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Electronic Shielding Parameters and Anisotropic Mössbauer Patterns in Dysprosium Ethyl Sulfate

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The Mössbauer effect of the 26-keV gamma transition in Dy^{161} was employed to study hyperfine interactions in single crystals of DyES at 4.2°K. The Dy nuclei experience a magnetic hyperfine interaction $g_0\beta_N H_{\rm eff}$ of -446 ± 12 Mc/sec, with $H_{\rm eff}$ parallel to the c axis of the crystal. The hyperfine field and Mössbauer patterns (parallel and perpendicular to the c axis) are readily interpreted in terms of the symmetry of the hyperfine interaction from the ground Kramers doublet. The measurement of the electric quadrupole interaction is of interest because the $4f$ contribution to the electric field gradient (EFG) is often dominant in rare-earth ions; however, for the ground doublet of DyES, this gradient is very small. This fact allowed a simple and direct measurement of the lattice contribution to the EFG. From this result the ratio $(1-\gamma_\infty)/(1-\sigma_2)$ was found to be 262, where γ_∞ is the lattice Sternheimer factor and σ_2 represents the shielding of the $4f$ electrons from the crystalline field. The resolution of the paramagnetic hyperfine spectra was interpreted to show that electronic relaxation times were longer than 10^{-8} sec.

RECENT Mössbauer investigations of hyperfine interactions in paramagnetic ions have demonstrated that in suitable systems at low temperatures an effective paramagnetic hyperfine field exists at the nucleus. This implies that by suitable choice of host lattice, anisotropic spectra may be observed[1] by obtaining Mössbauer spectra with source γ rays parallel or perpendicular to the internal paramagnetic field direction. Additional useful information may also be derived from the measured quadrupole interaction in the paramagnetic ion. In the following we report an experiment with a single crystal of DyES where the anisotropic effects are easily observed and where sufficient data are available in the literature to allow interpretation of the measured EFG. The quadrupole interaction yields Sternheimer[2] and related shielding factors which agree well with independent measurements of similar quantities in different rare-earth ions.[3–5]

A source of Gd^{161} was used in a high-velocity Mössbauer apparatus similar to that described by Cohen, McMullin, and Wertheim.[6] Large (15 g) single DyES crystals were grown from aqueous solution. The external morphology of the crystals allowed easy identification of the c axis. Absorber slabs were cut parallel and perpendicular to the c axis and then polished to a thickness of 1 mm and an area of 2 cm^2.

The properties of rare-earth ions in the ES lattice have been extensively investigated; in particular, Powell and Orbach[7] have determined from experimental data the effective crystal field parameters V_n^m for Dy^{3+} in DyES. Thus the energies and wave functions for the lower Dy^{3+} stark levels spanned by the ground $J=15/2$ manifold are known.[7] The first excited level is at 23°K, and only the ground doublet is populated at 4.2°K. The latter has effective g tensor: $g_z=10.75$, $g_x=g_y=0$.

It is known that whenever the effective g tensor of the ground doublet is highly anisotropic, the low-temperature spin-spin and spin-lattice relaxation times are much larger than the reciprocal Larmor frequencies of the Mössbauer levels in Dy^{161}.[8,9] This enables one to observe paramagnetic hyperfine interactions in the helium temperature range, even in concentrated paramagnetic salts. The results of experiments with polycrystalline and oriented single-crystal sections are shown in Fig. 1, The data are consistent with the hfs pattern from the ground doublet; the experimentally determined interactions are $g_0\beta_N H_{\rm eff}(4.2°{\rm K})=-446\pm12$ Mc/sec and $e^2qQ=-632\pm24$ Mc/sec. These parameters result from analysis of the line positions using a nuclear spin Hamiltonian with collinear magnetic field and axially symmetric quadrupole interaction.

The data of Fig. 1(a) and 1(c) show clearly that $H_{\rm eff}$ coincides with the crystal c axis. The angular dependence of the $E1$ γ-ray transitions with $\Delta m=0$ is proportional to $2\sin^2\theta$, while for $\Delta m=\pm1$ transitions the dependence is $(1+\cos^2\theta)$, where θ is measured relative to the crystal c axis. With the source parallel to the c axis the $\Delta m=0$ transitions have vanishing intensity. When the source is perpendicular to the c axis the intensity, relative to the random distribution, of the $\Delta m=0$ transitions increases by a factor of 2. In Fig. 2 we show theoretical spectra for the various orientations: the agreement with experiment is excellent.

