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F Centers in Thorium Oxide*

V. I. Neeley
Battelle Memorial Institute, Pacific Northwest Laboratories, Richland, Washington

AND

J. B. Gruber† and W. J. Gray
Washington State University, Department of Physics, Pullman, Washington

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Single crystals of ThO_2 grown in our laboratory have been subjected to ionizing radiations of 2-MeV electrons, Co^{60} γ rays, and 150-keV x-rays. The electron-spin-resonance spectrum of these irradiated single crystals indicates that an electron is trapped near an O^{--} vacancy in the crystal lattice of ThO_2. The ESR spectrum is the same regardless of which radiation was used to bombard the samples. Optical and ESR low-temperature studies have demonstrated that no paramagnetic ion impurities are present in the samples prior to irradiation, and similar studies performed on irradiated samples indicate that the observed signal is not the result of valence changes produced by irradiation of ions in the crystal. The observed spectrum can be interpreted as due to a defect having local tetrahedral symmetry which is very slightly distorted axially along the body diagonal in the over-all cubic symmetry of the ThO_2 lattice. Room-temperature g values are $g_{\parallel}=1.9739$ and $g_{\perp}=1.9644$. The linewidth at half-maxima ranges from approximately 32 G at room temperature to less than 1.5 G near liquid-helium temperature. All evidence so far examined leads us to conclude that we have observed the ThO_2 *F* center.

I. INTRODUCTION

During the past several years there has been interest in the results of the electron spin resonance and optical spectra of trivalent rare earth ions doped into single crystals of ThO_2.[1–3] Most recently tetravalent actinide ions and the rare earth Tb^{4+} have been successfully incorporated into the ThO_2 lattice and their optical and electron spin resonance spectra are presently being studied.[4] The fact that large strain-free, defect-free single crystals of ThO_2 can be grown containing tetravalent actinide ions has prompted us to use these ions as probes in the study of ThO_2 lattice dynamics.

Thorium oxide is a simple cubic array of oxygen ions with thorium ions located at alternate body centers.[1] Each O^{--} ion is found at the center of a tetrahedron of Th^{4+} ions, while each Th^{4+} ion is found at the center of a cube with eight O^{--} ions at the corners. The ThO_2 structure is isomorphic with CaF_2 and has a space-group symmetry of O_h.

The success in growing these crystals led us to attempt a study of defects in ThO_2 single crystals produced by various irradiations. To our knowledge, previous attempts to observe the *F* center or other types of centers in single crystals of ThO_2 have been unsuccessful.[5] The detection of a ThO_2 defect center, believed to be an *F* center, discussed in this paper, is thought to be due to the use of high quality, strain-free crystals which produced virtually no line broadening in the ESR spectrum.

II. GROWTH OF SINGLE-CRYSTAL THORIUM OXIDE

It has been demonstrated[3] that single crystals of ThO_2, ranging in size from 1 to 200 mm^3, can be grown from either PbO-PbF_2 or BiO_3-PbF_2 flux systems. The melts from which the largest ThO_2 crystals have been grown contain 7 mole% ThO_2, 15 mole% Bi_2O_3, and 78 mole% PbF_2. The bismuth-oxide and lead-fluoride chemicals were reagent grade and the thorium oxide purchased from Trona was spectroscopically analyzed to be at least 99.9% pure. Additional chemical purification was carried out in our laboratory so that the flux and ThO_2 material used was better than 99.99% free of paramagnetic ion impurities. The powders were mechanically mixed and fused in tightly covered platinum crucibles. The crucibles were heated by two super Kanthal elements in a temperature controlled muffle-type furnace. A description of the growth and separation of the ThO_2 crystals from the solidified flux can be found elsewhere.[3] The crystals obtained were generally cubic in habit. Although every batch of crystals contained some with occlusions and macroscopic defects, at least 20% of the crystals ranging in size from 1 to 5 mm on a side were clear and free of obvious defects under microscopic examination. X-ray crystallography revealed these crystals to be cubic and further optical and ESR studies on these crystals doped with tetravalent actinide ions indicate that the crystals are cubic.

Optical spectra of undoped single crystals of ThO_2 revealed no trace of rare earth or actinide ion impurities. The paramagnetic resonance spectrum of selected single

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[3] J. B. Gruber, U. S. Atomic Energy Commission Progress Report, No. San-34-120-2 (unpublished) for Contract USAEC-AT(11-1)-34, Project 120, (1966)—references to earlier work on thorium oxide carried out under this contract are listed in this report.

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[5] W. Low and D. Shaltiel, Phys. Rev. **115**, 424 (1959).

