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N. Edelstein and W. Easley

September 1967

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ABSTRACT

The g value anisotropies of the ground crystal field states of the nominally $^8S_{7/2}$ ions, Am^{2+} and Cm^{3+}, have been measured in cubic symmetry in CaF_2 at 35 Gc and magnetic fields of approximately 5500 gauss by epr spectroscopy. From the magnitude of these anisotropies the $\Gamma_6 - \Gamma_8$ zero field splittings of 13.4 ±0.5 cm^{-1} and 18.6 ±0.5 cm^{-1} have been deduced for Cm^{3+} and Am^{2+} respectively. These splittings are about 250 times greater than for the corresponding lanthanides, Gd^{3+} and Eu^{2+}. It is shown that the large intermediate coupling effects in the actinide ions can account qualitatively for these differences.

I. INTRODUCTION

The lanthanide series has been extensively investigated in crystals of the fluorite type by electron pramagnetic resonance (epr) and optical spectroscopy. The trivalent ions in these crystals may be found in various symmetry sites depending upon the conditions under which the crystals were grown.[1] The divalent ions are found in sites of cubic symmetry. Two of the most studied lanthanide ions are Gd^{3+} and Eu^{2+}, the half-filled shell ($4f^7$, $^8S_{7/2}$) configuration. For these ions in cubic symmetry the crystal field splittings are readily measured although the mechanisms causing these splittings are not well understood.[2]

We have previously reported the spin Hamiltonian parameters for Am^{2+} and Cm^{3+}, the $5f^7$ actinide analogs for Eu^{2+} and Gd^{3+}.[3] The earlier epr measurements were done at 9.2 Gc and temperatures of 4° K and 1° K, and were obtained for these actinide ions doped in CaF_2 in sites of cubic symmetry. For Cm^{3+}, spin Hamiltonian parameters for two different trigonal sites were also measured.[4] No resonance lines due to actinide ions were seen at 77° K. In this paper we report epr measurements made at 35 Gc on Am^{2+} and Cm^{3+} in cubic crystal field sites in the CaF_2 lattice. The larger magnetic field mixes into the ground crystal field state (Γ_6) the next highest crystal field state (Γ_8) which causes the measured g values to be anisotropic. From the anisotropy of the g value we have determined the zero field splitting in these two ions. We also show that the simple point charge model qualitatively explains the magnitude of the effects.

II. EXPERIMENTAL

Single crystals of actinide doped CaF_2 were grown as oriented cylinders by the Bridgman-Stockbarger technique. Optical quality pure CaF_2 was used for all experiments.[5] A 4 mm cylinder of single-crystal CaF_2 in a known orientation (for example, the cylinder axis parallel to the 110 direction) was placed in the bottom of a carbon crucible. Powdered CaF_2 to which had been added 2 wt percent PbF_2, was placed on top of the crystal and an acid solution of the actinide ion in minimum volume (10-50 λ) was pipeted onto the powder. The crucible was then placed in an evacuated tube furnace and raised into the hot zone such that the powder and the top part of the oriented cylinder melted. After soaking for about an hour or so, the crucible was slowly lowered from this hot region down to a region near room temperature. A disk of the oriented cylinder containing the actinide ions was cleaved from the main crystal and placed in a thin-walled teflon cylinder which was plugged with polystyrene foam. The teflon cylinder was glued with stopcock grease to the bottom of a TE_{01n} cylindrical cavity such that the cylinder axis of the crystal was parallel to the axis of rotation of the D.C. magnetic field. It is estimated that the orientation of the crystal is known to about ±2°. In this way, the magnetic field could be rotated in a particular plane of CaF_2.

For the experiments described in this paper we used approximately equimolar amounts of Am^{243} (nuclear spin I = 5/2) and Cm^{244} (I = 0) in one crystal. When the crystals were initially grown or annealed, the actinide ions were in the trivalent state. However, due to the high level of radioactivity caused mainly by the alpha emission from the Cm^{244} nucleus ($t_{1/2}$ = 18.1 yr) part of the Am^{3+} was reduced to the divalent state and part of the Cm^{3+}

was oxidized to Cm^{4+}.[4] At the time the measurements were done, the ratio of Am^{2+} to Cm^{3+} in cubic sites was approximately 10:1.

