Ultraviolet Absorption Spectra in Ruby*

A. Linz, Jr., and R. E. Newnham

*Laboratory for Insulation Research, Massachusetts Institute of Technology,
Cambridge, Massachusetts*

(Received March 6, 1961)

The optical properties of highly doped rubies have been investigated. Al_2O_3 and Cr_2O_3 form a complete solid-solution series; single crystals containing up to 5 mole % chromia were grown by the Verneuil technique. The optical absorption of a group of ultraviolet crystal-field bands near 3400 A was studied as a function of temperature, crystal orientation, and chemical composition. The intensity of these absorption bands varies with the square of the Cr concentration, perhaps indicating strong chromium-pair interactions.

THE absorption spectra of rubies have been studied extensively in recent years. Several groups of absorption bands in the visible are well known and have been correlated with transitions to energy levels calculated from crystal field theory.[1] These include two strong broad bands at 3900 and 5500 A, and two groups of weak narrow bands, at 4700 and 6900 A. In addition, the existence of some weak narrow bands in the ultraviolet has been noted previously,[2,3] but no details have been published to permit comparison with crystal field theory.

Single crystals of Cr-doped Al_2O_3 containing up to five percent Cr_2O_3 were grown with a modified Verneuil burner.[4] Feed materials were obtained from co-precipitated $NH_4(Al,Cr)$ alums calcined at 950°C for two hours. Lattice-parameter measurements and chemical analyses were employed to establish their homogeneity and composition. Since approximately 70% of the chromia vaporizes during the growth process, it was necessary to recheck the composition of the single-crystal boules. Boules containing more than 5% Cr_2O_3 were usually inhomogeneous and full of bubbles.

The lattice parameters of the chromium oxide-aluminum oxide system were measured over the entire range of compositions using feed materials calcined at 1450°C.
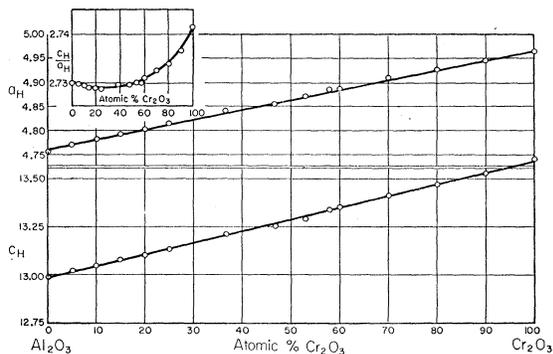

FIG. 1. Room-temperature lattice parameters and axial ratio as a function of composition in the Al_2O_3-Cr_2O_3 series.

Measurements on intermediate compositions were hampered by a marked broadening of the high-order x-ray diffraction spectra, possibly arising from the difference between the ionic radii of trivalent Al and Cr. Further studies might yield additional evidence relevant to the ion compression theory proposed by Orgel.[5] The values of a and c, the hexagonal unit-cell dimensions, are shown as a function of composition in Fig. 1. Both change smoothly between the end-member values, closely approximating Vegard's rule. The axial ratio remains constant to 50 mole % Cr and then rises gradually to the value for Cr_2O_3. This effect may be caused by the Cr-Cr interactions along the c axis between nearest cation neighbors. The lattice parameters of aluminum oxide crystals containing 0 to 2% Cr were identical, within experimental error, with those measured by Swiss workers.[6] There was no indication of the discontinuity near 8% reported by Thilo et al.[7]

Optical measurements were carried out on five single-crystal specimens containing 0.08, 0.35, 1.40, 2.55, and 4.25% chromia; thin sections (2.0 to 0.2 mm), oriented both perpendicular and parallel to the optic axis, were cut from each boule. An extended ultraviolet-range Beckman DK-1 spectrophotometer with a tungsten light source and quartz optics was used to record the absorption spectrum of the ruby specimen, positioned in the exit beam. A calcite air-gap Glan-Thompson prism was used as a polarizer. The results permitted verification of all the spectra from 3000 to 7500 A reported by McClure,[1] plus the ultraviolet bands near 3400 A shown in Fig. 2 and compiled in Table I. The intensities of these ultraviolet spectra were studied as a function of temperature, polarization direction, and Cr content.

The precise number of bands in the group is difficult to ascertain because some are extremely weak while others lie so close together they can scarcely be resolved. Some absorption bands are less sensitive to temperature than others, but nearly all increase in intensity as the temperature is lowered (Fig. 2). The intensities also show a marked dependence on crystal

[1] See D. S. McClure, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1959), Vol. 9, p. 490.
[2] S. F. Jacobs, Ph. D. thesis, Johns Hopkins University, 1956 (unpublished).
[3] W. Low, J. Chem. Phys. **33**, 1162 (1960).
[4] A. Linz, Jr. (to be published).