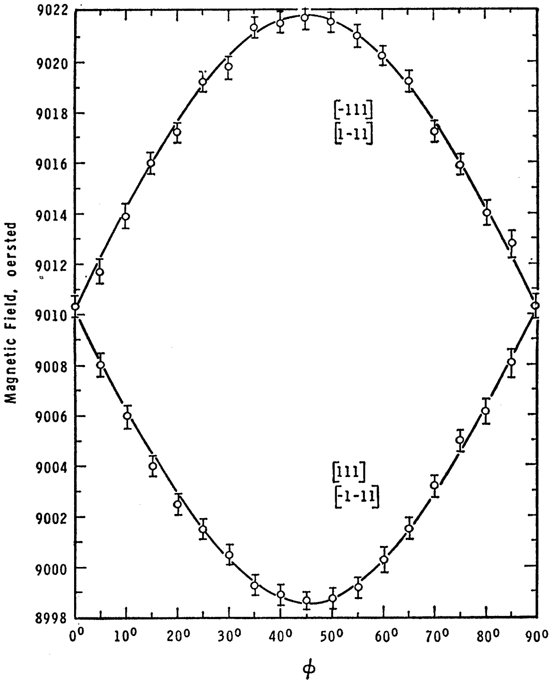

FIG. 1. Irradiated ThO_2 single crystal aligned with microwave field along [100] direction and external magnetic field rotated in a plane perpendicular to [100] direction. Room-temperature spectrum.

crystals taken at room and at liquid-helium temperatures revealed no trace of paramagnetic ion impurities or defects produced in the growth and annealing processes.

III. DEFECT CENTER FORMATION TECHNIQUES

Several small crystals ranging from 30 to 50 mg (1 to 2 mm on a side) were bombarded with 2-MeV electrons. The beam current used was 50 μA and was applied for 5 min from a Van de Graaff accelerator. The single crystals were attached to a cold finger which was immersed in a liquid-nitrogen Dewar. The crystals were then immediately placed in a cylindrical cavity (TE_{011} mode) of an ESR spectrometer. A Strand Labs 602EPR spectrometer operating at 24.83 GHz was used together with a Hoffman Labs liquid-helium Dewar system. The observed room-temperature spectrum agreed with that observed when crystals irradiated by a CO^{60} source (2×10^9 R) and by 150 keV x-ray (50 mA for 1.5 h) were examined under similar experimental conditions. Low-temperature measurements of the spectra near liquid-helium temperature gave no shift in the position of the lines, but the full width of the lines at half-maxima reduced from approximately 32 G to less than 1.5 G.

Optical spectra of irradiated and nonirradiated ThO_2 single crystals were taken on a Cary 14-R spectrophotometer.

IV. DISCUSSION

The observed spectrum can be described by a spin Hamiltonian of the form

$$H=g\beta\mathbf{H}\cdot\mathbf{S},$$

where $|\mathbf{S}|=\frac{1}{2}$.

The angular dependence of the resonance spectrum is given by

$$h\nu=g\beta H,$$

where $g=(g_{\parallel}^2\cos^2\theta+g_{\perp}^2\sin^2\theta)^{1/2}$ and θ is the angle between the crystal symmetry axis and the applied external magnetic field.[6] For pure tetrahedral symmetry the g value should be isotropic; however, the observed spectrum indicates the center has a slightly anisotropic g value with a distortion axis along the body diagonal of the over-all cubic lattice of ThO_2.

Two sets of spectra were observed, corresponding to two different orientations of the crystal in the microwave field.

In the orientation for Fig. 1, the crystal was aligned with the microwave magnetic field along the [100] direction in the crystal and the external magnetic field, H was rotated in a plane perpendicular to the [100] direction. The angular dependence of the two resonance lines in Fig. 1 agree well with that expected for a defect center on the assumption of a slightly distorted local tetrahedral symmetry with room-temperature values of $g_{\parallel}=1.9739\pm0.0010$ and $g_{\perp}=1.9664\pm0.0010$ relative to DPPH. Orientation studies used to determine the g value were made at liquid-helium temperature as well. Within the experimental capabilities of the instrument, the g values were essentially the same although the uncertainty in the value was reduced manyfold.

