

Optical Properties of SrTiO₃ in the Region of the Absorption Edge*†

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The absorption coefficient, reflectivity, and electroreflectance of SrTiO₃ in the neighborhood of the fundamental absorption edge are reported. The absorption coefficient shows an exponential rise with incident energy (Urbach rule) over five orders of magnitude. Its logarithm has a slope of $1/kT$. The data indicate that the band gap of SrTiO₃ is about 3.4 eV. Additional results for reduced SrTiO₃ show that Redfield's model for an exponential edge is not applicable to this material. The reflectivity indicates structure in the region of 3.4 eV and the electroreflectance shows an appreciable signal from 2.5 to 5.0 eV with some structure near 3.4 eV. The electroreflectance signal appears to be due to some process other than the Franz-Keldysh effect. It could be due to a shift or splitting in the major oscillator (4.4 eV) responsible for the refractive index, with induced lattice polarization.

I. INTRODUCTION

THE nature of the transition giving rise to the absorption edge in SrTiO₃ is of considerable interest. The calculated band structure of Kahn and Leyendecker¹ (KL) indicates that the lowest conduction band (Δ_2') is very narrow with the minimum at the zone edge (Fig. 1). Measurements of magnetoresistance² and the Shubnikov-de Haas effect³ suggest that the minima lie along [100] directions, while piezoresistance measurements have been interpreted⁴ as indicating an additional, slightly lower extremum at the center of the zone.

Based upon the KL results, Casella⁵ has derived optical selection rules for cubic SrTiO₃. In the dipole approximation, direct transitions from the upper valence band ($\Gamma_{15}-\Delta_1-X_4'$) to the conduction band are allowed only at $k=0$. If the lowest conduction minima lie at the edge, the possibility of indirect transitions from the $k=0$ valence-band maximum exists. He has also considered a model in which the order of the Δ_1 and Δ_5 valence bands are inverted and the transition is direct at the Brillouin zone face.

The effects of stress and electric field on the band structure and optical transitions have been discussed by Casella,⁵ Froya and Boddy,⁶ and by Brews.⁷ Brews has determined the order of the Stark levels by repeating the KL calculation in a quantitative manner, including electric-field-induced deformations.

Some earlier work on optical transitions in SrTiO₃ has been performed. Noland⁸ has reported the edge to be

at 3.22 eV. Cardona⁹ sees a small bump in the reflectivity at 3.2 eV which he attributes to the $\Gamma_{15} \rightarrow \Gamma_{25}'$ transition; he terms this the fundamental absorption edge. In an attempt to verify these results and perhaps determine the nature of the transition, we undertook an examination of the absorption edge of SrTiO₃ utilizing the techniques of absorption, reflectivity, and electroreflectance.

II. EXPERIMENTAL

All of the material used was obtained commercially¹⁰ in the form of single-crystal boules approximately 2 cm in diameter and 3 cm long. The oxidized samples used in the absorption measurements were cut from the boule with a diamond saw, ground to size, and polished with Al₂O₃ abrasives. Final sample thicknesses were 2.06 cm, 3 mm, 0.75 mm, 0.25 mm, and 0.053 mm. A 0.5-mm-

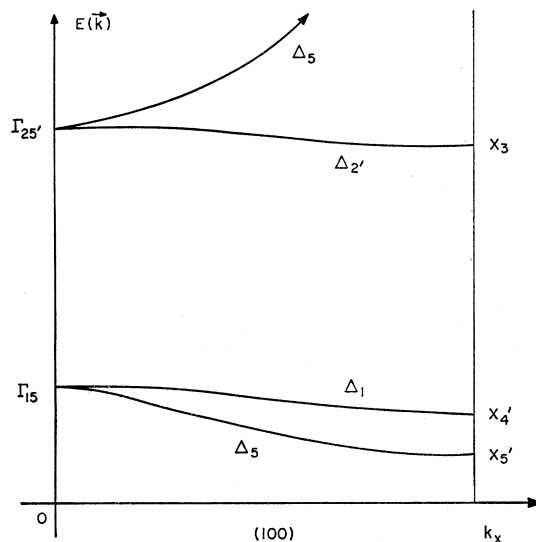


FIG. 1. Schematic of the band energies, $E(\mathbf{k})$, in SrTiO₃ for the cubic phase. Results are taken from Ref. 1. The wave vector \mathbf{k} is along the [100] axis.

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¹ A. H. Kahn and A. J. Leyendecker, Phys. Rev. **135**, A1321 (1964).