When admixtures, from higher electronic states, into the ground muliplet are negligible, it may be shown that a proportionality exists between effective hyperfine and g tensor for a Kramers doublet with $S=\frac{1}{2}$. The relation is $g_i=({\rm const})A_i$, where $i=x,y,z$. Thus the hyperfine field may be written $g_0\beta_N H_{\rm eff}=kg_z$ where

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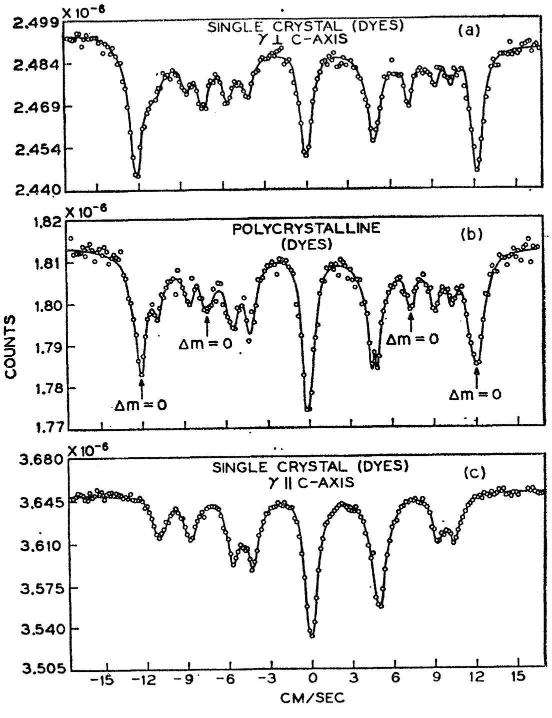

FIG. 1. Mössbauer spectra of Dy^{161} in oriented and polycrystalline absorbers of DyES.

$k = 41.5 \pm 1$ Mc/sec for DyES. The constant k should be independent of the particular compound investigated, as long as the assumption about admixtures remains valid. To show this we give in Table I a representative list of measured hyperfine interactions from which k may be deduced. The maximum "free ion" g_z value is 19.7 and should correspond to the case of magnetically ordered systems where the ground state is $|\pm J_z\rangle = |\pm 15/2\rangle$ to a very good approximation. Within experimental error the value of k is the same except for intermetallic compounds containing $3d$ elements, where additional contributions to the internal field are evident.[10]

A detailed investigation of spin-lattice relaxation in concentrated DyES has shown that the zero-field relaxation time at 4.2°K is approximately 10^{-6} sec.[11] Our results at this temperature indicated relaxation times of duration longer than 10^{-8} sec. The effects of relaxation on the spectrum have been simulated by applying solutions of the modified Bloch rate equations to the case of the Mössbauer effect. The resulting spectra show a dependence on an effective relaxation time τ which is a measure of the electronic relaxation time.[12] The range of relaxation times over which the Dy^{161} Mössbauer spectra are appreciably affected is limited to the range $5 \times 10^{-11} \leq \tau \leq 10^{-8}$ sec.

TABLE I. Comparison of hyperfine fields and effective g tensors in several dysprosium compounds.

Compound	$g_0\beta_N H_{\mathrm{eff}}$ (Mc/sec)	g_z	k	Reference
DyES	-446 ± 12	10.75	41.6 ± 1.0	this work
DyAlG	-769 ± 15	18.2	42.2 ± 1.0	9
Dy	-825 ± 30	19.7	41.9 ± 2	10
$DyAl_2$	-830 ± 30	19.7	42.2 ± 2	10
$DyFe_2$	-940 ± 30	19.7	48.2 ± 2	10

Of main interest is the determination of the large negative quadrupole interaction, -632 Mc/sec. The EFG at the Dy^{3+} nucleus arises in part from the known deviations from spherical symmetry of the crystalline electric field (CEF) which partially removes the degeneracies of the $4f$ shell and yields the ground Kramers doublet which now contributes to the EFG. However, the total EFG also arises in large part from the non-$4f$ subshells which are distorted by both the CEF and the $4f$ crystal field levels. It is generally assumed and experimentally verified that the "antishielding" due to the CEF and "shielding" due to the $4f$ levels are proportional to the direct and in principle

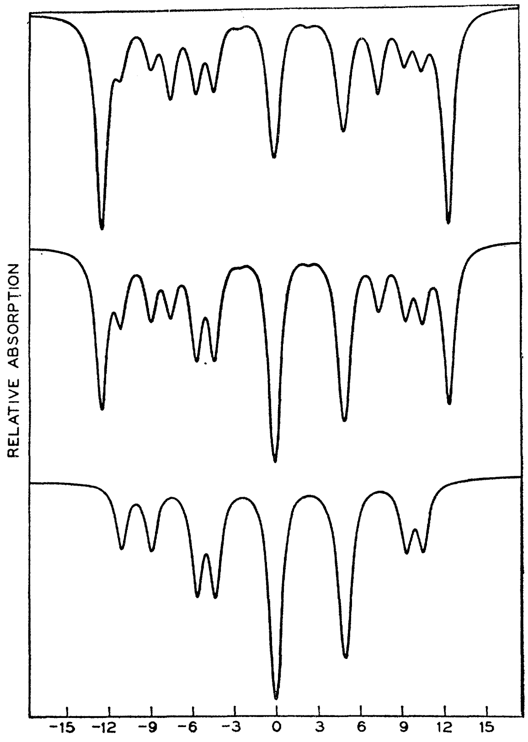

FIG. 2. Theoretical absorption spectra of DyES with an effective relaxation time $\tau \cong 10^{-8}$ sec.

