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

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The paramagnetic resonance spectrum of Yb^{3+} and Er^{3+} in ThO_2 has been investigated at 10.5 kMc/sec over the temperature range of 4 to 2°K. Sites of cubic symmetry as well as axial sites due to nearby charge compensation were observed. Both cubic spectra gave isotropic g values with $g=3.423\pm0.001$ for Yb^{3+} and $g=6.753\pm0.005$ for Er^{3+}, and these values are in good agreement with the predicted values for Γ_7 doublets. Temperature variation showed that these were the lowest states. For both ions in dilute crystals the linewidth was ≤ 0.5 Oe, and in heavily doped crystals the linewidth was 3 to 4 G. Nearby charge compensation in the Yb^{3+} case produces four sites of trigonal symmetry with [111] axes, while in the Er^{3+} case the preponderant axial site had tetragonal symmetry with three [100] axes. For Yb^{3+}, $g_{\parallel}=4.772\pm0.002$ and $g_{\perp}=2.724\pm0.001$, and one-third the trace of the g tensor was 3.407. For Er^{3+}, $g_{\parallel}=3.462\pm0.003$ and $g_{\perp}=7.624\pm0.005$, and one-third the trace of the g tensor was 6.240. The linewidths obtained for the axial sites were broader than those for cubic sites and varied with angle. Evidence for macroscopic crystalline imperfections was also found.

I. INTRODUCTION

The electron-spin-resonance (ESR) spectra of many rare-earth ions in crystal fields of cubic symmetry[1] have been observed in eightfold coordination, e.g., CaF_2, and sixfold coordination, e.g., CaO. The ground state is predicted to be different in the two cases because of the reversal in sign of the fourth-order term in the crystal potential. Rare-earth ions can be incorporated into ThO_2 crystals in the Th position with cubic symmetry preserved. Gd^{3+} has been observed in ThO_2 (Ref. 2) in sites of cubic symmetry. The absence of isotopes with nuclear moments (Th and O) eliminate a major source of line broadening. We report here the observation of the ESR of two more rare-earth ions in sites of cubic and axial symmetry in ThO_2. These ions, Yb^{3+} and Er^{3+}, were incorporated in synthetic ThO_2 crystals during growth.[3]

ThO_2 is a simple cubic array of oxygen ions with thorium ions at alternate body centers. The space-group symmetry is O_h^5, the structure being isomorphous with CaF_2. The substitution of a trivalent rare-earth ion into the Th^{4+} site should not alter the original cubic symmetry of the crystal field. However, charge compensation must take place, and if the charge compensation is in the vicinity of the rare-earth ion, there will be departures from cubic symmetry. For example, an oxygen vacancy in the nearest-neighbor position will produce trigonal symmetry about the [111] axis of the cube. For charge compensation in an interstitial body-centered site, two kinds of axial symmetry are possible. If the rare-earth ion is in a nearest-neighbor Th^{4+} site, the crystal field will have tetragonal symmetry about the [100] direction. Should the rare-earth ion be in a next-nearest-neighbor site the field will have trigonal symmetry about the [111] direction. The perturbation of the cubic crystal field due to the charge compensation should decrease with increasing distance from the rare-earth ion.

II. CRYSTAL GROWTH

The thorium oxide crystals used in this study were grown from a molten salt solvent, $Li_2O\cdot 2WO_3$ containing one weight percent B_2O_3, at 1225–1275°C. Nucleation and growth of these crystals resulted from gradual mass transfer of dissolved ThO_2 nutrient along a temperature gradient in the solution. Covered platinum containers were used in air atmosphere. The details of the crystal growth are to be described elsewhere.[3]

The purity of all the starting materials in these syntheses was greater than 99.93 wt%. The resulting crystals were (near to) water-white octahedra [with (111) facets] up to 3 mm on an edge. Representative undoped crystals were analyzed by emission spectroscopic methods; less than 500 ppmW, 100 ppm Li, and 100 ppm B were detected. The first crystals grown contained about 1.0 wt% Er^{3+} or Yb^{3+}; later crystals were doped to an estimated level of one-twentieth this concentrasion. The mosaic spread of an undoped crystal was determined by x-ray double-crystal diffraction from one of the major (111) faces. The linewidth of the diffracted x-ray beam at half maximum was 0.05°.

