

MAGNETIC MOMENT REDUCTION VIA THE ORBIT-LATTICE
INTERACTION FOR Ce^{3+} IN RARE-EARTH ETHYL SULFATES*

R. J. Birgeneau†

Hammond Laboratory, Yale University, New Haven, Connecticut

(Received 12 June 1967)

Data and calculations are presented for Ce^{3+} in a number of ethyl sulfates which show clearly that there is a large magnetic moment anomaly arising from the virtual phonon mechanism postulated by Inoue.

In rare-earth salts it is often found that the calculated g values differ from the experimental ones by an amount which is well outside of experimental error. In most cases, this discrepancy has been attributed to an "orbital reduction" arising from covalent bonding with the ligands.¹ Indeed, it has been suggested that the orbital reduction factor could be used directly to obtain information about the covalency parameters.² An alternative explanation, however, was offered by Inoue,³ who pointed out that there could also be a correction to the magnetic moment of the ground state due to a virtual phonon mechanism in which the excited states are admixed into the ground state through the simultaneous action of both the Zeeman and the orbit-lattice interaction. Inoue carried out explicit calculations using a semi-empirical point-charge model for Tm^{+2} and Ho^{+2} in CaF_2 and found that she was able to obtain order-of-magnitude agreement for the observed g shifts, although in both cases the effect is rather small so that the approximate agreement can only be regarded as encouraging rather than as unambiguous proof.

In this Letter we present data and calculations for Ce^{3+} in the ethyl sulfate which, as we shall show, presents an almost ideal test

of Inoue's hypothesis since (a) the magnetic-moment reduction is anomalously large, (b) it is found to be only slightly dependent on the splitting of the first excited state (which varies by a factor of 4 going from LaES to YES as host lattice), (c) information is available about the strength of the orbit-lattice coupling in each of the host lattices, and (d) the relatively high rare-earth point symmetry and the small value of J ($J = \frac{5}{2}$) result in very simple wave functions.

The crystal field analysis of Ce^{3+} in the ethyl sulfate has been carried out in detail elsewhere,⁵ and for our purposes here it is sufficient to quote the results. The energy levels and wave functions for the $J = \frac{5}{2}$ manifold of Ce^{3+} in CeES are given in Table I. The experimental and theoretical results for the g values of the $|\frac{5}{2}, \pm\frac{5}{2}\rangle$ state together with the splitting of the $|\frac{5}{2}, \pm\frac{1}{2}\rangle$ state are presented in Table II for Ce^{3+} in a number of ethyl sulfates. From Table II it may be seen that in each case there is a significant discrepancy between the experimental and theoretical values for g_{\parallel} although this discrepancy is only slightly dependent on the host lattice. At the same time, however, the splitting between the $|\frac{5}{2}, \pm\frac{1}{2}\rangle$ and $|\frac{5}{2}, \pm\frac{3}{2}\rangle$ states changes from -3.9 to 17.4 cm^{-1} . It should

Table I. Energy levels and wave functions for Ce^{3+} in CeES.^a

Energy (cm^{-1})	Wave function	Calculated		Experimental	
		g_{\parallel}	g_{\perp}	g_{\parallel}	g_{\perp}
0.0	$0.995 \frac{5}{2}, \pm\frac{5}{2}\rangle \mp 0.012 \frac{7}{2}, \pm\frac{5}{2}\rangle \mp 0.103 \frac{7}{2}, \pm\frac{7}{2}\rangle$	4.138	0.20	3.760 ^d	0.21
4.7 ^{b,c}	$0.997 \frac{5}{2}, \pm\frac{1}{2}\rangle \pm 0.077 \frac{7}{2}, \pm\frac{1}{2}\rangle$	1.010	2.454	± 0.005	± 0.03
94.5 ^b	$ \frac{5}{2}, \pm\frac{3}{2}\rangle \mp 0.019 \frac{7}{2}, \pm\frac{3}{2}\rangle$	2.537	0	1.00 ^e	2.20
				± 0.02	± 0.2
			

^aCalculated using $A_2^0 \langle r^2 \rangle = 9.0$ cm^{-1} , $A_4^0 \langle r^4 \rangle = -42$ cm^{-1} , $A_6^0 \langle r^6 \rangle = -45$ cm^{-1} , $A_6^6 \langle r^6 \rangle = 680$ cm^{-1} , where the latter two are extrapolated from the other concentrated rare-earth salts.