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calculable contributions from these sources.[3] In the notation of Ref. 3 the total EFG is written

$$e\hat{q}_{zz}=(1-\gamma_\infty)e\hat{q}_{zz}^{(\mathrm{Lat})}+(1-R)e\hat{q}_{zz}^{(4f)}, \qquad (1)$$

where γ_∞ and R are the lattice and atomic Sternheimer[2] factors.

The direct lattice contribution eq^{Lat} is related to the experimentally determined coefficient V_2^0 by

$$Qe^2q^{\mathrm{Lat}}=-4[QV_2^0/(1-\sigma_2)\langle r^2\rangle_{4f}],$$

where σ_2 is another shielding factor used to describe the shielding of the $4f$ electrons, principally by the $5s^2p^6$ subshells.[13–16] Measuring the quadrupole moment Q in barns, and with $V_2^0=119.2$ cm^{-1},[7] $\langle r^2\rangle_{4f}=0.726a_0^2$,[17] we find the result

$$\begin{aligned}&\tfrac{1}{4}(1-\gamma_\infty)e^2Qq^{\mathrm{Lat}}\\&\quad=-0.176[(1-\gamma_\infty)/(1-\sigma_2)]Q\ \text{Mc/sec.} \qquad (2)\end{aligned}$$

The $4f$ contribution to the electric field gradient can be estimated easily by using Powell and Orbach's wave function for the ground Kramers doublet ($|\pm\rangle$), together with an estimate of the free-ion $4f$ contribution

$$\begin{aligned}\langle+|\tfrac{1}{4}e^2qQ(1-R)q^{4f}|+\rangle&=\frac{\langle+|3J_z^2-J^2|+\rangle}{\langle J_z=J|3J_z^2-J^2|J_z=J\rangle}\\&\quad\times\{\tfrac{1}{4}e^2qQ(1-R)q^{4f}(\text{free ion},\ J_z=J)\}. \qquad (3)\end{aligned}$$

The free-ion value of $\frac{1}{4}e^2qQ$ is obtained in magnetic Dy alloys of cubic structure (e.g., $\mathrm{DyAl_2}$ and $\mathrm{DyFe_2}$) and has value[10] $+630\pm60$ Mc/sec. We make the reasonable assumption that the shielding factor R is independent of environment,[2] and the desired matrix element in Eq. 3 is found to be -38 Mc/sec. From Eq. (1) it follows that $e^2Qq^{\mathrm{Lat}}(1-\gamma_\infty)=-480$ Mc/sec and by Eq. (2) we obtain the result, with $Q=2.6$,[18]

$$(1-\gamma_\infty)/(1-\sigma_2)\equiv\alpha=262.$$

TABLE II. Shielding factor ratios for several rare-earth ions. The quantity α is the ratio $(1-\gamma_\infty)/(1-\sigma_2)$.

Ion	Config.	α	Reference	σ_2 ($\gamma_\infty=-80$)
$\mathrm{La^{3+}}$	$4f^0$	-300 ± 40	3	1.27
$\mathrm{Eu^{3+}}$	$4f^6$	300 ± 40	3	0.73
$\mathrm{Gd^{3+}}$	$4f^7$	193 ± 40	3	0.58
$\mathrm{Dy^{3+}}$	$4f^9$	262 ± 30	this work	0.69
$\mathrm{Tm^{3+}}$	$4f^{12}$	250	2	0.68
$\mathrm{Lu^{3+}}$	$4f^{14}$	140 ± 20	3	0.42

According to Sternheimer (1963)[2] and Freeman and Watson,[19] γ_∞ is about -80 so σ_2 is approximately 0.69.

Barnes *et al.*[3] have noted that fairly reliable estimates of γ_∞ are available which show this factor to be essentially constant throughout the rare-earth series. On the other hand, theoretical calculations of σ_2 tend to show greater variation with method of calculation. The experimental determinations of the ratio α in six rare-earth elements in the ethyl sulfate lattice are listed in Table II. Blok and Shirley have noted the general decrease in value of $|\alpha|$ with increasing number of $4f$ electrons.[4] With a reasonable fixed value of $(1-\gamma_\infty)$, the trend in the parameter σ_2 is also to decrease in a similar manner. This trend and the measured values of σ_2 are in agreement with recent theoretical calculations[20,21]: For example Sternheimer finds the values $\sigma_2(\mathrm{Pr^{3+}})=0.68$ and $\sigma_2(\mathrm{Tm^{3+}})=0.50$.[20] It should be mentioned here that implicit in the above discussion of α is accurate knowledge of the nuclear quadrupole moments involved. However, a probable error here of ~10% will not greatly alter the conclusions reached above.

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