The angular dependence of the magnetic field for distortion axes along the [111] and [−1−11] lines is given by

$$H=(\sqrt{3}h\nu/\beta)[g_{\parallel}^2+2g_{\perp}^2+(g_{\parallel}^2-g_{\perp}^2)\sin2\phi]^{-1/2},$$

where $g_{\parallel}$ and $g_{\perp}$ have been given previously, and where ϕ is the angle between the applied external magnetic field and the [001] direction of the cube. The field dependence for the [−111] and [−1−11] lines is given by

$$H=(\sqrt{3}h\nu/\beta)[g_{\parallel}^2+2g_{\perp}^2-(g_{\parallel}^2-g_{\perp}^2)\sin2\phi]^{-1/2}.$$

For an orientation of the external magnetic field along the [001] direction, a complete coalescence of the two sets of lines was observed.

In the second orientation for Fig. 2, the crystal was aligned with the microwave magnetic field parallel to a (110) plane and the external magnetic field H was rotated in an equivalent perpendicular (110) plane. In this particular orientation, two ⟨111⟩ distortion axes

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[6] W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960); B. Bleaney and K. W. H. Stevens, Rept. Progr. Phys. **16**, 108 (1953).

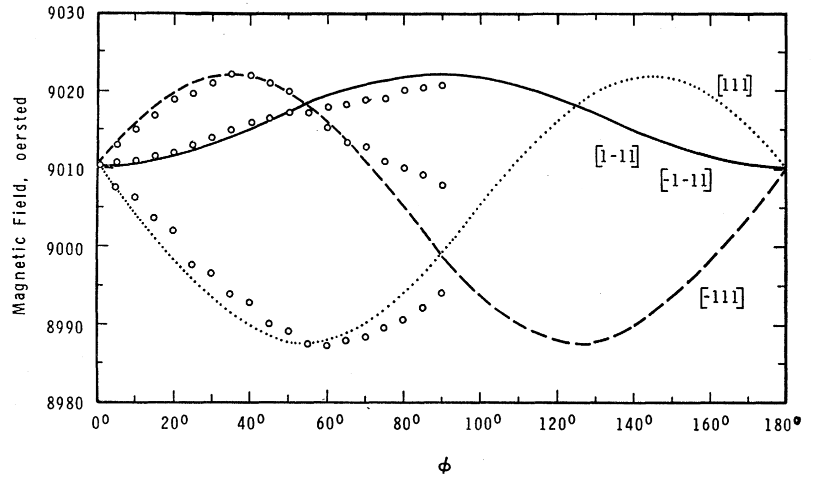

FIG. 2. Irradiated ThO$_2$ single crystal aligned with microwave field parallel to a (110) plane and external magnetic field rotated in an equivalent perpendicular (100) plane. Room-temperature spectrum.

lie in the plane of rotation of the magnetic field and the other two make equal angles with the magnetic field. Thus we should expect two lines differing in phase by $\theta = \arccos\frac{1}{3}$ (the angle between the $\langle 111 \rangle$ directions in the plane) from the two axes in the plane of rotation, and one line from the other two axes.

The field variation of the lines of Fig. 2 corresponding to the [1−11] and [−1−11] axes are given by

$$H = (\sqrt{3}h\nu/\beta)[3g_\perp^2 + (g_\parallel^2 - g_\perp^2)\cos^2\phi]^{-1/2},$$

and that for the [111] and [−111] axes are, respectively

$$H = (\sqrt{3}h\nu/\beta)[g_\parallel^2 + 2g_\perp^2 + (g_\parallel^2 - g_\perp^2) \times (\sin^2\phi + \sqrt{2}\sin 2\phi)]^{-1/2},$$

and

$$H = (\sqrt{3}h\nu/\beta)[g_\parallel^2 + 2g_\perp^2 + (g_\parallel^2 - g_\perp^2) \times (\sin^2\phi - \sqrt{2}\sin 2\phi)]^{-1/2}.$$

The angular variation of the observed room-temperature spectrum is in agreement with the calculated variation using the room-temperature values of $g_\parallel$ and $g_\perp$ as given earlier. For this particular crystal orientation all lines of the spectrum should coalesce when the magnetic field is along the [100] direction. Because of a slight misalignment (less than $\frac{1}{2}$ deg) of the crystal along a (110) plane in the microwave field, the observed lines do not strictly follow those calculated from the equations above; however, if one corrects for this misalign-