^bG. O'Leary and R. Wheeler, private communication.

^cA. H. Cooke, S. Whitley, and W. P. Wolf, Proc. Phys. Soc. (London) **68**, 415 (1955).

^dJ. Dweck and G. Seidel, Phys. Rev. **146**, 359 (1966).

^eG. S. Bogle, A. H. Cooke, and S. Whitley, Proc. Phys. Soc. (London) **64A**, 931 (1951).

Table II. Crystal-field splittings, g values, and magnetic moment reduction factors for Ce^{3+} in several ethyl sulfates.

Host lattice	$E \pm\frac{1}{2}\rangle - E \pm\frac{5}{2}\rangle$ (cm^{-1})	Experiment		Calculation g_{\parallel}	Experiment	$\Delta g_{\parallel}/g_{\parallel} \times 100$ Calculated	
		g_{\parallel}	g_{\perp}			Model I	Model II
LaES	-3.9 ^a	3.70 ± 0.02	0.20 ± 0.02	4.139	-10.6	-6.7	-10.9
CeES	4.7	3.76 ± 0.005	0.21 ± 0.03	4.138	-9.2	-5.4	-9.2
SmES	11.5 ^b	3.79 ± 0.02	0.22 ± 0.02	4.137	-8.4	-4.7	-8.3
YES	17.4 ^c	3.81 ± 0.01	0.20 ± 0.02	4.136	-7.9	-4.3	-7.6

^aD. P. Devor and R. H. Hoskins, Bull. Am. Phys. Soc. 6, 364 (1961).

^bRef. 8.
^cRef. 7.

be noted also that g_{\perp} is constant to within the experimental error over the range.

Spin-lattice relaxation measurements have also been carried out on Ce^{3+} in a number of ethyl sulfates by the workers at Berkeley.⁶⁻⁸ In each case, it is found that the dominant relaxation process is the Orbach process⁹ arising from the first excited state, although for Ce^{3+} in YES the Raman process is also clearly distinguishable. From the point of view of the magnetic moment reduction, the most significant result of the relaxation experiments is that from the dependence of the numerical coefficient in the Orbach process on the splitting of the first excited state, it may be inferred that for Ce^{3+} in the ethyl sulfates from LaES to YES, the strength of the orbit-lattice coupling is roughly independent of the host lattice.⁸ This considerably simplifies the problem of calculating the systematics of the magnetic moment reduction.

Let us now consider the possible causes of the magnetic moment reduction. The most obvious mechanism, and indeed the one originally suggested by Elliott and Stevens on the basis of the LaES and CeES data alone,¹⁰ is a small C_{3v} distortion from the C_{3h} symmetry, which would serve to admix the $|\pm\frac{5}{2}\rangle$ and $|\pm\frac{1}{2}\rangle$ states. However, the contribution of this effect to both g_{\parallel} and g_{\perp} for the $|\frac{5}{2}, \pm\frac{5}{2}\rangle$ state would vary approximately as $1/(E_{\pm\frac{1}{2}} - E_{\pm\frac{5}{2}})^2$, and from Table II it may be seen clearly that this is not so. For the same reason, odd-parity crystal-field terms introduced by configuration mixing may be ruled out as appreciable contributors. In addition, covalency may be

ruled out since a 10% orbital reduction due to covalency would necessitate overlap and covalent contributions to the static crystal field far larger than the actual crystal field.¹¹ Thus, we are apparently left with only the virtual phonon mechanism.

It is clear that a calculation from first principles of the magnetic moment reduction due to the orbit-lattice interaction is prohibitively difficult for a system as complicated as the ethyl sulfates (or even, for that matter, much simpler systems). In order to estimate the magnitude of the effect, however, we have carried out calculations using a phenomenological model which included the following approximations: (a) Orbach's phenomenological form for the one-phonon relaxation perturbation⁹ (as modified by Scott and Jeffries⁶) is used, (b) the lattice vibrations are treated by the Debye model, (c) the error in using approximation (a) is minimized by scaling the orbit-lattice Hamiltonian so as to bring the theoretical Raman relaxation time into agreement with experiment, and (d) only the zero-point phonon contribution is included.¹² It should be noted that because of the simplicity of the wave functions for Ce^{3+} in the ethyl-sulfate, group-theoretical problems inherent in using approximation (a) are, in fact, avoided.