² H. P. R. Frederikse, W. R. Hosler, and W. R. Thurber, Phys. Rev. **143**, 648 (1966).

³ H. P. R. Frederikse, W. R. Hosler, W. R. Thurber, J. Babiskin, and P. G. Siebenmann, Phys. Rev. **158**, 775 (1967).

⁴ O. N. Tufte and E. L. Stelzer, Phys. Rev. **141**, 675 (1966).

⁵ R. C. Casella, Phys. Rev. **154**, 743 (1967).

⁶ A. Froya and P. J. Boddy, Phys. Rev. **153**, 606 (1967).

⁷ J. R. Brews, Phys. Rev. Letters **18**, 662 (1967).

⁸ J. A. Noland, Phys. Rev. **94**, 724 (1954).

⁹ M. Cardona, Phys. Rev. **140**, A651 (1965).

¹⁰ National Lead Co.

thick sample of hydrogen-reduced SrTiO_3 (carrier concentration $n \approx 10^{19}/\text{cm}^3$) was also prepared in this manner. Samples thinner than 0.053 mm could not be obtained; an attempt was made to produce them by evaporation techniques, but was unsuccessful.

Reflectivity measurements were performed on two of the above samples (etched in hydrofluoric acid) and on a 3-mm-thick, polished and etched sample of reduced SrTiO_3 ($n \approx 7 \times 10^{19}/\text{cm}^3$). This last sample and two others of differing carrier concentration were used in the electroreflectance experiment.

Absorption measurements were made in a commercial double-beam spectrophotometer.¹¹ A "cold-finger"-type Dewar was used for low-temperature measurements. The cryogenic liquids used were nitrogen, helium, and a mixture of dry ice and alcohol. Reduction of the data from optical density to absorption coefficient was achieved by a method similar to that of Marple.¹² The apparent absorption was determined over a range of wavelength large enough to allow an extrapolation to the point where data were off scale. This extrapolated curve was subtracted from the data, and the resulting "corrected" values were substituted into the simple form of Beer's law $I/I_0 = e^{-\alpha x}$. The five sets of points obtained by the above method were plotted yielding a composite curve.

The selected thicknesses of samples were such that there was a considerable amount of overlap of points from any one sample with adjacent samples. Deviations from the composite absorption curve were found only at the bottom and top of each individual sample curve. These deviating points were not used.

The approximation used can be justified as follows. Once the optical density of the sample rises above about 0.3, multiple reflections no longer need to be taken into account. Also since the reflectivity of SrTiO_3 varies only a small amount ($\sim 6\%$) and smoothly in the wavelength range covered, the subtraction of the extrapolated background should be sufficient correction for the surface reflection losses. We feel that this approximation fails only at the bottom of each individual sample curve where the points deviate from the composite curve. The region of deviation at the top of each sample curve is due to stray light.

Room-temperature reflectivity was measured throughout the range from 2.5 to 4 eV using a 600-line/mm grating monochromator and a 150-W high-pressure xenon arc source. The detector was an S-5 response photomultiplier coated with sodium salicylate. Detector and sample were placed on a device that could be rotated such that the detector was placed alternately in the direct beam from the monochromator and in the reflected beam from the sample. The light was incident on the sample at an angle of $\sim 80^\circ$ to the surface. Data were obtained point by point throughout the region.

Electroreflectance data were taken at room temperature by the technique of Shaklee *et al.*¹³ The monochromator used was a 1200-line/mm grating instrument. The light source was a 150-W xenon arc, and the detector was a sodium-salicylate-coated photomultiplier. The method was modified by the use of semiconductor-electrolyte interfaces for both contacts to the sample.

III. RESULTS

Our composite absorption edge curve for stoichiometric SrTiO_3 is shown in Fig. 2. As is evident, the absorption edge in the region measured is exponential over approximately five orders of magnitude at room temperature. The data at lower temperatures do not cover as large a range but, where measured, are still exponential. From these curves the constants in Urbach's rule $\{\alpha = \alpha_0 \exp[-\sigma(E_0 - E)/kT]\}$ were determined. We find

$$\alpha_0 = 1.3 \times 10^4 \text{ cm}^{-1},$$

$$\sigma = 1.0,$$

$$E_0 = 3.37 \text{ eV}.$$

Attempts to extend the data to α 's larger than 10^3 cm^{-1} were frustrated by our inability to obtain sufficiently thin samples. Within experimental error, the data for