The epr measurements were made at 1° K with a conventional superheterodyne spectrometer operating at approximately 34.5 Gc. The magnetic field was produced by a 12-inch rotating magnet and measured with an nmr gaussmeter whose frequency was monitored by a frequency counter. A small piece of Tm^{2+} in CaF_2 was placed in the cavity and the isotropic resonance from the Γ_7 state was used as an internal reference.[6] The frequency of the signal klystron was measured with a high-Q wavemeter.

III. PRELIMINARY DISCUSSION AND RESULTS

A free ion placed in a crystalline electric field undergoes a splitting of its total angular momentum J which is dependent upon the symmetry of the electrostatic field. We are interested in the case of a J = 7/2 state placed in a cubic symmetry site in the CaF_2 lattice. From group theoretical arguments, the J = 7/2 state in zero magnetic field will split into two doubly degenerate states, Γ_6 and Γ_7, and one quartet state, Γ_8. The Hamiltonian for this problem including the Zeeman effect caused by an external magnetic field may be written

$$H = g_J \beta \vec{H}.\vec{J} + B_4(O_4^0 + 5\, O_4^4) + B_6(O_6^0 - 21\, O_6^4) \qquad (1)$$

The first term represents the Zeeman interaction where g_J is the Landé g value for the lowest free ion level, β is the Bohr magneton, and $\vec{H}$ is the

external magnetic field. The last two terms represent the effect of the cubic crystalline field on the J = 7/2 manifold, where we consider B_4 and B_6 as adjustable parameters related to the strength of the crystalline field. The O_n^m terms are angular momentum operators of the appropriate symmetry.[7]

For the zero magnetic field case we find an exact solution for this Hamiltonian applied to the J = 7/2 manifold, the energies of the levels being given in terms of $b_4 = 60B_4$ and $b_6 = 1260B_6$. The energy level diagram is shown in Fig. 1. If we choose the energy of the Γ_6 state to equal zero, the second column in Fig. 1 shows the relative energies. If the crystal field splitting is much greater than the Zeeman interaction, then the zero field wavefunctions will be an accurate representation and can be used to calculate g values of the crystal field energy levels.[7] For the cases under consideration here we have neglected J mixing by the crystal field because the next free ion level is on the order of 17,000 cm^{-1} higher in energy.[8] We have used the zero field wavefunctions to calculate g values and interpret our epr results at X band, 9.2 Gc and approximately 1500 gauss, and have shown that the Γ_6 state has the lowest energy for Am^{2+} and Cm^{3+} in cubic symmetry and is isotropic to within our experimental error.[3] Our earlier results are given in Table I.

At higher magnetic fields the Zeeman term will become important and will cause an anisotropy in the epr spectrum of the Γ_6 state since this interaction will mix the Γ_8 with the Γ_6 state. From the magnitude of the anisotropy we can determine the splitting of the $\Gamma_6 - \Gamma_8$ levels. The experimental data are shown as circles in Fig. 2. We have plotted the g value of the Γ_6 state for both Cm^{3+} and Am^{2+} as a function of the angle of the magnetic field with respect to the unit cell axis of the CaF_2 lattice. The magnetic field was

rotated in the [110] plane of CaF_2. The hyperfine coupling constant of Am^{243} was isotropic to within our experimental error of ~1% on this particular measurement. In order to determine the values of the parameters b_4, b_6, and g_J which would reproduce the experimental data, the Hamiltonian (Eq. 1) was applied to the J = 7/2 manifold which resulted in an 8 × 8 matrix with elements in terms of the above parameters, the magnetic field H, and the direction cosines of H relative to the cubic axes of CaF_2. A computer program was written which diagonalized the 8 × 8 matrix and calculated the g value for the ground Kramers doublet state. The values of b_4, b_6, and g_J were varied until the best fit to the experimental data was found.[9] The calculated fits for Am^{2+} and Cm^{3+} are shown in Fig. 2 along with the values for the parameters. The solid line is the calculated g value for Am^{2+}, the dotted line is for Cm^{3+}.

