

Electron Spin Resonance of Rare-Earth Ions in CeO_2 : Yb^{3+} and Er^{3+} †

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The paramagnetic resonance spectrum of Yb^{3+} and Er^{3+} in single crystals of CeO_2 has been measured at 10 Gc/sec and 4°K. In sites of cubic symmetry, the ground states in both cases are found to be isotropic Γ_7 doublets with $g = 3.424 \pm 0.001$ for Yb^{3+} and $g = 6.747 \pm 0.006$ for Er^{3+} . Hyperfine structures for the odd isotopes were resolved with $A(\text{Yb}^{171}) = (877.1 \pm 1.0) \times 10^{-4} \text{ cm}^{-1}$, $A(\text{Yb}^{173}) = (242.0 \pm 0.3) \times 10^{-4} \text{ cm}^{-1}$, and $A(\text{Er}^{167}) = (232.1 \pm 0.3) \times 10^{-4} \text{ cm}^{-1}$. Nearby charge compensation produces sites of axial symmetry. For Yb^{3+} , one set of axes is along the four $\langle 111 \rangle$ crystal directions with $g_{11} = 4.733 \pm 0.004$ and $g_{\perp} = 2.744 \pm 0.002$. For Er^{3+} two different axial spectra were measured, also with trigonal symmetry about the $\langle 111 \rangle$ directions. For one set $g_{11} = 10.25 \pm 0.05$ and $g_{\perp} = 4.847 \pm 0.005$, and for the other set $g_{11} = 4.539 \pm 0.005$ and $g_{\perp} = 7.399 \pm 0.007$. In most crystals the linewidths were 20 Oe; however, in some crystals in which no cubic sites were found, the axial linewidths were greater than 50 Oe. Comparisons of the axial g -tensor traces with the cubic g tensor and the magnitude and sign of $\Delta g = g_{11} - g_{\perp}$ are the basis for a discussion of the possible nature of the charge compensation producing the axial symmetry.

I. INTRODUCTION

TRIVALENT rare-earth ions have usually been observed to occupy sites of axial symmetry in crystals.^{1,2} Results of recent research have shown they may also occupy cubic sites in the alkaline earth oxides and fluorides.² The rare-earth ion replaces the divalent metal ion and the sites may exhibit either cubic or axial symmetry depending upon the proximity of the necessary compensating charge. Under some circumstances a divalent rare-earth ion may be formed³ which eliminates the necessity for a compensating charge. Recently we have reported⁴ the observation of trivalent rare-earth ions in tetravalent thorium sites of ThO_2 (isomorphous with CaF_2) which displayed both kinds of symmetry.

A simple point-charge-model calculation for the cubic crystal field due to the eight nearest-neighbor oxygens predicts the sign of the fourth- and sixth-order parameters in the potential expansion.⁵ The ground states for the paramagnetic ions are determined by the ratio of these two parameters but the point-charge approximation is not sufficient to give the correct ratio. The cubic crystal field splits the J ground state into a number of sublevels and the g value of a sublevel will only be a function of this ratio when the sublevel is a repeated irreducible representation of the cubic double group.⁶ The g values observed for Yb^{3+} and Er^{3+} occupying cubic symmetry sites in ThO_2 were in good agreement

with the values predicted for Γ_7 doublets.⁴ Since the Γ_7 is not a repeated representation for $J = \frac{7}{2}$ (Yb) or $J = 15/2$ (Er) the ratio cannot be determined precisely. However, an upper and lower limit can be set,⁵ for Yb^{3+} : $1 > |x| > 0.2$ and for Er^{3+} : $0.45 > |x| > 0$ (in Lea, Leask, and Wolf's notation). For the latter case, $|x|$ is expected to be very close to 0.45, since the isoelectronic Ho^{2+} has been shown to have a different ground state (Γ_6) than Er^{3+} (Γ_7) in the same crystal CaF_2 ,⁷ indicating that its $|x|$ is greater than 0.45. The difference in the $|x|$ values of Ho^{2+} and Er^{3+} was attributed to a difference in ionic size.⁷ It would be interesting to see if this ratio changes for these ions in other eight-fold coordinated cubic crystals.

Isomorphous CeO_2 was used as a host crystal for this study. The O-O distance in CeO_2 is 5.411 Å, which is smaller than in ThO_2 where the distance is 5.600 Å. In addition to a comparison of g values in CeO_2 and ThO_2 , other properties of the resonance spectra which can be compared for the two crystals are: hyperfine structure of the odd isotopes, linewidths, relative abundance of cubic and axial sites, and the characteristics of some of the axial sites which are present.