The actual calculations have been carried out using two different models. In the first model, the water molecules, ethyl radicals, sulfate radicals, and rare-earth ions are assumed to move as units. In the second model the carbon, sulfur, oxygen, and rare-earth ions are treated equally, but the hydrogens,

because of their light mass, are excluded. The calculated magnetic moment reduction for these two approximations are listed in Table II. It may be seen that the agreement is extremely satisfying. In both cases, the order of magnitude is correct, and most importantly, the systematics of the g_{\parallel} shift are well explained. In fact, for model II, the calculated and experimental g shifts correspond almost exactly for each host lattice, although this exact numerical agreement should be regarded as somewhat fortuitous considering the large number of approximations in the theory.

Thus it may be seen that Ce^{3+} in the ethyl sulfates gives a rather straightforward and convincing verification of the basic correctness of Inoue's hypothesis. In this case there is also a simple physical interpretation of the anomaly. At any given time, due to the thermal and zero-point vibrations, the symmetry at the rare-earth site is less than C_{3h} , so that the $|\frac{5}{2}, \pm\frac{5}{2}\rangle$ and $|\frac{5}{2}, \pm\frac{1}{2}\rangle$ states are admixed. The effect of this admixture, however, is always to reduce the net magnetic moment of the $|\frac{5}{2}, \pm\frac{5}{2}\rangle$ state. Thus the time-averaged magnetic moment is less than one would calculate on the basis of a static crystal field. In the present case the effect is large both because the states are very close together and because their magnetic moments are quite different.

Finally, we should note that these results have several significant consequences. First of all, it is clear that since the magnetic moments may differ considerably from what one would calculate using a static model, great caution should be used in employing g values to obtain information about static-crystal-field parameters. Secondly, our results, together with Inoue's original calculations, indicate that in most cases the virtual phonon mechanism will mask the covalency contribution so that orbital reduction factors may not be used to obtain information about covalency in rare-

earth salts.

We would like to thank Dr. G. Larson, Dr. R. Orbach, and Dr. W. P. Wolf for a number of helpful comments. We are grateful to Mr. G. O'Leary and Professor R. G. Wheeler for communicating their results prior to publication. We would also like to thank Dr. W. P. Wolf for his critical reading of the manuscript. Finally, we are grateful to Professor J. Van Vleck for the loan of his copy of Dr. Inoue's thesis.

*Work supported in part by the U. S. Atomic Energy Commission.

†Present address: Clarendon Laboratory, Oxford, England.

¹See, for example, B. Bleaney, Proc. Roy. Soc. (London) 277, 289 (1964); W. Low and R. S. Rubins, Phys. Rev. 131, 2527 (1963); J. C. Eisenstein, in Proceedings of the First International Conference on Paramagnetic Resonance (Academic Press, Inc., New York, 1963).

²J. H. M. Thornley, Proc. Phys. Soc. (London) 88, 325 (1966).

³M. Inoue, Phys. Rev. Letters 11, 196 (1963).

⁴J. A. A. Ketelaar, Physica 4, 619 (1937); D. R. Fitzwater and R. E. Rundle, Z. Krist. 112, 352 (1959).

⁵R. J. Birgeneau, to be published.

⁶P. L. Scott and C. D. Jeffries, Phys. Rev. 127, 32 (1962).

⁷G. H. Larson and C. D. Jeffries, Phys. Rev. 141, 461 (1966).

⁸G. H. Larson, Phys. Rev. 150, 264 (1966).

⁹R. Orbach, Proc. Roy. Soc. (London) A264, 458 (1961).

¹⁰R. J. Elliott and K. H. Stevens, Proc. Roy. Soc. (London) A215, 437 (1952).

¹¹J. Axe and G. Burns, Phys. Rev. 152, 331 (1966).

¹²The validity of assumption was tested by measuring the temperature dependence of the g values for Ce^{3+} in LaES. It was found that for the range from 4.2 to 1.3°K, g_{\parallel} for both the $|\pm\frac{1}{2}\rangle$ and $|\pm\frac{3}{2}\rangle$ states was independent of temperature to well within the experimental error. Thus the thermally populated phonons make a negligible contribution to the magnetic moment reduction at these temperatures.