III. Yb^{3+}

A. Theory

The electronic configuration of Yb^{3+} is $4f^{13}$ with a ground state of ${}^2F_{7/2}$. A cubic field will split the eightfold degenerate ${}^2F_{7/2}$ level into a fourfold Γ_8, a twofold Γ_6, and a twofold Γ_7. The Γ_6 and Γ_7 doublets will have isotropic splitting factors in an applied magnetic field. The splitting of the Γ_8 quartet will depend upon orientation of the applied field with respect to the crystal axes.[4] With eightfold coordination, the lowest level is expected

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to be a Γ_7 or a Γ_6 depending upon the ratio of the fourth- and sixth-order cubic-field parameters.[5] Yb^{3+} in CaF_2 (Ref. 6) and CdF_2 (Ref. 7) have been observed with the Γ_7 doublet lowest. With sixfold coordination, the Γ_6 state is expected to be lowest regardless of the ratio of the cubic-field parameters. A Γ_6 doublet was found to be lowest in the case of Yb^{3+} in CaO.[8]

B. Experimental

Crystals of Yb^{3+}:ThO_2 were investigated by electron spin resonance at 4°K and at a frequency of 10.4 Gc/sec with a spectrometer of the Hirshon-Fraenkel type.[9] Two different types of spectra were observed corresponding to different point symmetries. One of the spectra was isotropic with rotation of the magnetic field and was attributed to a paramagnetic ion in a cubic site. The other spectrum, upon rotation of the magnetic field, had axial symmetry about the four [111] directions of the crystal.

The isotropic spectrum consisted of a strong central line and two sets of weaker lines. This spectrum can be described by a spin Hamiltonian of the form

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

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

$$g=3.423\pm0.001,$$

$$A_{5/2}=151.3\pm0.20\ \mathrm{Oe}(241.8\pm0.3\times10^{-4}\ \mathrm{cm}^{-1}),$$

$$A_{1/2}=548.8\pm0.6\ \mathrm{Oe}(877.0\pm1.0\times10^{-4}\ \mathrm{cm}^{-1}).$$

These spins are in agreement with the two known odd isotopes, Yb^{173} ($I=\frac{5}{2}$) and Yb^{171} ($I=\frac{1}{2}$).[10] An estimate of the observed relative intensity ratios of the six-line set ($I=\frac{5}{2}$), the two-line set ($I=\frac{1}{2}$) and the central line ($I=0$) was 0.21:0.18:0.61. The ratios of the natural abundances, (Yb^{173}) 0.16:(Yb^{171})0.14:(all even-even isotopes)0.70, are in reasonable agreement.

The observed g value is in good agreement with the value calculated for a Γ_7 doublet[11]

$$0.8660|\pm\tfrac{5}{2}\rangle-0.500|\mp\tfrac{3}{2}\rangle$$

gives

$$g=3g_{\mathrm{Landé}}.$$

Atomic-beam measurements[12] give

$$g_{\mathrm{Landé}}(\mathrm{Tm^I})=1.14122\pm0.00015.$$

The $g_{\mathrm{Landé}}(\mathrm{Tm^I})$ is not expected to be appreciably different from $g_{\mathrm{Landé}}(\mathrm{Yb^{IV}})$. The predicted g value is therefore

$$g=3.42366.$$

The measured value of the $I=\frac{5}{2}(Yb^{173})$ hyperfine constant was obtained using third-order terms[13] in the spin Hamiltonian. Since transitions with the same $|m_I|$ have the same even-order terms, differences between them will cancel the fourth-order terms. The hyperfine term for the $I=\frac{1}{2}(Yb^{171})$ nucleus was determined using the Breit-Rabi equation.[14] The ratio of the moments is

$$\mu_{173}/\mu_{171}=(A_{173}/A_{171})\times(\tfrac{5}{2}/\tfrac{1}{2})=1.378\pm0.003,$$

assuming no hyperfine anomaly. The value given by Cooke and Park[15] is 1.39±0.01, and the value by Low[16] is 1.375±0.005. All of these values are in reasonable agreement.

The concentration of the axial centers was approximately half that of the isotropic centers. Since no resonances were observed in an undoped ThO_2 crystal grown under the same conditions, we have assumed that the axial lines are also Yb^{3+} with charge compensation. Because of the low intensity and width of the axial lines, we were unable to observe the hyperfine interactions with the odd Yb isotopes.

For observation of the axial spectrum, the crystal was oriented so that the magnetic field rotated in a (110) plane. With this rotation, the field could be directed along the [100], [110], and [111] directions. The two [111] axes not in this plane make equal angles with any particular direction of the magnetic field. For centers with axial symmetry along [111] directions, we would therefore expect to observe three lines of intensity ratios 1:1:2. All lines should coalesce when the field is along a [100] direction since the four [111] axes make the same angle with this direction. The two lines of lower intensity should exhibit the same angular variation with rotation of the field but be out of phase by the actue angle, $\theta=\cos^{-1}\frac{1}{3}$, which is the angle between the two [111] directions in the plane.