II. EXPERIMENTAL

The CeO_2 crystals were grown from $\text{Li}_2\text{O} \cdot 2\text{WO}_3$ solvent at 1000–1200°C by either a thermal-gradient⁸ or a slow-cooling technique. The resulting crystals were colored (reddish amber) octahedra with dimensions up to 2 mm on an edge. Spectrochemical analysis of optically clear crystals free from inclusions showed no Li or W. (The limit of detection was 100 ppm Li and 500 ppm W.) Approximately 0.1 to 0.5% by weight of 99.9% pure Yb_2O_3 or Er_2O_3 was mixed with reagent grade CeO_2 (G. Frederick Smith Chemical Company) and single crystals were grown. Electron-spin-resonance measurements were made at liquid-helium temperatures

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¹ K. D. Bowers and J. Owen, Rept. Progr. Phys. **18**, 304 (1955); J. W. Orton, *ibid.* **22**, 204 (1959); W. Low, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Suppl. 2.

² K. Heuer, Phys. Status Solidi **4**, 461 (1964).

³ Donald S. McClure and Zoltan J. Kiss, Microwave Res. Inst. Symposia Ser. **13**, 357 (1963).

⁴ M. M. Abraham, R. A. Weeks, G. W. Clark, and C. B. Finch, Phys. Rev. **137**, A138 (1965).

⁵ K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962); M. T. Hutchings, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. XVI, p. 227.

⁶ H. Bethe, Ann. Physik **3**, 133 (1929).

⁷ H. R. Lewis and E. S. Sabisky, Phys. Rev. **130**, 1370 (1963); W. Hayes, G. D. Jones, and J. W. Twidell, Proc. Phys. Soc. (London) **81**, 371 (1963).

⁸ C. B. Finch and G. W. Clark, J. Appl. Phys. **26**, 2143 (1965).

using a conventional reflection-type superheterodyne spectrometer operating at ~ 10 Gc/sec. The samples could be rotated⁴ in the microwave cavity while the resonance signal on an oscilloscope was simultaneously observed, allowing very accurate alignment of various crystal directions with the external magnetic field.

A. Yb³⁺

The observed spectrum displayed absorption lines whose positions were both isotropic and anisotropic with respect to magnet field orientation, corresponding to cubic and axial local symmetries, respectively. The isotropic lines were completely described by the spin Hamiltonian

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + A\mathbf{I} \cdot \mathbf{S},$$

with $S = \frac{1}{2}$, $I = 0$, $\frac{1}{2}$, or $\frac{5}{2}$.

$$g = 3.424 \pm 0.001,$$

$$A_{5/2}(\text{Yb}^{173}) = 151.4 \pm 0.2 \text{ Oe}[(242.0 \pm 0.3)10^{-4} \text{ cm}^{-1}],$$

$$A_{1/2}(\text{Yb}^{171}) = 548.7 \pm 0.6 \text{ Oe}[(877.1 \pm 1.0)10^{-4} \text{ cm}^{-1}].$$

These values are, within experimental error, the same as those obtained for Yb³⁺ in sites of cubic symmetry in ThO₂.⁴

Some of the anisotropic lines were observed to have the orientation dependence characteristic of axial symmetry about the four $\langle 111 \rangle$ crystal directions. The measured g values were

$$g_{11} = 4.733 \pm 0.004,$$

$$g_{1} = 2.744 \pm 0.002,$$

which is similar to one of the axial spectra observed⁴ in ThO₂ where $g_{11} = 4.772$ and $g_{1} = 2.724$. In fact, the trace of the g tensor is the same in both crystals,

$$\frac{1}{3}(g_{11} + 2g_{1}) = 3.407,$$

and presumably the axial sites are caused by the same charge compensating mechanism.

The widths of each of the lines were approximately 20 Oe and were, at least in part, attributed to paramagnetic impurities initially present in the CeO₂. One impurity definitely present was Gd, whose resonance spectrum was observed. (It was very useful in checking the alignment of the crystals.) The intensity ratio of the cubic spectrum to the sum of the axial spectra varied for crystals prepared under different growth conditions.

Cubic sites were not observed in some crystals but axial sites were observed in all crystals. Interestingly, the absence of the cubic sites was associated with the slow-growing technique.