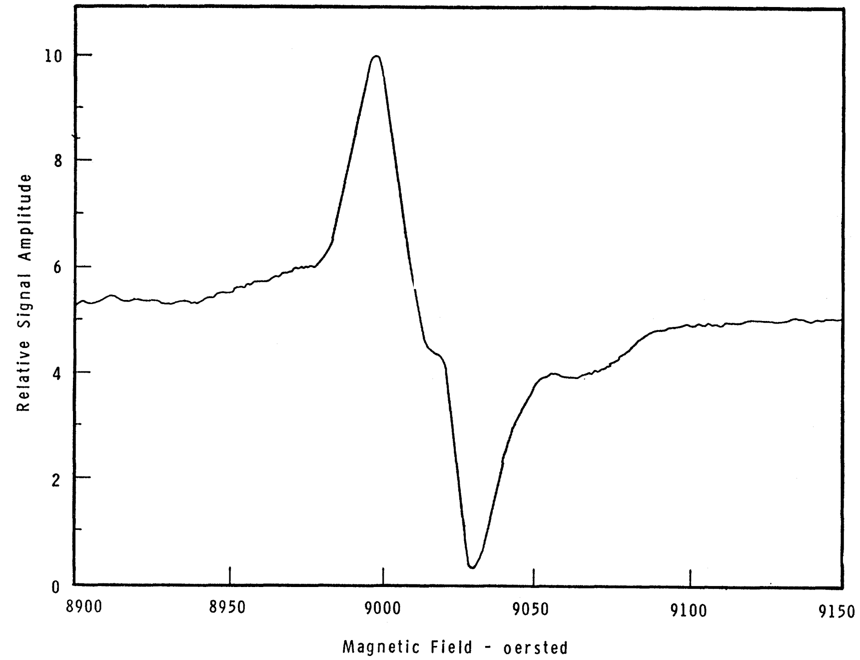

FIG. 3. Room-temperature spectrum of irradiated ThO$_2$ single crystal aligned as indicated in Fig. 1. Spectrum taken at $\Phi = 0°$.

ment the coalescence of the [111] and [−111] lines will be observed at $\phi=90°$. This misalignment has been taken into account in estimating the ESR linewidth at room temperature and at liquid-helium temperature. (See Fig. 3.)

V. EVIDENCE FOR AN *F* CENTER IN ThO_2

Numerous optical and ESR studies have been performed on *F* centers in the monovalent alkali halides[7] and on *F* centers in divalent alkaline earth oxide single crystals[8] which yield information on the expected properties of an *F* center in ThO_2.

Some work on the optical-absorption spectrum of crystalline thoria has been reported by several groups of investigators.[9,10] By heating the crystals in air and in vacuum at different temperatures, Bodine and Thiess[10] obtained the red and yellowish colored crystals previously described by Weinrich and Danforth.[9] The crystals heated in vacuum or in hydrogen at 1800°C showed an anomalous absorption peak around 4000 Å which was attributed to oxygen vacancies or interstitial thorium ions (oxygen deficient).

Prior to irradiation our crystals are perfectly colorless and show no absorption in the visible or near infrared. The transmission cutoff for our crystals appears around 3000 Å. On irradiation, the crystals take on a dark yellowish cast. Since the crystals bleach very readily, it has been difficult to obtain the spectra of these irradiated samples. However, an anomalous absorption peak appears around 4300 Å, and the general cutoff of the crystal in the ultraviolet is around 3400Å. Within minutes of scanning with the Cary 14R spectrophotometer, the crystals are bleached and the spectrum is identical to that of unirradiated crystals.

One possible suggestion as to why the optical spectrum of excited states of the *F* center is so difficult to detect may be that the excited states of a Th^{3+}-like ion center have an energy spectrum[11] that lies near the band gap in ThO_2.

Bleaching of the ESR *F* center signal has been observed under infrared irradiation. Although this observation appears to be contradictory to the previous suggestion, it may be that electrons bleached from other shallow defects by infrared radiation are trapped at the *F* center sites producing F′ centers which are nonparamagnetic and result in an apparent bleaching of the *F*-center ESR signal. Low-temperature monochroniatic excitation optical studies are now in progress and appear promising enough to be reported later.

Reasons for the abundance of negative-ion vacancies in ThO_2 single crystals are thought to be similar to reasons given by Wertz[12] and co-workers, explaining the abundance of positive-ion vacancies in MgO and other alkaline earth oxide crystals.[12] Their arguments for this phenomenon have been that, for the divalent alkaline earth oxides, the principal impurities are trivalent. In order to have proper charge compensation the crystal tends to have one positive-ion vacancy for every two of the trivalent impurities that are substitutionally admitted into the crystal, which results in hole centers (V_1 center) after minor irradiation.