Unique values of b_4 and b_6 could not be determined from this analysis as the anisotropy depended only on the $\Gamma_6 - \Gamma_8$ splitting. Therefore, there are any number of values of b_4 and b_6 which can give the same splitting. The Γ_7 level is so relatively high in energy that our data are not sensitive to its position. We have determined the magnitude of the $\Gamma_6 - \Gamma_8$ splitting as 13.4 ±0.5 cm^{-1} for $Cm^{3+}:CaF_2$ and 18.6 ±0.5 cm^{-1} for $Am^{2+}:CaF_2$. The g_J values were found to be 1.9261 ±0.001 and 1.9258 ±0.001 for Cm^{3+} and Am^{2+}, respectively. The absolute values of g_J are measured to the accuracy shown; however, the relative measurement of the two g_J values is about one order of magnitude better.

In the lanthanide series a recent survey has shown that for trivalent rare earth ions in cubic sites in the CaF_2 lattice, the fourth order term b_4 is about an order of magnitude larger than the sixth order term b_6.[1] This

ratio is also true for Eu^{2+} in the CaF_2 lattice. We have made this assumption, $b_6 < b_4$, for Cm^{3+} and Am^{2+} and show in Fig. 3 the energy level diagrams for the crystal field levels with the values of $b_6 = 0$, and $-.1\ cm^{-1}$. For the purpose of comparison, we show the energy diagram of Gd^{3+} and Eu^{2+} doped in CaF_2 in Fig. 4. It is instructive to see how the Zeeman interaction mixes the crystal field levels for Cm^{3+}. Fig. 5 shows the energies of the crystal field levels as a function of magnetic field applied in the [100] direction.

IV. DISCUSSION

Our experimental results show that the crystal field splittings of the nominally $^8S_{7/2}$ actinide ions are approximately 250 times larger than the corresponding lanthanides. Clearly such a large effect must arise from the differences of the electronic structures of the two sets of ions. Such differences are quite significant and arise because of the intermediate coupling effects induced by the relatively large spin orbit coupling energies of the actinide ions. The spin orbit interaction matrix elements are diagonal in J but are not diagonal in L and S, so states of the same J but different L and S will be mixed.[10] For example, the leading terms of the ground state wavefunction of Gd^{3+} have been given by Wybourne as[11]

$$\psi(Gd^{3+}, J=7/2) = 0.987|^8S\rangle + 0.162|^6P\rangle - 0.012|^6D\rangle + \ldots \qquad (2)$$

which shows that for Gd^{3+} the ground state is approximately 98% pure $^8S_{7/2}$. Recent work on the optical spectra of Cm^{3+} has shown that the leading terms

for the Cm^{3+} ground state wavefunction are[8]

$$\psi(Cm^{3+}, J=7/2) = 0.891|^8S\rangle + 0.414|^6P\rangle - 0.090|^6D\rangle + \ldots \qquad (3)$$

so that it is only 79% pure $^8S_{7/2}$. However, the fourth order crystal field operator will not split any of the three terms listed above nor will there be any non-zero matrix elements between any combination of them. Therefore, the contribution to the zero field splitting from the intermediate coupled wavefunction will come from a large number of small terms. We will now calculate the zero field splitting caused by these terms using the electrostatic point charge model.

The theoretical expression for B_4 in the approximation of the electrostatic model may be written[12]

$$B_4 = A_4^o\langle r^4\rangle\ (1-\sigma_4)\ \langle\psi_J\|\beta\|\psi_J{}'\rangle \qquad (3)$$

where A_4^o represents the sum of all the charges in the lattice at a particular point, $\langle r^4\rangle$ is the expectation value for the magnetic electrons, $\langle\psi_J\|\beta|\psi_J{}'\rangle$ is the fourth degree operator equivalent factor. The expression $(1-\sigma_4)$ takes into account shielding effects, where σ_4 is the fourth degree shielding parameter. Since we have a good wave function for Cm^{3+}, we will carry out the above calculation for the ions Cm^{3+} and Gd^{3+}. We will assume $\sigma_4 = 0$ (no shielding effects).