B. Er³⁺

Again the observed absorption spectrum was composed of some lines whose positions were orientation-independent and some lines whose positions varied with orientation. The isotropic lines were described by the

spin Hamiltonian

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + A\mathbf{I} \cdot \mathbf{S},$$

with $S = \frac{1}{2}$, $I = 0$, or $\frac{7}{2}$.

$$g = 6.747 \pm 0.006,$$

$$A_{7/2}(\text{Er}^{167}) = 73.7 \pm 0.1 \text{ Oe}[(232.1 \pm 0.3)10^{-4} \text{ cm}^{-1}].$$

Within experimental error, the results are the same as those obtained for Er³⁺ in cubic sites of ThO₂.⁴

Two different sets of anisotropic lines were observed, both possessing axial orientation dependence about the four $\langle 111 \rangle$ crystal directions but with different g tensors. For one set

$$g_{11} = 10.25 \pm 0.05,$$

$$g_{1} = 4.847 \pm 0.005,$$

and

$$\frac{1}{3}(g_{11} + 2g_{1}) = 6.65,$$

while for the other set

$$g_{11} = 4.539 \pm 0.005,$$

and

$$g_{1} = 7.399 \pm 0.007,$$

$$\frac{1}{3}(g_{11} + 2g_{1}) = 6.45.$$

An axial spectrum which was observed for Er³⁺ in ThO₂,⁴ having symmetry along the three $\langle 100 \rangle$ crystal directions, had parameters

$$g_{11} = 3.462 \pm 0.003,$$

$$g_{1} = 7.624 \pm 0.005,$$

and

$$\frac{1}{3}(g_{11} + 2g_{1}) = 6.24.$$

In all CeO₂ crystals more than one axial spectrum was observed. However, because of the profusion of lines, only two spectra were measured. All crystals had a variety of axial sites but in some crystals no cubic sites were found. Linewidths were approximately 20 Oe except in the latter crystals in which the axial linewidths were larger than 50 Oe. As in the Yb case, these latter crystals were grown by the slow-growth technique.

III. DISCUSSION

The cubic spectra of both Yb³⁺ and Er³⁺ in CeO₂ are essentially the same as in ThO₂ and may be compared (Table I) with the results obtained in isomorphous CaF₂ and CdF₂ by other workers for X band (10 Gc/sec) frequencies.

For Yb³⁺, the g value varies with the magnetic field in CdF₂ because of the closer proximity of the excited Γ_8 state and is lower at higher frequencies.⁹ In CaF₂ the observed g values are independent of field within experimental error.¹⁰ The fact that the Yb g values for the

⁹ V. K. Konyukhov, P. P. Pashinin, and A. M. Prokhorov, *Fiz. Tverd. Tela* **4**, 246 (1962) [English transl.: *Soviet Phys.—Solid State* **4**, 175 (1962).]

¹⁰ W. Hayes and J. W. Twidell, *J. Chem. Phys.* **35**, 1521 (1961).

TABLE I. Data for Yb³⁺ and Er³⁺ in CaF₂, CdF₂, ThO₂, and CeO₂.

	Lattice constants ^a Å	g^b (Calc.)	g (Expt.)	Yb ³⁺ A^{171} (10 ⁻⁴ cm ⁻¹)	A^{178} (10 ⁻⁴ cm ⁻¹)	g^b (Calc.)	Er ³⁺ g (Expt.)	A^{167} (10 ⁻⁴ cm ⁻¹)
CaF ₂	5.4626	3.4237	3.426 ± 0.001 ^c	886.5 ± 1.5 ^c	243.2 ± 0.4 ^e	6.772	6.785 ± 0.002 ^d	225.5 ± 3.0 ^d
CdF ₂	5.3880	3.4237	3.4359 ± 0.0008 ^e	883.0 ± 1.5 ^e	242.0 ± 0.4 ^e	6.772	6.758 ± 0.010 ^f	231.0 ± 3.0 ^f
ThO ₂	5.600	3.4237	3.423 ± 0.001 ^b	877.0 ± 1.0 ^b	241.8 ± 0.3 ^b	6.772	6.752 ± 0.005 ^b	232.6 ± 0.3 ^b
CeO ₂	5.4110	3.4237	3.424 ± 0.001 ^{g,h}	877.1 ± 1.0 ^g	242.0 ± 0.3 ^g	6.772	6.747 ± 0.006 ^{g,i}	232.1 ± 0.3 ^g

^a American Society for Testing and Materials X-Ray Powder File, Sets 1-5, revised (1960).

^b See Ref. 4.

^c W. Low, Phys. Rev. **118**, 1608 (1960). A value of 3.443 ± 0.002 is reported by W. Hayes and J. W. Twidell, in Ref. 10.

^d J. M. Baker, W. Hayes, and D. A. Jones, Proc. Phys. Soc. (London) **73**, 942 (1959); M. Dvir and W. Low, *ibid.* **75**, 136 (1959); Ref. 12.

^e See Ref. 9.

^f G. M. Zverev, L. S. Kornienko, A. M. Prokhorov, and A. I. Smirnov, Fiz. Tverd. Tela **4**, 392 (1962) [English transl.: Soviet Phys.—Solid State **4**, 284 (1962)].

^g This paper.