The observed spectrum was in good agreement with this hypothesis of a [111] axis for the axial centers. For an orientation of the field along the [100] direction, almost complete coalescence of all the lines in the axial spectrum was observed. The accuracy of the crystal alignment was estimated from the residual separation

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of the lines. The field was within 0.25° of the [100] direction. Upon rotation of the field this small misalignment caused the more intense line to be resolved into two lines of equal intensity quite close together. The two remaining lines were observed to have the predicted angular variation with relation to the field. The minimum and maximum fields for these lines were, respectively, parallel and perpendicular to the two [111] directions in the (110) plane. The more intense line (actually two close lines) also had the same maximum field when the field along a [110] direction (perpendicular to the two [111] axes). These observations show that the centers have their charge compensation along the [111] directions.

Measurements were also made whereby the crystal could be rotated in a vertical plane while simultaneously observing the resonance signals. A (111) face of the crystal was glued with rubber cement to a nylon disc whose axis passed through the narrow wall of the microwave cavity (rectangular TE_{102} mode) to an external gear which could be rotated. The accurate alignment of a crystal [100] direction with the field was achieved and all of the lines from sites with [111] axes coalesced.

The measured g values were

$$g_\perp = 2.724 \pm 0.001,$$
$$g_{||} = 4.772 \pm 0.002.$$

For small axial distortions of the cubic field, the trace of the g tensor is expected to be conserved,[17] i.e.,

$$(g_{||} + 2g_\perp)/3 \cong g_{\text{isotropic}},$$
$$g_{\text{isotropic}} = 3.423,$$

and

$$(g_{||} + 2g_\perp)/3 = 3.407,$$

which is in reasonable agreement. A measure of the axial field strength is the anisotropy $|g_{||} - g_\perp| = 2.05$, a value intermediate to those found in the alkaline earth fluorides, where values in the neighborhood of three and one were observed.[18]

An additional complication of the axial spectra was observed. Each of the axial lines was split into two lines whose separation was a function of orientation. The maximum separation of ~30 Oe decreased to zero when the field was parallel or perpendicular to the axes. Different intensity ratios for the two lines were found in different crystals from the same crystal growth run.

One of the crystals used for the above measurements was examined by an x-ray rocking-curve technique. One major subgrain boundary was found for reflection from a (111) facet, with an angle of ~5 min. Assuming that this subgrain boundary extends throughout the crystal, we calculate from the equation

$$2g\delta g = (g_{||}^2 - g_\perp^2) \sin 2\theta\delta\theta$$

a maximum separation of ~20 Oe between the axial lines in each of the subgrains. The separation should be zero at 0° and 90° as was observed. Further work on this hypothesis is required.

The width of the cubic lines in the heavily doped crystals, was $\Delta H = 3.5$ Oe invariant with rotation of the magnetic field. The axial lines were found to vary in width from ~6 Oe ($H_\perp$) to 3 Oe ($H_{||}$) as the field was rotated, and are much smaller than those found in Yb:CaO.[8] The relative intensities of the axial and cubic lines were constant over the temperature range ≈1.5 to ≈50°K. At the lowest temperature, ≈1.5°K, an estimate of the spin-lattice relaxation time T_1 of the central cubic line gave $\sim 10^{-3}$ sec. At ≈77°K, this line was found to have a width of ~30 Oe. The other lines were not observed.

The width of the central cubic line was measured in crystals which had been doped at ~1/20 the doping level of the crystals used in the above measurements. Several low-doped crystals were placed in the cavity, and the measurement was made at ≈1.5°K. The linewidth was ≤0.5 Oe. Therefore, the linewidth in the heavily doped crystal is due to spin-spin interactions and to small perturbations of the cubic crystal field. In the heavily doped crystals, we suppose these small perturbations to arise from charge compensation in remote sites giving a very small anisotropy in the g value. The large number of these remote sites would result in an isotropic inhomogeneous broadening of the cubic lines. There are two contributions to the linewidth from spin-spin interactions, (1) interactions between identical sites which would cause homogeneous broadening and, (2) interactions between dissimilar sites which would cause inhomogeneous broadening. Our experiments do not distinguish between these contributions to the linewidth.

