UCRL-10844

University of California

Ernest O. Lawrence Radiation Laboratory

QUADRUPOLE ANTISHIELDING IN THE RARE EARTHS

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-10844

For Journal; J. Chem. Phys.

UNIVERSITY OF CALIFORNIA

Department of Chemistry and
Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

QUADRUPOLE ANTISHIELDING IN THE RARE EARTHS

Johan Blok and D. A. Shirley

June 1963

QUADRUPOLE ANTISHIELDING IN THE RARE EARTHS*

Johan Blok and D. A. Shirley

Department of Chemistry and
Lawrence Radiation Laboratory
University of California
Berkeley, California

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) Eu^{3+} $4f^6(^7F_0)$, Gd^{3+} $4f^7(^8S_{7/2})$, and 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

*This 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 Edmonds[2] 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 $3\,Q\gamma_N A_2^0/I(2I-1)$), a comparison of experimental V_2^0's with the radial moments[4] $\langle r^2 \rangle_{4f}$, 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-sum calculations)[7] for Pr^{3+} in $LaCl_3$ with the experimental V_2^0 of 14½ 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 Burns[8] 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 500 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 $\gamma_E A_2^0$ and a $\gamma_E A_2^0$ for Ce^{3+} in this lattice[10] as filled triangles in Fig. 1. It seems likely that this parameter actually passes through zero and that Edmond's value of $\gamma_E A_2^0$ for La^{3+} is positive. We note that the correlation is preserved because the extrapolated magnitude of $\gamma_E A_2^0$ is unchanged.

REFERENCES

1. B. R. Judd, C. A. Lovejoy, and D. A. Shirley, Phys. Rev. 128, 1733 (1962).

2. D. T. Edmonds, Phys. Rev. Letters 10, 129 (1963).

3. B. R. Judd, Proc. Roy. Soc. A232, 458 (1955).

4. A. J. Freeman and R. E. Watson, Phys. Rev. 127, 2058 (1962).

5. R. M. Sternheimer, Phys. Rev. 95, 736 (1954).

6. R. J. Blin-Stoyle and M. A. Grace, Handbuch der Physik Vol. 42, p. 555 (Springer-Verlag, Berlin, 1957).

7. Eugene Y. Wong and Isaac Richman, J. Chem. Phys. 36, 1889 (1962).

8. Gerald Burns, private communication to B. R. Judd.

9. John B. Gruber, J. Chem. Phys. 38, 946 (1963).

10. R. J. Elliott, and K. W. H. Stevens, Proc. Roy. Soc. A219, 387 (1953).

Table 1.

Rare-Earth Ion	$\gamma_N A_2^0$ in 10^4 cm^{-1} a_o^{-2}				Reference
	Double nitrate		Ethylsulfate		
	Calc.	Obs.	Calc.	Obs.	
La^{3+}	(1.13)	1.13	(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 Lu^{3+} doesn't substitute isomorphously into the double nitrate lattice.

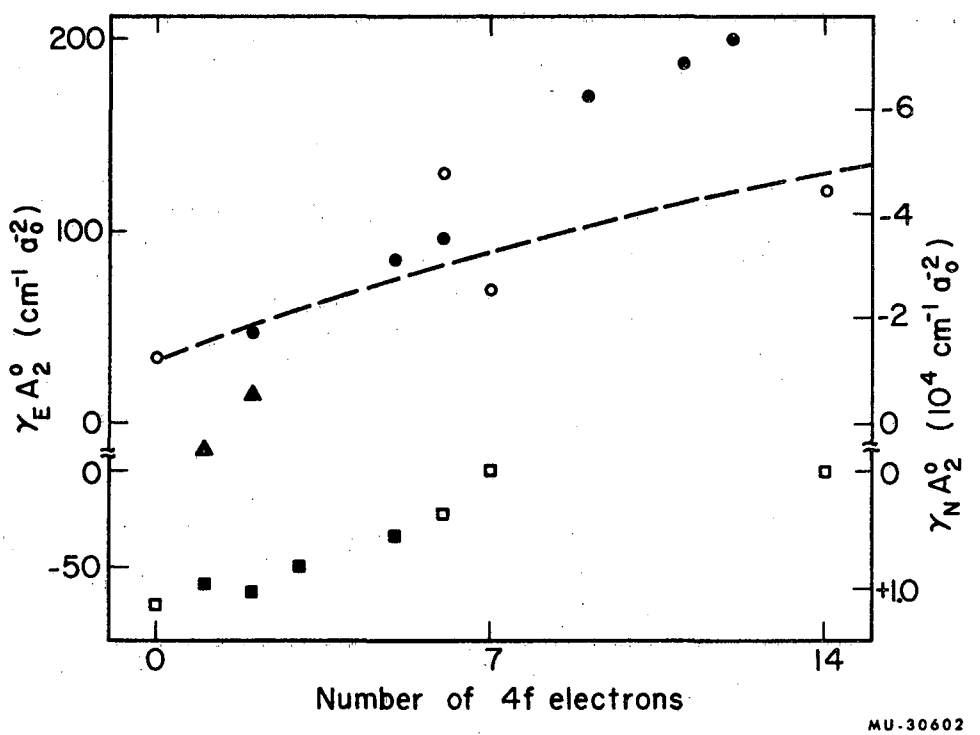
200
100
0
0
-50
-6
-4
-2
0
0
+1.0
0
7
14
Number of 4f electrons
$\gamma_E A_2^0$ (cm^{-1} a_0^{-2})
$\gamma_N A_2^0$ (10^4 cm^{-1} a_0^{-2})
MU-30602

Fig. 1

Figure Caption

Fig. 1. Correlation plot of $\gamma_E A_2^0$ ($= V_2^0 \langle r^2 \rangle^{-1}$) and the quadrupole antishielding term $\gamma_N A_2^0$ for rare-earth ions in the ethylsulfate (circles) and double nitrate (squares) lattices. Filled (open) symbols denote $\gamma_E A_2^0$ ($\gamma_N A_2^0$) and should be read with left (right) ordinate scale. Dashed curve for ethylsulfate represent qualitatively the type of behavior to be expected for $\gamma_N A_2^0$ if γ_N decreases in magnitude from -80 to -50 between Ce^{3+} and Yb^{3+}, as suggested by Wikner and Burns. Triangles are discussed in text.

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.