^h Y. Komet, W. Low, and R. C. Linares give a value of 3.427 ± 0.001 in Phys. Letters **19**, 473 (1965).

ⁱ W. Low and Y. Komet give one value as 6.748 ± 0.008 in Bull. Am. Phys. Soc. **10**, 699 (1965), and Y. Komet, W. Low, and R. C. Linares give a value of 6.759 ± 0.005 in Phys. Letters **19**, 473 (1965).

oxides⁴ are closer to the first-order predicted values than in the fluorides¹¹ implies that the crystal field splitting is larger in the oxides. Another indication of this is the disappearance of the Yb³⁺ resonance in CdF₂ at 20°K,⁹ while the resonance may still be observed above 77°K in ThO₂.⁴

For Er³⁺, the levels are expected to be much closer,⁷ and it is quite surprising that the ThO₂ and CeO₂ spectra are so similar despite their different lattice spacings. It would be desirable to determine the field dependence of the Er³⁺ isotropic g value in both oxides.

For both Yb³⁺ and Er³⁺ axial spectra in these oxides it is expected for small perturbations of the cubic crystal field and for positive charge compensation that $g_{11} > g_{\text{cubic}} > g_{\perp}$.^{4,12} When this was true, the average value ($\frac{1}{3}$ trace) of the g tensor was close to the cubic g value, indicating small axial perturbations¹³ of the cubic sites.

For Yb I¹⁴ and II (Table II) the axial perturbation could be due to charge compensation either at the nearest-neighbor oxygen site (e.g., O vacancy or OH⁻) or at the nearest interstitial site along the same [111] direction (e.g., impurity atom). In the first case we would expect the Δg to be larger than that observed, assuming the situation is the same as in the fluorides

where Δg 's greater than 3 were observed.¹⁵ We must recognize, however, that there is mainly ionic bonding in the fluorides while the bonding in the oxides is partially covalent.

Er II and III have negative Δg 's and a large shift of the g -tensor trace from the cubic g value. The distortion of the cubic crystal field in these two cases is so great as to invalidate the perturbation treatment. The [100] axis for Er II is unequivocal evidence that the charge compensation is in the nearest-neighbor interstitial site. Since Er III has a smaller Δg than Er II we infer that the Er III is due to charge compensation in the next-nearest-neighbor interstitial site. Because of the closeness of other levels in the case of Er³⁺, distortions of the cubic crystal field by an interstitial ion would have a larger effect on the g values than in the case of Yb³⁺. For Er I, a possible implication of the large positive Δg , is that the charge compensation takes place at the nearest-neighbor oxygen site rather than the nearest interstitial site along the (111) direction. We suggest, therefore, that charge compensation at an oxygen site does not distort the cubic field as much as an ion in the nearest or next-nearest interstitial position. That is, the oxygen site compensation only adds a second-order term to the Hamiltonian without affecting the fourth- and sixth-order terms of the cubic crystal field Hamiltonian, while the introduction of an interstitial ion not only adds a second-order term but affects the higher order terms as well. These speculations on the nature of the axial sites are plausible but other interpretations are possible. An investigation of the conditions which determine the relative abundance and character of the cubic and axial sites is desirable.

Although linewidths in the ThO₂ crystals varied with different growth conditions, extremely narrow lines less than $\frac{1}{2}$ Oe were observed⁴ in some cases and it is believed the same will be true in CeO₂ when we can obtain cerium of higher purity.

¹⁵ U. Ranon and A. Yaniv, Phys. Letters **9**, 17 (1964).

TABLE II. Axial sites.

	Axis	g_{11}	g_{\perp}	$\Delta g = g_{11} - g_{\perp}$	$\frac{1}{3}(g_{11} + 2g_{\perp})$
Yb:ThO ₂ I	[111]	4.772 ± 0.002	2.724 ± 0.001	2.048	3.407
Yb:CeO ₂ II	[111]	4.733 ± 0.004	2.744 ± 0.002	1.989	3.407
Er:CeO ₂ I	[111]	10.25 ± 0.05	4.847 ± 0.005	5.40	6.65
Er:ThO ₂ II	[100]	3.462 ± 0.003	7.624 ± 0.005	-4.162	6.24
Er:CeO ₂ III	[111]	4.539 ± 0.005	7.399 ± 0.007	-2.860	6.45

¹¹ W. Low, Phys. Rev. **118**, 1608 (1960); see also Ref. 9.

¹² U. Ranon and W. Low, Phys. Rev. **132**, 1609 (1963).

¹³ H. R. Lewis and E. S. Sabisky, Phys. Rev. **130**, 1370 (1963).

¹⁴ The use of Roman numerals in this paper is only for the purpose of classifying the axial sites.