IV. Er^{3+}

A. Theory

The electronic configuration of Er^{3+} is $4f^{11}$ with a ground state $^4I_{15/2}$. In a cubic field, the sixteenfold degeneracy will split into three Γ_8 quartets, a Γ_6 doublet, and a Γ_7 doublet. For eightfold coordination, either a Γ_6 or Γ_7 doublet is expected to be lowest,[11] depending upon the ratio of the fourth- and sixth-order cubic field terms. Observations[19] on Er^{3+}:CaF_2 have shown that the Γ_7 doublet is lowest. With sixfold coordination, a Γ_8 quartet was found to be lowest in Er^{3+}:MgO[20] and in Er^{3+}:CaO.[8]

B. Experimental

Crystals of ThO_2 doped with Er_2O_3 were grown by the same process as the Yb^{3+}-doped crystals. The spectra observed in these crystals were quite similar to the spectra of the Yb:ThO_2 in that both cubic and axial

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centers were found. The cubic spectrum had a strong central line and eight weaker lines of equal intensity. The only odd Er isotope is Er^{167} with $I=\frac{7}{2}$ (Ref. 21) and a natural abundance of 23%. The observed ratio of the sum of the intensities of the hyperfine lines to the central line was in good agreement with this natural abundance. The spin Hamiltonian used was

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

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

$$g=6.752\pm0.005,$$

$$A_{7/2}=73.8\pm0.1 \text{ Oe}[(232.6\pm0.3)\times10^{-4}\text{ cm}^{-1}].$$

The Γ_7 doublet[22]

$$0.6332|\pm13/2\rangle+0.5819|\pm\tfrac{5}{2}\rangle -0.4507|\mp\tfrac{3}{2}\rangle-0.2393|\mp11/2\rangle,$$

gives

$$g=g_{\text{Landé}}17/3.$$

Atomic-beam measurements[23] give

$$g_{\text{Landé}}(\text{Ho}^{\text{I}})=1.19515\pm0.00010,$$

a value which is not expected to be appreciably different from $g_{\text{Landé}}$ (Er$^{\text{IV}}$). Using this $g_{\text{Landé}}$, the theoretical g value is

$$g=6.772.$$

For a Γ_6 doublet, $g=5g_{\text{Landé}}=5.975$.

Our measured $g=6.752$ is in reasonable agreement with the theoretical value for a Γ_7 doublet.

The linewidth at half-maximum aplitude of the "cubic" lines was 4 Oe in the heavily doped crystals, and was ≤0.5 Oe in the lightly doped crystals. No variation with temperature from 1.5 to 4°K was observed. The spin-lattice relaxation time was considerably shorter than the time found for Yb as expected, but it did not contribute to the linewidth in this temperature range. Broadening of the line was observed upon warming to 20°K and above 20°K became so broad as to be unobservable. The observed linewidth in the heavily doped crystals is assumed to have the same origins as attributed previously to the Yb "cubic" lines.

The concentration of centers with axial symmetry was approximately half that of the cubic centers. Due to the width and low intensity of the axial lines, we were unable to observe the hyperfine interactions with the odd Er isotope.

The most intense lines in the axial spectra were found to have tetragonal symmetry about the three [100] directions with

$$g_{\parallel}=3.462\pm0.003,$$
$$g_{\perp}=7.624\pm0.005.$$

By rotating the crystal, exact alignment of a crystal [111] direction with the external magnetic field was obtained. The coalescence of these lines for this orientation verified our identification of the axes.

The linewidth varied with orientation from ∼20 Oe($H_{\perp}$) to ∼40 Oe$H_{\parallel}$). The axial lines were seven times broader than the Yb axial lines. It is to be noted that in both cases the greater width was associated with the smaller g values and the narrower width with the larger g value. The width and intensity of the lines were invariant with respect to temperature from ∼1.5 to 4°K. This invariance indicates that spin-lattice interactions do not make an appreciable contribution.

The doubling of the axial lines that was observed in Yb:ThO$_2$ was also found in the Er:ThO$_2$ crystals, despite the difference in linewidth.

Lines of weaker intensity and smaller width due to other centers were present. Because of their low intensity, the symmetry axes of these centers were not determined.

The trace of the g tensor is

$$(g_{\parallel}+2g_{\perp})/3=6.24,$$

where $g_{\text{isotropic}}=6.752$. The deviation from $g_{\text{isotropic}}$ is over 10 times larger than for Yb.

The axial anisotropy

$$|g_{\parallel}-g_{\perp}|=4.162$$

is also much larger than for Yb.