Bleaney[12] has performed the lattice summation for the CaF_2 lattice considering the first four shells of ions surrounding the trivalent ion. He has

also estimated the polarization effects of a trivalent ion occupying a Ca^{2+} position. He gives the formula for trivalent ions (in cm^{-1}).

$$B_4 = -659\langle r^4\rangle\langle\psi_J\|\beta_J\|\psi_J'\rangle \qquad (4)$$

where r is expressed in Ångstroms. Dr. M. Wilson[13] from Argonne National Laboratory has performed a Hartree-Fock calculation and provided us with the value $\langle r^4\rangle = 3.69$ a.u. for the trivalent Cm ion. The matrix element remaining $\langle\psi_J\|\beta\|\psi_J'\rangle$ may be written as the summation of terms of the type[10,14]

$$16\left[\frac{14(2J-4)!}{11(2J+5)!}\right]^{1/2}(-1)^{S+L'+J+k}(2J+1)\begin{Bmatrix} J & J & k \\ L' & L & S \end{Bmatrix}\langle f^n\alpha SL\|U^{(k)}\|f^n\alpha' SL'\rangle \qquad (5)$$

where k = 4. The values of the reduced matrix elements for k = 2,3,4,5, and 6 have been tabulated for all f^n configurations by Nielson and Koster.[15] A computer program has been written[9] which will calculate operator equivalent factors for intermediate coupled wavefunctions. The values of the operator equivalent factors, α, β, γ for the 50-term Cm^{3+} wavefunction are given in Table II. A similar calculation for Cm^{3+} but with a wavefunction which was derived from extrapolated parameters has been performed by Dr. S. Feneuille.[16] We have checked the relevant parts of his calculation with ours. We also list in Table II the operator equivalent factors for Gd^{3+} calculated from an intermediate coupled wavefunction which was obtained from electrostatic and spin orbit coupling parameters which best reproduced the spectra and intensities of this ion in solution.[17]

We now calculate

$$b_4\ (Cm^{3+}) = 60B_4\ (Cm^{3+}) = -0.24\ cm^{-1} \tag{6}$$

and similarly

$$b_4\ (Gd^{3+}) = 60B_4\ (Gd^{3+}) = -4.7 \times 10^{-4}\ cm^{-1} \tag{7}$$

where we have used for Gd^{3+}, $\langle r^4 \rangle = 1.52$ a.u. obtained from the work of Freeman and Watson.[18] These numbers can be compared to the experimental values

$$b_4\ (Cm^{3+})_{exp} \approx -1.12\ cm^{-1} \tag{8a}$$

$$b_4\ (Gd^{3+})_{exp} = -46 \times 10^{-4}\ cm^{-1}\ . \tag{8b}$$

We may also take the ratio of the calculated parameters and compare them with the ratio of the experimental parameters. We find

$$\frac{b_4\ (Cm^{3+})_{exp}}{b_4\ (Gd^{3+})_{exp}} = 243 \tag{9}$$

and

$$\frac{b_4\ (Cm^{3+})_{calc}}{b_4\ (Gd^{3+})_{calc}} = \frac{\langle r^4 \rangle_{Cm^{3+}}\ \langle \psi_J \| \beta_J \| \psi_J' \rangle_{Cm^{3+}}}{\langle r^4 \rangle_{Gd^{3+}}\ \langle \psi_J \| \beta_J \| \psi_J' \rangle_{Gd^{3+}}} = 511 \tag{10}$$

The signs of the calculated b_4 parameters agree with experiment but the magnitudes are off. However it has been shown that the lattice summation term (A_4^o) in the simple point charge model is not a good approximation and one must consider the extended nature of the induced moments.[19] For this reason the comparison of the ratio of the calculated b_4 terms to the ratio of the experimental b_4 terms is a more valid criterion. We find that these ratios differ by approximately a factor of two. Considering the uncertainties in the parameters used, this agreement shows the intermediate coupling mechanism accounts qualitatively in a very satisfactory manner for the difference in the crystal field splittings between the half-filled shell configurations of the lanthanide and actinide ions.

For the case of Gd^{3+} in $La(C_2H_5SO_4)_3 \cdot 9H_2O$, Wybourne[11] has pointed out that the intermediate coupling mechanism gives rise to a contribution of the wrong sign to the value of b_2^o (relative to the experimental value) because the Stark levels of the $^6P_{7/2}$ state are ordered oppositely to those of the $^8S_{7/2}$ ground state. Apparently the sign of b_2^o is determined by another mechanism. Kim and Moos[20] have recently measured b_2^o for Eu^{2+} in $LaCl_3$ and have found that it is approximately fifty times larger than that for Gd^{3+} in $LaCl_3$. They have attributed this ratio to the difference in electronic properties of Eu^{2+} and Gd^{3+}; specifically to the lowering in energy of the excited configurations in Eu^{2+}. They show that their results are in accord with the assumption that configuration interaction and intermediate coupling are the dominant mechanisms for the observed splittings but suggest that the relative importance of these two mechanisms are different for the ground and excited states. Accordingly, they suggest that Wybourne did not completely

