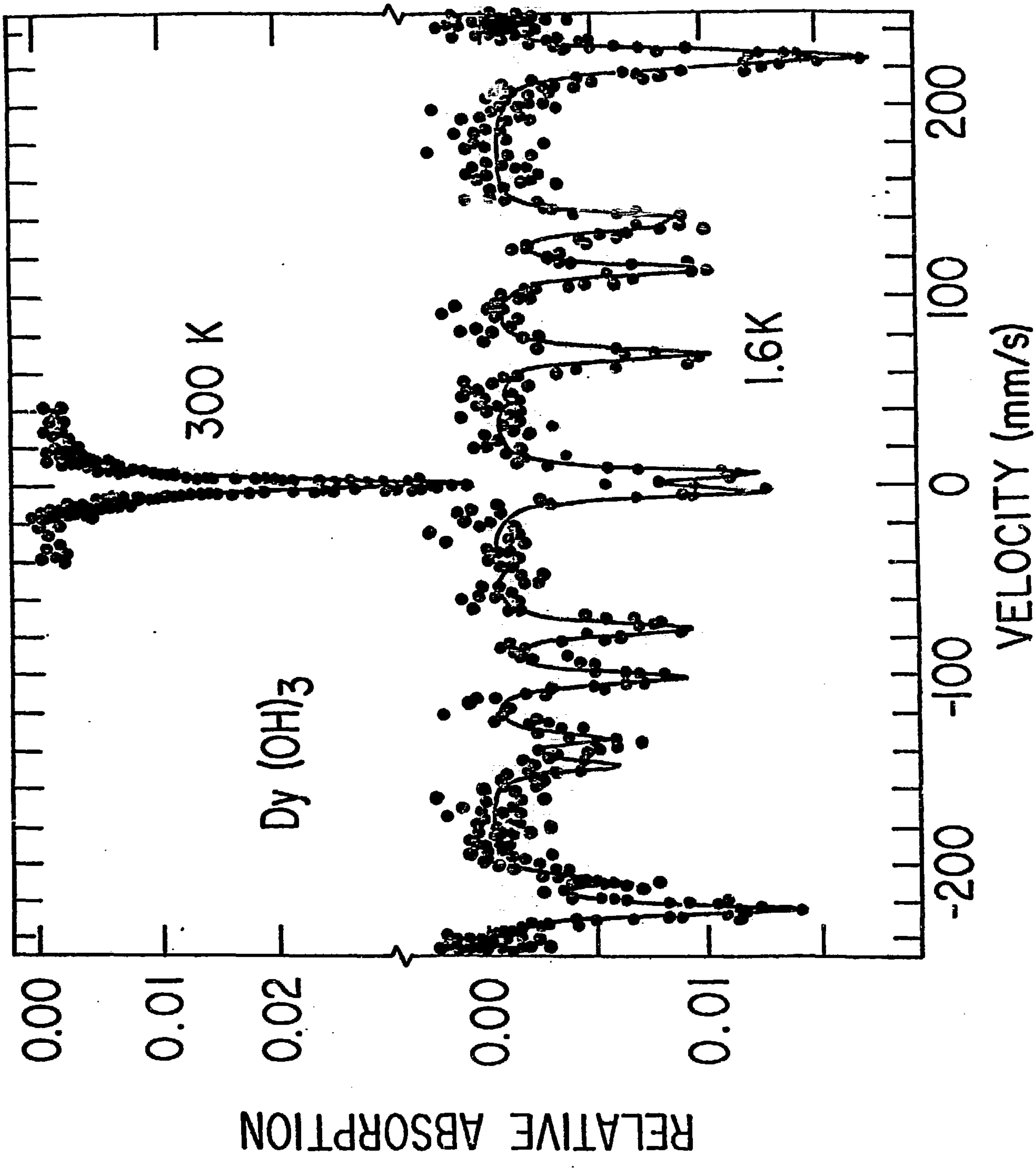
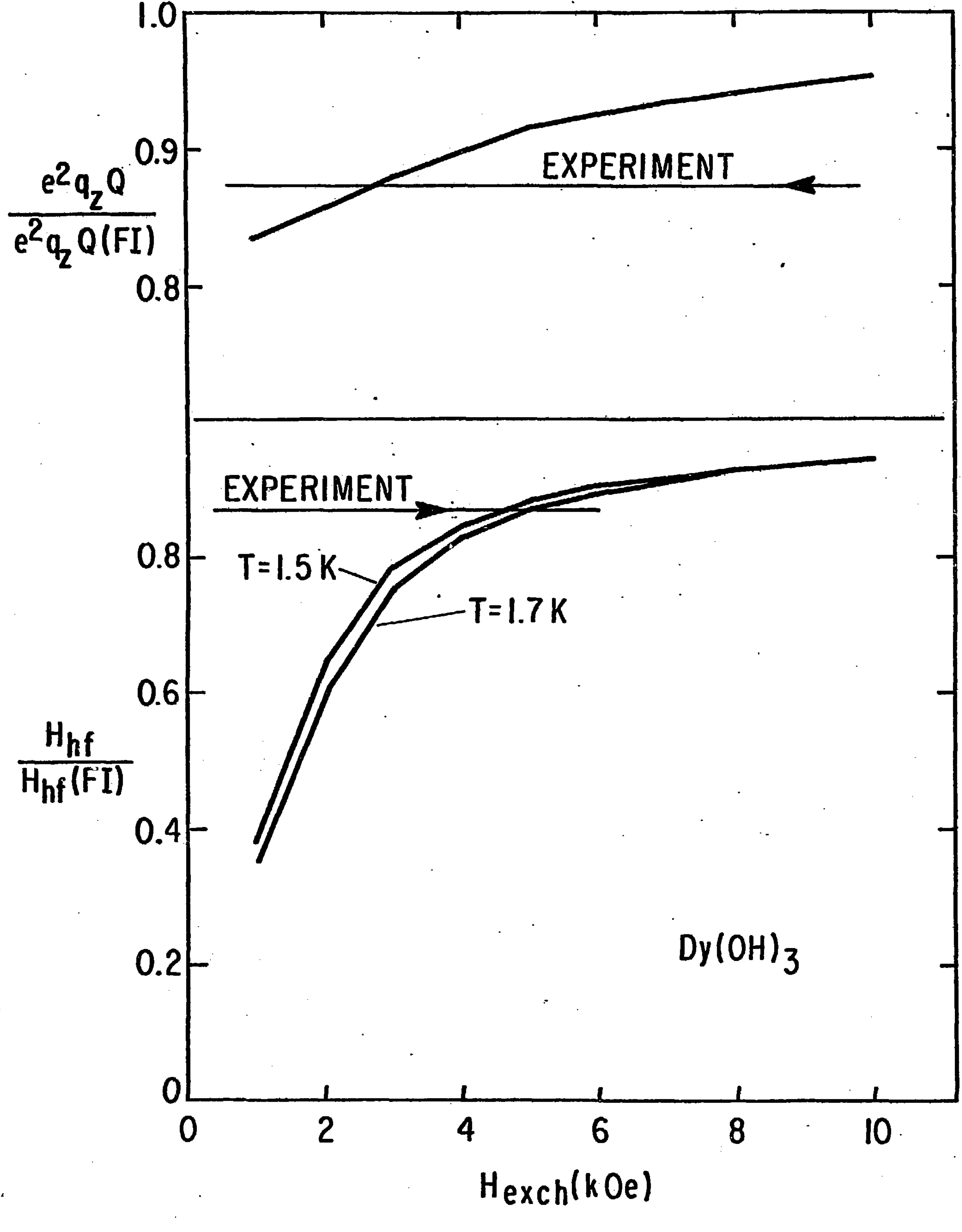

Dy (OH)3
300 K
1.6K
0.00
0.01
0.02
0.00
0.01
RELATIVE ABSORPTION
-200
-100
0
100
200
VELOCITY (mm/s)

Fig 1



1.0
0.9
0.8
$\frac{e^2 q_z Q}{e^2 q_z Q(FI)}$
EXPERIMENT
EXPERIMENT
T=1.5 K
T=1.7 K
0.8
0.6
0.4
0.2
0
$\frac{H_{hf}}{H_{hf}(FI)}$
Dy(OH)$_3$
0
2
4
6
8
10
H_{exch}(kOe)

Fig. 2