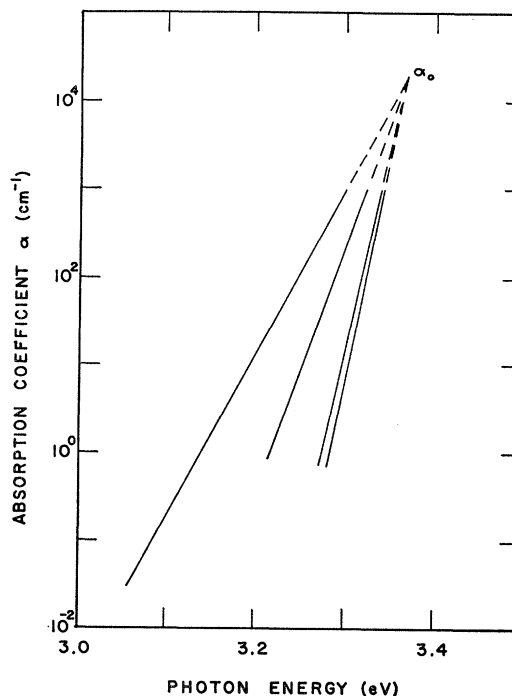


FIG. 2. Composite absorption coefficient (α) curve for several samples of SrTiO_3 , illustrating the Urbach rule. $\alpha_0 = 1.3 \times 10^4 \text{ cm}^{-1}$ at 3.37 eV. From left to right, temperature was room temperature, cooled by dry ice and alcohol, by liquid nitrogen, and by liquid helium.

¹¹ Applied Physics Corporation Model 14.

¹² D. T. F. Marple, *Phys. Rev.* **150**, 728 (1966).

¹³ K. L. Shaklee, F. H. Pollak, and M. Cardona, *Phys. Rev. Letters* **15**, 883 (1965).

the reduced and stoichiometric samples are identical at liquid nitrogen as well as at room temperatures.

The reflectivity from 2.5 to 4 eV is shown in Fig. 3. We detect structure in the region of 3.4 eV; considering the width of this "maximum," there is no essential disagreement with the value of 3.2 eV found by Cardona.⁹ The reflectivity was not carried beyond 4 eV since it has been measured previously⁹ and our primary interest was in the details near the absorption edge.

Figure 4 shows our room-temperature results together with those of Cardona (obtained by Kramers-Kronig inversion⁹). The agreement is reasonably good.

Electroreflectance in the range of 2.5 to 5.5 eV is shown in Fig. 5. Again structure is evident at 3.4 eV.

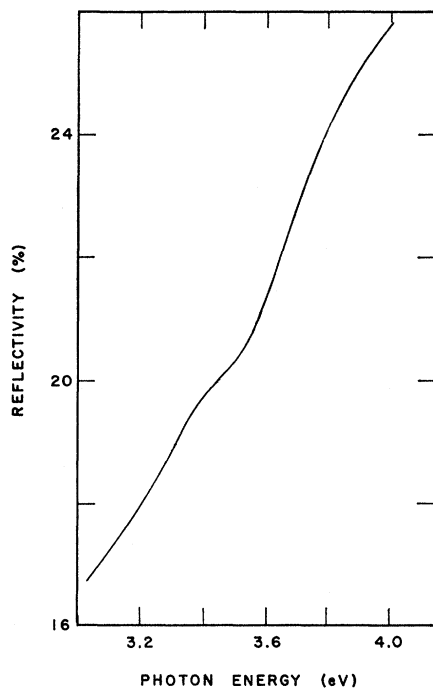


FIG. 3. The room-temperature reflectivity of SrTiO_3 in the range from 3.0 to 4.0 eV. The data were obtained on the 2.06-cm-thick sample used in the absorption measurements. The results have not been normalized (see Ref. 9).

The peak at 3.7 and the shoulder at 4.8 eV are close to the reflectivity peaks seen by Cardona,⁹ and designated by him as A_1 and A_2 . The data for SrTiO_3 and KTN^{6,14} are similar in that the structure is broad and that changes of bias tend to make peaks appear and disappear, or shift position.

It should be noted that there is appreciable electroreflectance signal at 2.5 eV which is more than 0.6 eV below the energy at which α is of the order of 1 cm^{-1} .

IV. DISCUSSION

As is well known, energy dependence of the absorption edge should show power-law dependences for vari-

¹⁴ A. Frova and P. J. Boddy, Phys. Rev. Letters 16, 688 (1966).