account for the effects of configuration interaction. It has been shown that configuration interaction effects for rare earth ions are, for the most part, linear and can be accounted for in terms of a shielding factor which for b_2^0 is written as σ_2.[21] It has also been shown that $\sigma_2 > \sigma_4 > \sigma_6$.[22,23] The result of our calculation for the value of b_4 (Gd^{3+} in CaF_2) is qualitatively consistent with the arguments of Kim and Moos,[20] in that we would expect the configuration interaction mechanism to be less important for b_4, and, therefore, the intermediate coupling mechanism might dominate. We have shown that the intermediate coupling mechanism gives at least the correct sign. This qualitative argument is supported by the fact that b_4 (Gd^{3+}) $\simeq$ b_4 (Eu^{2+}) for cubic sites in CaF_2.

The g_J values mentioned earlier are in quite good agreement with the earlier values of g_J for Cm^{3+} measured by Abraham, Judd, and Wickman[24] and by Conway et al.[8] However, it is rather surprising that the <u>relative</u> values of g_J found for Am^{2+} and Cm^{3+} are to within experimental error (±.0002) the same. From the arguments of Judd et al.[24] we would expect the g_J value of Cm^{3+} to be less than that of Am^{2+}. The reason for this is that the spin orbit coupling constant for trivalent Cm is larger than for divalent Am and so intermediate coupling effects should be more important for Cm^{3+}. We list for comparison in Table III the g_J values for Am I[25] (spectroscopic notation) and Am III and a number of lanthanide atom-divalent ions, the electronic configurations differing only by a filled s shell. The g_J values for the ions were calculated from epr data using zero field crystal field wavefunctions.[7,12,28] We see the difference between g_J for Am I - Am III ($5f^7\ 7s^2$ - $5f^7$) is as large as the largest lanthanide atom-ion shift,

Ho I - Ho III ($4f^{11}\ 6s^2$ - $4f^{11}$). These shifts and also the Cm IV, Am III shift might be ascribed to covalent bonding, but an orbit-lattice interaction of the type described by Inoue[29] and Birgeneau[30] produces the same sort of experimental results. It is interesting to note that Am III which is approximately 80% pure ^8S has a g_J shift relative to the atom that is as large as that found in Ho III, $4f^{11}$.

V. CONCLUSION

In this paper we have described measurements which give the zero field field splittings of the $5f^7$ ions, Am^{2+} and Cm^{3+}, in cubic symmetry in CaF_2. The parameters deduced from these experiments have been calculated using the point charge approximation. It has been shown that intermediate coupling, that is the mixing of states of the same J into the ground state by spin orbit coupling, can account qualitatively for the large difference in zero field splittings between the lanthanide and actinide ions of nominally ^8S character.

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Table I. Spin Hamiltonian Parameters for Am^{2+} and Cm^{3+} in Cubic Sites in CaF_2[3,4]. I is the nuclear spin and A is the hyperfine coupling constant.

Ion	g	I	$\lvert A \rvert (cm^{-1})$
$^{244}Cm^{3+}$	4.492 ±.002	0	
$^{241}Am^{2+}$	4.490 ±.002	5/2	.01837 ±.00002
$^{243}Am^{2+}$	4.490 ±.002	5/2	.01821 ±.00002

Table II. Calculated Operator Equivalent Factors for Cm^{3+} and Gd^{3+}.

Ion	$\langle \psi_J \lVert \alpha_J \rVert \psi_J' \rangle$	$\langle \psi_J \lVert \beta_J \rVert \psi_J' \rangle$	$\langle \psi_J \lVert \gamma_J \rVert \psi_J' \rangle$
Cm^{3+}	-1.397×10^{-3}	2.109×10^{-5}	-8.933×10^{-7}
Gd^{3+}	-5.460×10^{-5}	9.885×10^{-8}	-6.010×10^{-10}

Table III. The g_J Values for Am I - Am III and Various Lanthanide Atoms-Ions. The numbers in parentheses are the errors in the last significant figures.