DISCUSSION

For the axial spectra, we may approximate the crystal field by superposing a term $B_2{}^0O_2{}^0$ on the cubic field.[24] If the distortion is caused by positive charge compensation, then it is expected that for Yb^{3+}, $g_{\parallel}>g_{\text{isotropic}}>g_{\perp}$, and this is indeed the case. We would expect the sign of the charge compensation for Er^{3+} to be the same as for Yb^{3+} (both positive). The operator equivalent $\langle J\|\alpha\|J\rangle$ for Er^{3+} has the same sign as for Yb^{3+}, and therefore $g_{\parallel}$ should be greater than $g_{\perp}$, in this case too. This expectation is not realized, since the relative magnitude of $g_{\parallel}$ and $g_{\perp}$ in the Er:ThO$_2$ crystals is reversed with respect to Yn:ThO$_2$. This result may be due to the charge compensation at the axial center being a negative charge in contradiction to the expected positive charge compensation; or, more likely, the approximation of the axial distortion by a diagonal crystal-field term of the second order alone is not valid. The deviation of the g tensor trace from the cubic g supports this latter supposition. Using the formula[25]

$$\mu_n\langle r^{-3}\rangle=\frac{A}{g\beta}\,\frac{I}{2}\,\frac{\langle J\|\Lambda\|J\rangle}{\beta_n\langle J\|N\|J\rangle},$$

$$\mu_n(\text{Yb}^{171})\langle r^{-3}\rangle=6.038\pm0.006,$$
$$\mu_n(\text{Yb}^{173})\langle r^{-3}\rangle=8.323\pm0.008,$$
$$\mu_n(\text{Er}^{167})\langle r^{-3}\rangle=5.81(3)\pm0.01,$$

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where $\langle r^{-3}\rangle$ is in atomic units and μ_n is in nuclear magnetons. The values for $\langle r^{-3}\rangle$ given by Lindgren[26] yield

$$\mu_n(\mathrm{Yb}^{171})=0.50\,,$$
$$\mu_n(\mathrm{Yb}^{173})=0.68\,,$$
$$\mu_n(\mathrm{Er}^{167})=0.56\,.$$

The extremely small linewidth observed for the cubic lines in the low-doped crystals is, to our knowledge, the smallest yet observed for any rare earth in a solid. A line of this width should be very useful for self-ENDOR experiments.

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Superconductivity of α-Titanium Solid Solutions with Vanadium, Niobium, and Tantalum

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It was found that the hcp solid solutions of V, Nb, and Ta in α-Ti show a nearly linear increase in T_c. There is no difference in the effect of V, Nb, or Ta.

I. INTRODUCTION

IN the bcc β solid solutions of Ti-V, Ti-Nb, and Ti-Ta alloys the superconducting transition temperature T_c increases[1–4] with increasing valence-electron concentration. This is explained by an increase in the γ values, e.g., of the Ti-V alloys.[4] The influence of the elements of the Vth group of the periodic system V, Nb, and Ta on T_c of the hcp α solid solution has not been examined yet. All samples investigated up to now were beyond the solubility range of the α solid solution. For high-purity alloys this α solid solution range extends for the Ti-V and Ti-Nb alloys up to not more than 2.5 at.%.[5,6] According to our own investigations, the maximum solubility of Ta in Ti at 650°C is of approximately 5 at.%. At concentrations a little above the solubility limit the β phase is usually present in the form of filaments. These filaments have a lower Ti concentration and a higher T_c than the α phase matrix. This explains, for example, the difference in T_c between 1.8 and 5.8°K in a Ti-Nb alloy with about 3.5 at.% Nb when slowly cooled and water-quenched.[2] Intermediate phases and the formation of martensitic α′ do not seem to have a strong influence on T_c in this group of alloys.[7]

It was suggested that T_c of alloys in the α solid-solution range is not increased with decreasing Ti concentration.[2,8] In a newly published investigation[9] about superconductivity in hcp solid solutions of Ti-V and Ti-Nb, the composition of the investigated samples (4 at.%) was beyond the solubility range and therefore the results seemed to be doubtful despite the fact that it was stated that the rapidly quenched alloys are single phase up to more than 10 at.% in both cases. The bulk superconductivity may have been caused by an almost identical T_c of α and β or more probably by the formation of metastable phases during the rapid quenching.

We therefore started an investigation of the superconductivity of these alloys and took special care to prepare the samples under defined conditions and to avoid contamination by β filaments.

II. EXPERIMENTS

The starting materials were iodide titanium from Foote Mineral Company which was electron-melted and degassed. The purity of V, Nb, and Ta was 99.8%, the DPN hardness 60, 40, and 45, respectively. Ten-gram buttons were melted three times in an argon arc furnace to ensure homogeneity. The alloys prepared in this way show a Widmannstätten-type structure of transformed β. We therefore cold-rolled these alloys up to more than 40% deformation and annealed them at 650°C for 2 h in a closed titanium cylinder placed in an evacuated silica tube in order to avoid contamination by oxygen. According to the metallographical examination these

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