[5] L. E. Orgel, Nature **179**, 1348 (1957).
[6] J. P. Jan, S. Steinemann, and P. Dinichert, Helv. Phys. Acta **33**, 123 (1960).
[7] E. Thilo, J. Jander, H. Seemann, and R. Sauer, Naturwissenschaften **37**, 399 (1950).

TABLE I. Wavelengths of ultraviolet absorption bands at 77°K.

	$E \perp c$			$E \| c$	
No.	λ (A)	ν (cm^{-1})	No.	λ (A)	ν (cm^{-1})
1	3262	30 660	1	3268	30 600
2	3303	30 280	2	3295	30 350
3	3348	29 870	3	3300	30 300
4	3392	29 480	4	3327	30 060
5	3398	29 430	5	3343	29 910
6	3420	29 240	6	3347	29 880
7	3430	29 160	7	3377	29 610
8	3452	28 970	8	3402	29 390
9	3467	28 840	9	3415	29 280
10	3485	28 690	10	3430	29 160
			11	3450	28 990

orientation; the spectra for $E \perp c$ and $E \| c$ are shown in Figs. 2(a) and 2(b), respectively. The principal bands of the π spectrum ($E \| c$, $H \perp c$) occur at a higher energy than those of the a spectrum ($E \perp c$, $H \perp c$). The latter is identical with the σ spectrum ($E \perp c$, $H \| c$), indicating that the spectra are not associated with magnetic dipole transitions.[8]

The bands increase in intensity relative to other bands in the ruby spectrum as the Cr concentration is increased. Measurements of both peak and integrated
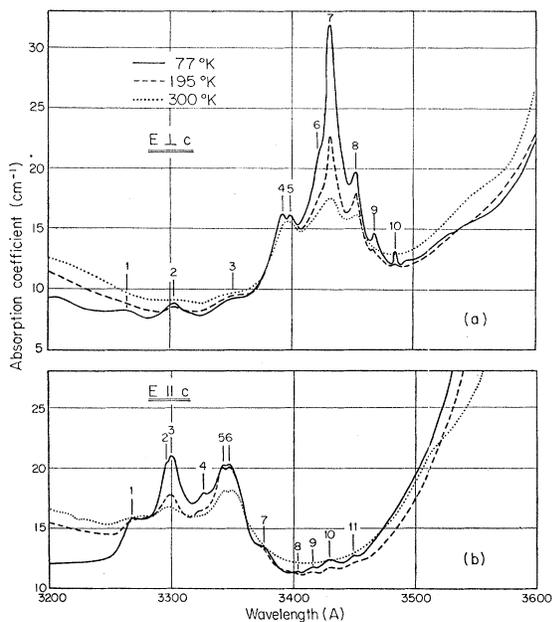

FIG. 2. Optical density of ruby containing 2.55% Cr_2O_3, recorded at various temperatures.

[8] E. V. Sayre, K. Sancier, and S. Freed, J. Chem. Phys. 23, 2060 (1955).
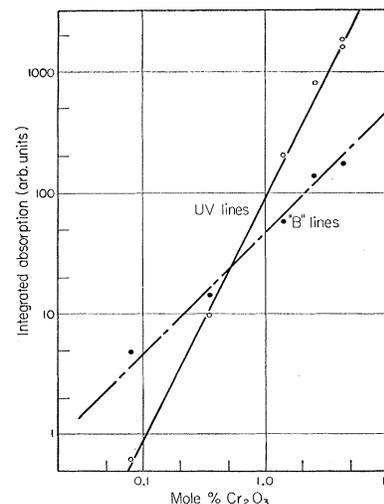

FIG. 3. Integrated absorption of the ultraviolet bands and the "B" lines as a function of the Cr content in ruby.

intensities for the ultraviolet bands indicated a dependence on the square of the concentration for both orientations. Similar observations on the sharp spectra near 4770 A (the "B" lines) showed their intensities to be linearly proportional to the Cr content (Fig. 3). Paramagnetic resonance absorptions and optical emission lines showing a dependence on the square of the composition have been observed previously.[9,10] Both were ascribed to exchange-coupled Cr^{3+} ion pairs, which also play a role in the ultraviolet spectra. The theoretical calculations of Tanabe and Sugano[11] suggest the most plausible explanation of the spectra. They predict transitions in the ultraviolet from the ground state $^4A_2(t^3)$ to several excited doublet states, $^2A_1$, $^2T_1$, $^2T_2$, and ^2E, all having a t^2e electronic configuration. It is conceivable that when two Cr^{3+} ions are close together the spin selection rules are weakened and the bands appear stronger than for isolated atoms in the lattice.

ACKNOWLEDGMENTS

[9] L. Rimai, H. Statz, M. J. Weber, G. A. deMars, and G. F. Koster, Phys. Rev. Letters 4, 125 (1960).

[10] A. L. Schawlow, D. L. Wood, and A. M. Clogston, Phys. Rev. Letters 3, 271 (1959).

[11] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan 9, 753 and 766 (1954).