	g_J	Δg_J(I - III)	Configuration	Term	Reference
Am I	1.937884(67)		$5f^7 7s^2$	$^8S_{7/2}$	25
		.012			
Am III	1.926(1)		$5f^7$	$^8S_{7/2}$	This Work
Eu I	1.99337(7)		$4f^7 6s^2$	$^8S_{7/2}$	26
		.0008			
Eu III	1.9926(3)		$4f^7$	$^8S_{7/2}$	27
Ho I	1.19516(10)		$4f^{11} 6s^2$	$^4I_{15/2}$	26
		.013			
Ho III	1.182(1)		$4f^{11}$	$^4I_{15/2}$	28
Tm I	1.14122(15)		$4f^{13} 6s^2$	$^2F_{7/2}$	26
		.007			
Tm III	1.134(1)		$4f^{13}$	$^2F_{7/2}$	12

FIGURE CAPTIONS

Fig. 1. The zero field splittings of a J = 7/2 manifold in cubic symmetry.

Fig. 2. The measured g value as a function of the rotation of the D.C. magnetic field in the 110 plane of CaF_2. The angle 0° corresponds to the 100 direction.

Fig. 3. The zero field splittings for the ions Cm^{3+} and Am^{2+} for the values of the fourth and sixth degree parameters shown.

Fig. 4. The zero field splittings for the lanthanide ions Gd^{3+} and Eu^{2+} in cubic symmetry. The data are taken from Table 2 in Reference 2.

Fig. 5. Calculated energy level diagram for the ground J = 7/2 state of Cm^{3+} in cubic symmetry as a function of magnetic field. The direction of the magnetic field is along a cube axis (100).