Similar arguments can be made for the existence of negative-ion vacancies (resulting in *F* centers) in thorium oxide crystals. If impurities go in substitutionally, the predominant impurity again will be a trivalent impurity; however, since the thorium ion is a tetravalent ion, a trivalent impurity would tend to be compensated by the existence of a negative-ion vacancy for every two trivalent impurities that are substitutionally admitted into the lattice. Under conditions predominant in the lattice, one may expect to find a reasonably large number of *F* centers produced by x-ray or electron bombardment, however, virtually no hole centers will be produced because the crystal contains very few positive-ion vacancies. The introduction of additional trivalent impurities should then enhance the concentration of these centers. In order to check this supposition, ESR experiments were conducted with single crystals of ThO_2 containing Er^{3+} and La^{3+}. Every attempt was made to carry out the irradiation experiments of the doped and undoped samples in the same way. The volume of each sample used was determined to within 1%, so that the number of spins per unit volume could be estimated. In all cases the defect ESR spectrum results indicated a greater number of defect centers produced in samples containing Er^{3+} and La^{3+} impurities, which is consistent with the above suggestions.

The linewidth of the *F* center electron-spin-resonance signal is generally expected to be quite narrow due to the fact that the electron is trapped in the negative-ion site and generally quite isolated from the surrounding lattice. This assumption depends a great deal on the depth of the trap and the type of positive ion in the lattice, the general result being that, as the positive-ion mass increases the linewidth increases due to increased spin-orbit interaction and the trap depth decreases. Alkaline earth oxide *F* centers are good examples of this phenomenon.[13] At room temperature the linewidth of the ThO_2 *F* center ESR signal was observed to be approximately 35 G (see Fig. 3) and reduced to approximately 1.5 G at liquid-helium temperature. Linewidth and ESR saturation properties are thus consistent with the above assumptions of the *F* center properties.

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Measurements were also made on ThO_2 crystals that contained strain facults. The general result of these experiments was to produce a severe line broadening due to the strain. High-purity natural ThO_2 ceramic materials were also investigated, but in no case could *F* centers be observed (assumed to be due to line broadening) and in each case ESR signals from gadolinium impurities were observed.

Optical and ESR low-temperature studies have failed to reveal any possibility of impurity ions becoming paramagnetic due to sample bombardment. The fact that no hyperfine splitting was observed in the ESR spectrum of irradiated samples would suggest that the signal is not the result of valence changes produced by irradiation of impurity centers in the crystal. Moreover, it appears unlikely that Th^{3+} (should it be produced by such irradiations) would have the magnetic properties we have observed. We have also demonstrated to our own satisfaction that the observed ESR signal is not associated with any surface effect.

An additional argument can be made on behalf of *F* centers in ThO_2 by recalling that previous studies[8] have shown that the g value for *F* centers tends toward lower and lower values below 2 with increasing atomic number of the metal cation. The small distortion of the *F* center can be accounted for by mechanisms none of which would seem to alter any of the arguments presented in favor of an *F* center. If one argues, as did Kahn and Kittel,[14] that an admixture of excited defect states into the ground S state is possible through spin-oribt interaction, then a change in g factor for the *F* center (using a molecular-orbital model) will be

$$\Delta g = -\tfrac{4}{3}(\lambda/\Delta)\epsilon^2/(1+\epsilon^2),$$

where λ is the spin-orbit coupling constant, Δ is the energy separation between S and P states, and ϵ is the electrostatic polarization of the thorium ions by the vacancy. If one estimates values of λ and Δ on the basis of Th^{3+}-like ions[11] and calculates a value of ϵ using modified hydrogenic wave functions, an order of magnitude for Δg of -0.02 is obtained, which yields a tentative value of $g \approx 1.98$. While the numerical value is only an approximation, all reasonable choices of values for λ, Δ, and ϵ indicate that the correction to the g value is in the right direction. One can admix other states of opposite parity into the ground-state wave functions through the crystal field which could account for the small anisotropy of the g value.

The observed change in linewidth from 32 to 1.5 G between room and liquid-helium temperature provides an interesting system for later spin-lattice studies. The *F* center may be a very useful probe in the study of the lattice dynamics of ThO_2 as well as other actinide and heavy metal oxides. Investigations of such series as the alkaline earth oxides have indicated that the effect of metal cations with increasing atomic number in the host crystal tends to produce *F* centers that are less and less tightly bound, and thus do indeed have stronger spin-lattice interactions, which accounts for the observed changes in linewidth as a function of temperature. Although effects of lattice distortions have not yet been examined in detail, it is hoped that continuing studies may explain why the room-temperature line is not a simple broad line but seems to have some structure associated only with high temperatures.

Nevertheless, as a result of the above arguments, it does not seem unreasonable to suggest that the observed spectrum is due to *F* centers in single crystals ThO_2.

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