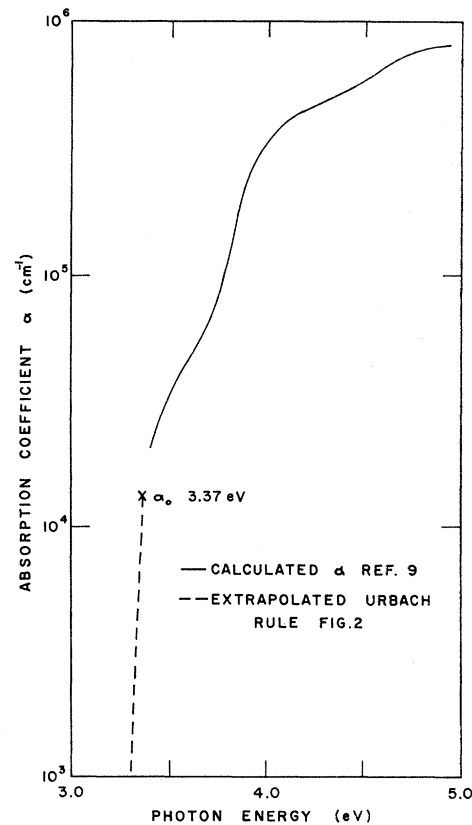


FIG. 4. Comparison of the absorption coefficient as calculated by Cardona (Ref. 9) with the extrapolated portion of the room-temperature curve in Fig. 2 of this paper.

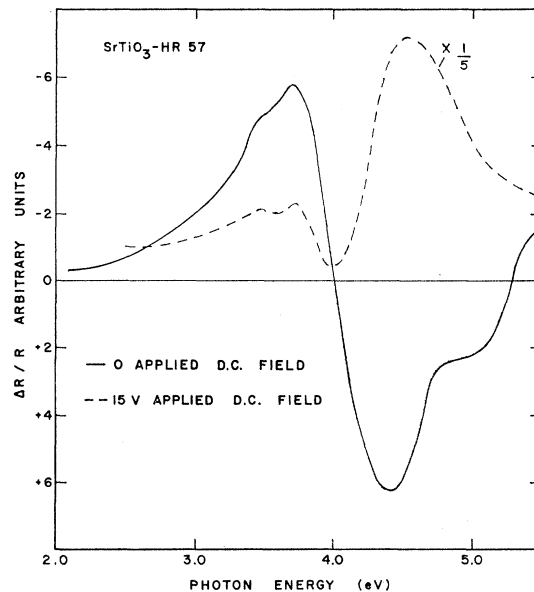


FIG. 5. The room-temperature electroreflectance of reduced SrTiO_3 .

ous zero- or one-phonon interaction models.¹⁵ However, the Urbach process giving rise to an exponential edge in most solids is not well understood, and the nature of the transition cannot be directly determined at this time. A number of models accounting for low-energy exponential tails of this type have been proposed.¹⁶⁻²¹ Of these, some invoke exciton states. These will not be discussed since there is no optical evidence for the presence of excitons in SrTiO₃. (Because of the large static dielectric constant, the binding energy for Wannier excitons would be very small, $\approx 10^{-5}$ eV at 77°K.) In addition, Mahan has shown¹⁹ that it is not necessary to postulate such states in order to derive an Urbach rule.

Redfield's mechanism of an internal Franz-Keldysh effect due to charged impurities¹⁸ would not be expected to apply to SrTiO₃. He proposes that his model should be applicable to the class of covalent, direct-gap semiconductors (apparently shown experimentally in the case of GaAs²¹) and not to materials which are essentially ionic. Our experiments show that it does not apply to SrTiO₃. His model requires a freeze-out of carriers to yield a temperature-dependent slope for the absorption edge. In the case of SrTiO₃, where there is no freeze-out in heavily reduced material,²² one would expect the slope of the edge to be insensitive to temperature if the model were applicable. However, heavily reduced SrTiO₃ exhibits an absorption edge that coincides (within experimental error) with that of stoichiometric material.

Mahan has derived an approximation to the Urbach rule for electrons in a parabolic conduction band having a linear interaction with longitudinal optical phonons, in a polar crystal. He uses only polar interactions but indicates that other types of electron-optical-phonon interactions will also produce an exponential tail.