Γ_7 ——— $-18b_4 - 12b_6$, $-32b_4 + 8b_6$

Γ_8 ——— $2b_4 + 16b_6$, $-12b_4 + 36b_6$

Γ_6 ——— $14b_4 - 20b_6$, 0

$$b_4 = 60\,B_4;\ b_6 = 1260\,B_6$$

Fig. 1 XBL674-2665-A

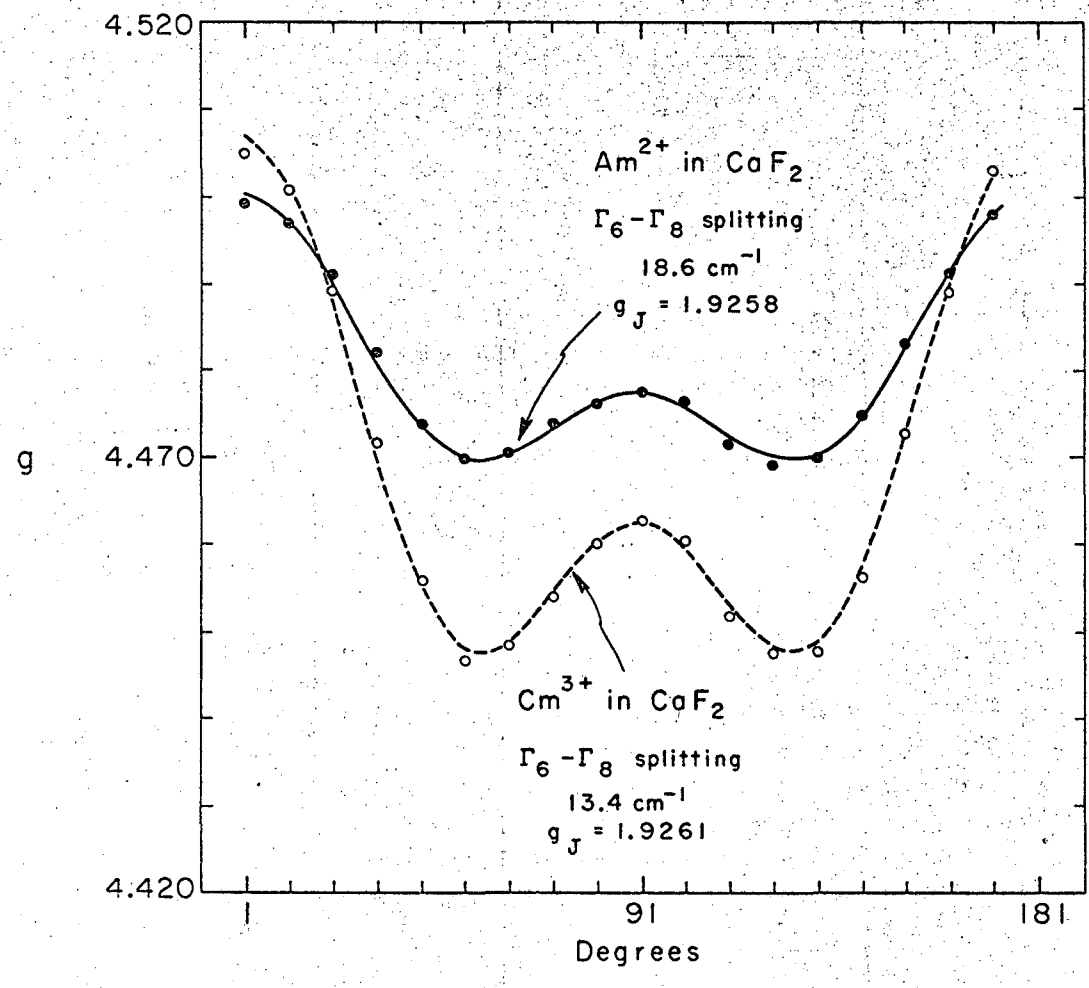


Fig. 2

XBL674-2667

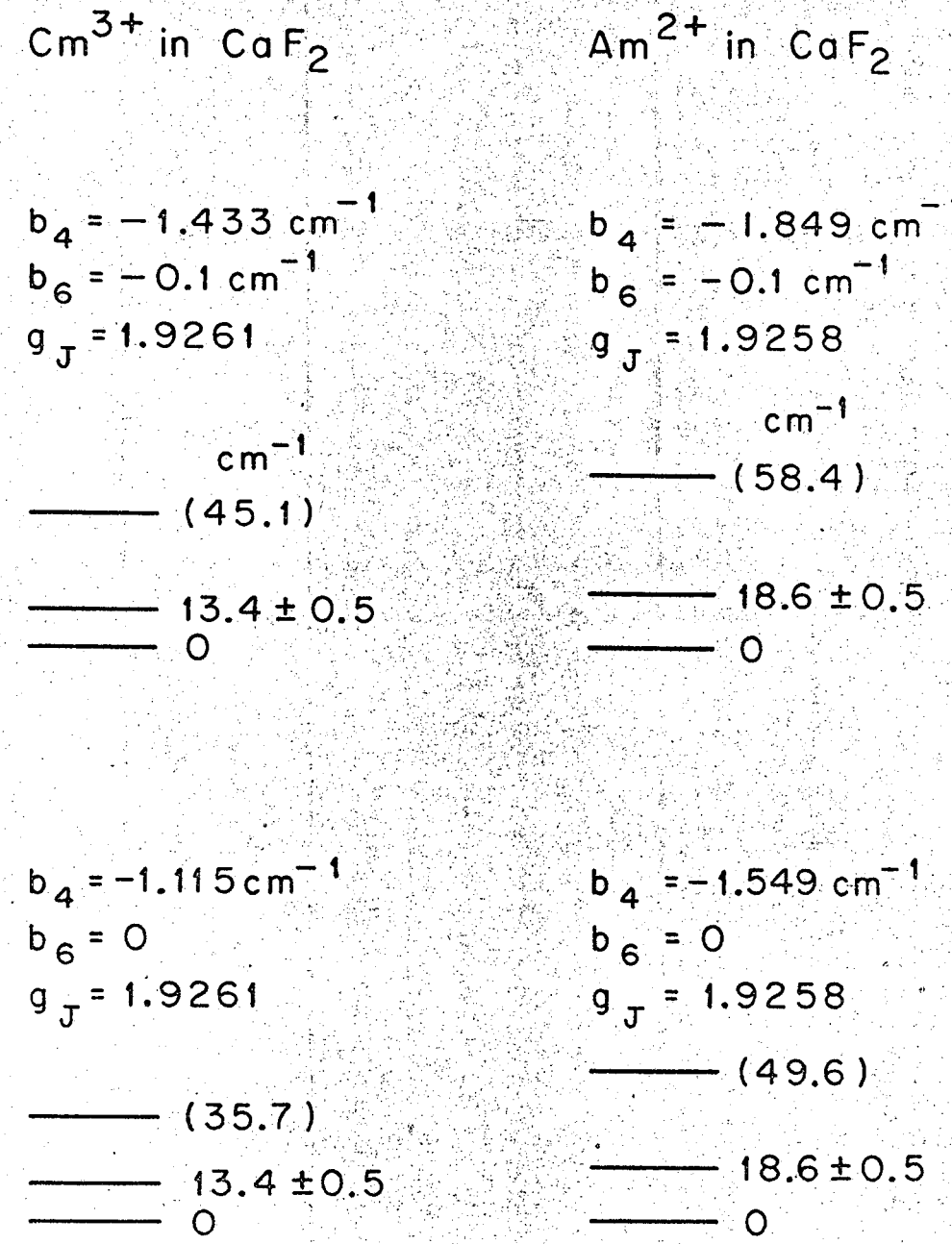
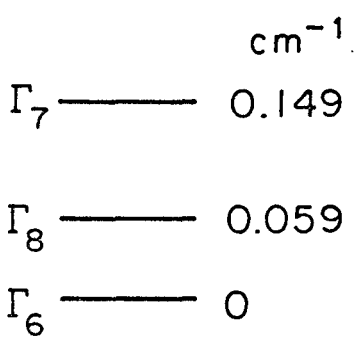


