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June 1963

QUADRUPOLE ANTISHIELDING IN THE RARE EARTHS^a

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Using recently determined quadrupole coupling constants for La^{3+} and Eu^{3+} in two ionic lattices^{1,2} and the known values^{3,4} of the crystal field parameter V_2^0 for other rare earths in these lattices, we have estimated contributions to the field gradient at the nucleus arising from polarization of the "closed" inner electron shells, by the crystal field, for all the rare earths. This effect is known as antishielding,⁵ because "closed-shell" electrons enhance the external crystal field gradient by a large (sometimes negative) factor.

The estimates were tested by nuclear orientation experiments on Eu^{154} , Gd^{159} , and Lu^{177} in cerium magnesium nitrate lattices and on Gd^{159} and Lu^{177} in crystals of neodymium ethylsulfate. These isotopes were grown into the crystals substitutionally as trivalent ions having the configurations (lowest levels) $\text{Eu}^{3+} 4f^6(7F_0)$, $\text{Gd}^{3+} 4f^7(8S_{7/2})$, and $\text{Lu}^{3+} 4f^{14}(1S_0)$. Field-gradient contributions other than antishielding either vanish (Gd^{3+} , Lu^{3+}) or are accountable (Eu^{3+}); thus these ions provide a reliable test of the theory. Quadrupole coupling constants were derived from the orientation data by the standard techniques of angular momentum theory.⁶ Agreement between the estimated and experimental field gradients was very satisfactory. We conclude that the systematics of antishielding in the fifteen rare earths (La^{3+} through Lu^{3+}) are well understood. This effect is an important contributor to the quadrupole coupling constants for

^aThis work was done under the auspices of the U. S. Atomic Energy Commission.

most rare earth ions in crystals, and the substantial experimental literature on this subject will require reinterpretation.

In estimating field gradients we followed the procedure used by Edmonds² for correlating data on La^{3+} and Eu^{3+} . Thus we assumed that the ratio of the quadrupole shielding factor for $4f$ electrons, γ_E , to the quadrupole antishielding factor for rare-earth nuclei, γ_N , is essentially constant, for a given lattice, throughout the $4f^N$ series. Since the experimental V_2^0 's obtained from optical spectroscopy are just $\gamma_E A_2^0 \langle r^2 \rangle_{4f}$ and the field gradient at the nucleus is proportional to $\gamma_N A_2^0$ (P in the spin Hamiltonian is $3 \gamma_N A_2^0 / I(2I-1)$), a comparison of experimental V_2^0 's with the radial moments⁴ $\langle r^2 \rangle_{4f}$, together with the experimental determination of γ_N/γ_E for one ion, yields field gradients for all the rare earths.

The accuracy of the constant γ_N/γ_E assumption is tested in Fig. 1, in which $\gamma_N A_2^0$ and $V_2^0 / \langle r^2 \rangle_{4f}$ are plotted for the rare-earth ethylsulfates and double nitrates. The ratio γ_N/γ_E decreases by about a factor of two throughout the rare earth series. Experimental and calculated hyperfine structure constants are given in Table 1. We find, in fair agreement with Edmonds, that the ratio γ_N/γ_E has an average value of about -400 in the ethylsulfate and -120 in the double nitrate lattice. In addition γ_N is negative.

The magnitude of γ_N is somewhat uncertain, because only the ratio γ_N/γ_E was measured. Comparing Wong's $A_2^0 \langle r^2 \rangle$ of 903 cm^{-1} (from lattice-sum⁵ calculations)⁷ for Pr^{3+} in LaCl_3 with the experimental V_2^0 of 147 cm^{-1} yields $\gamma_E \sim 1/20$ and therefore $\gamma_N \sim -20$. If $A_2^0 \langle r^2 \rangle$ is actually lower than this (ionic) estimate because of covalent bonding, both γ_E and γ_N would be larger in magnitude. Wikner and Burns⁸ have calculated γ_N , using Hartree wave functions, for Pr^{3+} and Tm^{3+} , and have estimated that γ_N ranges from -80 for Ce^{3+} to -50 for Yb^{3+} . This trend is in accord with the observed decrease in γ_N/γ_E (Fig. 1), although the above ionic model comparison yields a smaller magnitude for γ_N .

A new value of V_2^0 for Pr^{3+} in the ethylsulfate has been reported recently.⁹ We have plotted the corresponding $\gamma_{E2} A^0$ and a $\gamma_{E2} A^0$ for Ce^{3+} in this lattice¹⁰ as filled triangles in Fig. 1. It seems likely that this parameter actually passes through zero and that Edmond's value of $\gamma_{E2} A^0$ for La^{3+} is positive. We note that the correlation is preserved because the extrapolated magnitude of $\gamma_{E2} A^0$ is unchanged.

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Table 1.

Rare-Earth Ion	$\gamma_{N_2}^A \text{ in } 10^4 \text{ cm}^{-1} \text{ a}_o^{-2}$				Reference
	Double nitrate		Ethylsulfate		
	Calc.	Obs.	Calc.	Obs.	
La ³⁺	(1.13)	1.15	(1.22)	1.22	2
Eu ³⁺	.4	.38	-3.0	-4.8	1, this work
Gd ³⁺	~ 0	< .07	-3.3	-3.5	this work
Lu ³⁺	-	< 0.2 ^a	-4.8	-4.5	this work

^a It is possible that Lu³⁺ doesn't substitute isomorphously into the double nitrate lattice.

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Fig. 1

Figure Caption

Fig. 1. Correlation plot of $\gamma_{E^2}^A (= V_2^0 \langle r^2 \rangle^{-1})$ and the quadrupole antishielding term $\gamma_{H^2}^A$ for rare-earth ions in the ethylsulfate (circles) and double nitrate (squares) lattices. Filled (open) symbols denote $\gamma_{E^2}^A$ ($\gamma_{H^2}^A$) and should be read with left (right) ordinate scale. Dashed curve for ethylsulfate represent qualitatively the type of behavior to be expected for $\gamma_{H^2}^A$ if γ_H decreases in magnitude from -80 to -50 between Ce^{3+} and Yb^{3+} , as suggested by Wilmer and Burns. Triangles are discussed in text.

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