The allowed direct transitions for cubic SrTiO₃ as given by Casella⁵ are $\Gamma_{15} \rightarrow \Gamma_{25'}$, $\Delta_5 \rightarrow \Delta_2'$, $\Delta_5 \rightarrow \Delta_5$, and $X_{5'} \rightarrow X_3$. Cardona⁹ has assigned the fundamental band edge to $\Gamma_{15} \rightarrow \Gamma_{25'}$ at the zone center. However, the direct process $X_{5'} \rightarrow X_3$ at the zone edge (model 2 of Ref. 5) could also account for the observed transition²³

and would be more in accord with the [100] minima in the conduction band found by Frederikse *et al.*^{2,3} If indirect, the transition would probably be $\Gamma_{15} \rightarrow \Gamma_{25'} \rightarrow X_3$. Feldman and Horowitz²⁴ interpret their rotary transmission measurements of the stress-induced dichroism in SrTiO₃ as indicating that a direct transition at X is improbable. However, their data are not wholly incompatible with this transition or with a direct transition at Γ .

It was hoped that the electroreflectance (ER) spectrum would provide additional clues as to the nature of the edge transition, but this expectation was not realized. The breadth of the peaks observed and the manner in which these peaks change with applied bias indicate that the effect is not primarily due to the Franz-Keldysh effect. However, some inferences can be drawn about the optical behavior of SrTiO₃ under application of electric fields.

The approach used by Casella is helpful for a qualitative understanding of the observed ER spectrum. He has postulated a reduction of symmetry to C_{4v} under applied electric fields, due to large ionic displacements. This would lead to nontrivial Stark shifts and splittings of the bands. A similar viewpoint is also used by Prova and Boddy to interpret the ER spectra observed in KTaO₃, KTaO₃-KNbO₃, and BaTiO₃.⁶ They also feel that the applied electric field splits the degenerate levels associated with the transition-metal-oxygen octahedra by inducing a large lattice polarization, and that tunneling of the nature of the Franz-Keldysh effect plays only a small role. The reflectivity of SrTiO₃ is similar to that of BaTiO₃,⁹ and the ER of SrTiO₃ bears a striking resemblance to that of BaTiO₃, KTaO₃, and KTN.^{6,14} In view of this, it would not be surprising if a similar explanation were applicable here.

Cardona⁹ attributes the dispersion below the fundamental absorption edge mainly to the A_1 and A_2 virtual transitions (≈ 4.4 eV) and not to virtual transitions at E_0 (3.4 eV). High-precision measurements of the refractive index made by Malitson *et al.*²⁵ can be fitted to a Sellmeier relation with the major oscillator at about 4.4 eV. If this main oscillator were shifted or split by an applied electric field, we would expect to see changes in the refractive index throughout the visible region. These changes could lead to an ER signal throughout this spectral range. If the Franz-Keldysh effect alone were the major contributor to the ER spectrum, we would not expect to see appreciable signal at 2.5 eV, in contradiction to experimental observations.

V. CONCLUSIONS

The absorption edge of SrTiO₃ has been examined. It shows an exponential energy dependence (Urbach

¹⁵ J. Bardeen, F. Blatt, and L. H. Hall, in *Photoconductivity Conference*, edited by R. G. Breckenridge *et al.* (John Wiley & Sons, Inc., New York, 1956), p. 146.

¹⁶ R. S. Knox, *Solid State Phys.*, Suppl. 5, (1963).

¹⁷ Y. Toyozawa, *Progr. Theoret. Phys. (Kyoto)* 22, 455 (1959); Technical Report of the Institute for Solid State Physics, Report No. 119, Ser. A, 1964 (unpublished).

¹⁸ D. Redfield, *Phys. Rev.* 130, 916 (1963).

¹⁹ G. D. Mahan, *Phys. Rev.* 145, 602 (1966).

²⁰ B. Segall, *Phys. Rev.* 150, 734 (1966).

²¹ D. Redfield and M. A. Abromowitz, Columbia University Department of Electrical Engineering Technical Report No. 98 (unpublished).

²² H. P. R. Frederikse, W. R. Thurber, and W. R. Hosler, *Phys. Rev.* 134, A442 (1964).

²³ Di Domenico and Wemple [*Phys. Rev.* (to be published)] have assigned the transition in BaTiO₃, KTaO₃, and KTaO₃NbO₃, as due to a direct transition at the zone edge on the basis of Baer's Faraday rotation measurements [*J. Phys. Chem. Solids* 28, 677 (1967)] and their own results for the temperature dependence of the band-edge dichroism.

²⁴ A. Feldman and D. Horowitz (to be published).