Fig. 3

XBL674-2664-A

Gd^{3+} in CaF_2

$b_4 = -46.3 \times 10^{-4} cm^{-1}$
$b_6 = +1.0 \times 10^{-4} cm^{-1}$



Eu^{2+} in CaF_2

$b_4 = -57.9 \times 10^{-4} cm^{-1}$
$b_6 = +0.50 \times 10^{-4} cm^{-1}$

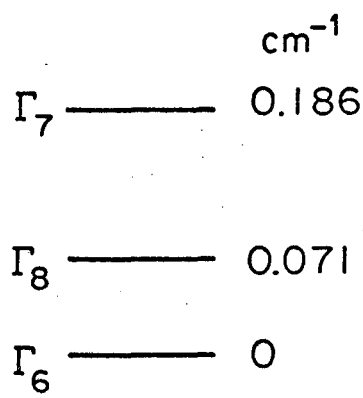


Fig. 4

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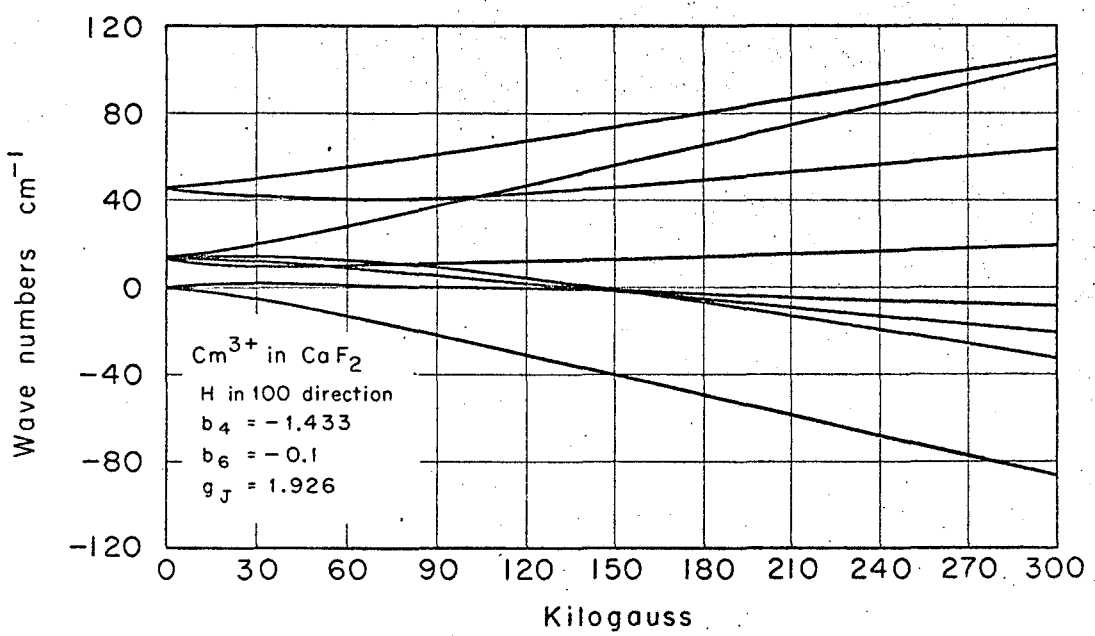

Fig. 5

XBL674-2666

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