²⁵ I. Malitson (private communication).

rule) over five orders of magnitude. There are difficulties with the interpretation of the observed data which prohibit assignment of the edge to either an indirect or a direct process. The ER data indicate that the observed results of this experiment are not consistent with the Franz-Keldysh effect. It can be more readily explained

on the basis of shifts or splitting in the major oscillator due to induced polarization.

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Electron Spin Resonance of Tripositive Curium in ThO_2 and CeO_2 †

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The ESR spectra of $^{244}\text{Cm}^{3+}$ -doped ThO_2 and CeO_2 single crystals were measured at approximately 10 Gc/sec and liquid-helium temperatures. Sites of cubic symmetry were observed in both hosts, with the crystal-field splitting being larger than the microwave quanta used. The ground states are Γ_6 doublets, indicating that the fourth-order parameter of the cubic crystal-field Hamiltonian is negative. For ThO_2 , the g value was 4.484 ± 0.002 , and for CeO_2 , it was 4.475 ± 0.002 .

INTRODUCTION

THE rare-earth elements (also called lanthanide or $4f$ elements) are characterized by the progressive filling of the $4f$ electronic shell. The f -electron orbits contract with increasing atomic number (lanthanide contraction) and are shielded by an outer closed shell of $5s$ and $5p$ electrons (with $5d$ and $6s$ valence electrons) from the local chemical environment. This is the reason for the close similarity in the chemical properties of the rare earths.

The possibility of a second rare-earth series beginning at uranium was postulated by Bohr.¹ Following the discovery of synthetic transuranium elements, Seaborg² proposed that actinium (element 89) was the analog of lanthanum (element 57) and that the $5f$ electronic shell was being filled. The $5f$ electron eigenfunctions have larger orbits and a lower binding energy than their corresponding $4f$ eigenfunctions; hence, their interaction with the local environment is greater. Further, the actinide contraction (the $5f$ electrons become shielded by an outer closed shell of $6s$ and $6p$ electrons) does not occur as rapidly. This results in a greater variety of valence states for the early actinides with the trivalent state becoming dominant in the later actinides.

When the $4f$ shell is half filled (Gd^{3+} and Eu^{2+}) the $^8S_{7/2}$ ground state has no orbital angular momentum and therefore the local crystal field has a smaller effect on the ground-state levels. The spin-lattice relaxation

times are long enough for paramagnetic-resonance spectra to be observed at room temperatures for these ions.

The actinide Cm^{3+} nominally has a $5f^7$ configuration and would be expected to exhibit similar resonance spectra. Indeed, early ESR work with Cm^{3+} in lanthanum trichloride and lanthanum magnesium nitrate crystals, unintentionally doped with chemically similar Gd^{3+} as well, erroneously attributed the Gd^{3+} spectra to Cm^{3+} .³ The experiments were performed at room temperature and 77°K only. The Cm^{3+} resonance was first correctly observed in lanthanum trichloride and lanthanum ethylsulfate single crystals at liquid-helium temperatures,⁴ and was not observable at 77°K due to the short spin-lattice relaxation time. This, in itself, was a clear indication of a larger crystal-field interaction than usual for S -state ions. The observation of only one absorption line instead of the usual seven lines was a further indication of the large interaction with the axial fields in these crystals.

The incorporation of Cm into various host lattices has become desirable and prompted us to incorporate Cm into the cubic fluorite lattices of ThO_2 and CeO_2 .

EXPERIMENTAL

The $^{244}\text{Cm}^{3+}$ -doped CeO_2 and ThO_2 single crystals were grown from $\text{Li}_2\text{O} \cdot 2\text{WO}_3$ flux by a previously described thermal-gradient technique.^{5,6} This method

³ M. Abraham, B. B. Cunningham, C. D. Jeffries, R. W. Kedzie, and J. C. Wallmann, *Bull. Am. Phys. Soc.* **1**, 396 (1956); P. Fields, A. Friedman, B. Smaller, and W. Low, *Phys. Rev.* **105**, 757 (1957).

⁴ Marvin Abraham, B. R. Judd, and H. H. Wickman, *Phys. Rev.* **130**, 611 (1963).

⁵ C. B. Finch and G. W. Clark, *J. Appl. Phys.* **36**, 2143 (1965).

⁶ C. B. Finch and G. W. Clark, *J. Appl. Phys.* **37**, 3910 (1966).

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¹ N. Bohr, *Nature* **112**, 30 (1923).

² G. T. Seaborg, *Chem. Eng. News* **23**, 2190 (1945); *Science* **104**, 379 (1946).