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Optical Absorption Spectra of the Ordered Phases in the Praseodymium Oxide–Oxygen System

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Optical absorption spectra were taken of oxides of praseodymium with compositions between Pr_2O_3 and PrO_2. The spectra of the green sesquioxides, A-form and C-form Pr_2O_3, were measured in a liquid helium cryostat at both 40 and 95°K. The spectra of $PrO_{1.51}$, $PrO_{1.54}$, $PrO_{1.57}$, $PrO_{1.58}$, $PrO_{1.60}$, $PrO_{1.62}$, $PrO_{1.67}$, $PrO_{1.71}$, $PrO_{1.76}$, $PrO_{1.78}$, $PrO_{1.80}$, $PrO_{1.82}$, and $PrO_{1.83}$ were measured using liquid nitrogen as the cryogenic fluid. Differences between the 40 and 95°K spectra of C-form and A-form sesquioxides enabled tentative assignment of the peaks in the visible region. The spectra of oxides with composition above Pr_2O_3 change in a regular manner as the oxygen content is increased consistent with the proposed phase relationships. The stable intermediate compositions have unique spectra while those of diphasic samples are combinations of the spectra of the stable phase on either side.

Introduction

The absorption spectra of the oxides of praseodymium reveal variations in the oxygen arrangement about the Pr^{3+} ion. The phase relations in the PrO_x–O_2 system are well established by tensimetric[1] and X-ray diffraction studies.[2,3]

There are two stable sesquioxides: the high-temperature A form which is hexagonal and the C form which is cubic. Between the sesquioxide and the dioxide, there are five stable ordered phases of narrow composition range. These are $PrO_{1.714}$ (Pr_7O_{12}), $PrO_{1.778}$ (Pr_9O_{16}), $PrO_{1.80}$ ($Pr_{10}O_{18}$), $PrO_{1.818}$ ($Pr_{11}O_{20}$), and $PrO_{1.833}$ ($Pr_{12}O_{22}$). These stable compositions from an homologous series R_nO_{2n-2}. There are also two nonstoichiometric phases at higher temperatures and pressures: σ below composition $PrO_{1.68}$ and α above composition $PrO_{1.72}$.

With the exception of the A-form sesquioxide, good single crystals of the stable compositions have not been available. However, a study of a crystal with gross composition $PrO_{1.71}$ was made using a precession camera,[4] but it was not possible to determine the structure completely. Thus, for the most part, studies of the structures of the oxides of praseodymium have been carried out using powdered samples. Very careful X-ray examination using a Guinier focusing camera[2] has led to characterization of the five distinct intermediate phases between Pr_2O_3 and PrO_2. However, because of the lack of information about the positions of the oxygens, only tentative structures can be proposed. The spectra published here show the effect of the oxygen arrangement as the composition is changed.

Experimental Part

The praseodymium oxide used as the starting material for all samples was obtained from the Lindsay Division of American Potash and Chemical Corp. with a stated purity of 99.999% with respect to other rare earths. PrO_x is hygroscopic and reacts with CO_2 so that prepared samples must be protected from the ambient atmosphere. Even in a desiccator, unprotected samples show hydroxide lines in their X-ray diffraction patterns after a few days. Because of this, samples were kept in sealed, evacuated tubes until ready to be examined.

The A-form sesquioxide was prepared by vacuum reduction of PrO_x at 1000°. The resulting oxide was a clear green. The C-form sesquioxide was prepared by hydrogen reduction of PrO_x at temperatures below 600°. This oxide was more yellowish than the A form. $PrO_{1.83}$ was prepared by heating PrO_x in flowing air to 900° and then annealing at 600° in the air for 1 day. Intermediate compositions were prepared by mixing C-form sesquioxide and $PrO_{1.83}$ in proper proportions, sealing in evacuated quartz tubes, and annealing at temperatures where the phase diagram shows an ordered phase. After annealing, the compositions were checked gravimetrically by reducing an aliquot to A form and calculating the original composition from the weight lost. Preparative conditions and analyses of the samples used for spectral measurements are shown in Table I.

In order to obtain a spectrum, the sample was mixed with Kel-F No. 90 grease to make a mull. The mull was applied to a sample holder which was attached to a conduction dewar. For the sesquioxides, copper wires ran across a quartz plate attached to a piece of copper. The mull was applied over the wires. For samples with compositions above the sesquioxide, the mulls were pressed between two quartz plates and slipped into a cylindrical holder. The temperature was monitored with a copper–constantan differential thermocouple. The spectra were taken by a Cary Model 14 recording spectrophotometer. The spectra of C-form and A-form sesquioxides were taken at 95 and 40 °K using both liquid nitrogen and liquid helium as the cryogenic fluid. The spectra of the oxides of intermediate composition were examined at about 120°K. A single crystal of A-form sesquioxide grown by flame fusion and provided by Dr. John B. Gruber[5] was examined at about 100°K.[6] Spectra in the infrared region were taken on a Beckman IR-12. Since Kel-F grease absorbs in the regions of interest, the oxide mulls were made with Fluorolube oil (manufactured by Hooker Chemical Corp.).

Results

The spectrum of the crystal of A-form sesquioxide, examined near 100°K, is shown in Figure 1. Mull

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(1) B. G. Hyde, D. J. M. Bevan, and L. Eyring, *Phil. Trans. Roy. Soc. London*, **A259**, 583 (1966).

(2) J. O. Sawyer, B. G. Hyde, and L. Eyring, *Bull. Soc. Chim. France*, 1190 (1965).

(3) R. P. Turcotte, J. M. Warmkessel, and L. Eyring, unpublished work.

(4) L. Eyring and N. C. Baenziger, *J. Appl. Phys. Suppl.*, **33**, 428 (1962).

(5) Department of Physics, Washington State University, Pullman, Wash.

(6) This work was carried out while J. M. W. was on an AEC summer fellowship at the Hanford Project of the Atomic Energy Commission, Richland, Wash., 1965.

Table I

Preparation of Samples Used for Spectral Measurements

Gravimetrically determined compn	Annealing temp, °C	Annealing time, days	X-ray results (lattice parameter, Å)	
$PrO_{1.508}$	500 (H_2 redn)	$^1/_6$	bcc (a = 11.140)	ϕ
$PrO_{1.536}$	605	1	bcc (a = 11.132)	ϕ
$PrO_{1.568}$	605	1	bcc (a = 11.123)	ϕ
$PrO_{1.580}$	524	2	bcc (a = 11.134) +	ϕ
			bcc (a = 11.093)	σ
$PrO_{1.608}$	605	1	bcc (a = 11.010)	σ
$PrO_{1.626}$	605	1	bcc (a = 11.086)	σ
$PrO_{1.670}$	605	1	bcc (a = 11.086) + rhombohedral $PrO_{1.714}$ lines	$\sigma + \iota$
$PrO_{1.714}$	600	1	Rhombohedral $PrO_{1.714}$ lines	ι
$PrO_{1.76}$	400	1	$PrO_{1.714}$ + $PrO_{1.778}$	$\iota + \zeta$
$PrO_{1.781}$	475	1	Triclinic $PrO_{1.778}$	ζ
$PrO_{1.802}$	400	2	Pseudo fcc (a = 5.482)	ϵ
$PrO_{1.819}$	400	3	Pseudo fcc (a = 5.478)	δ
$PrO_{1.833}$	600	1 (flowing air)	Pseudo fcc (a = 5.469)	β

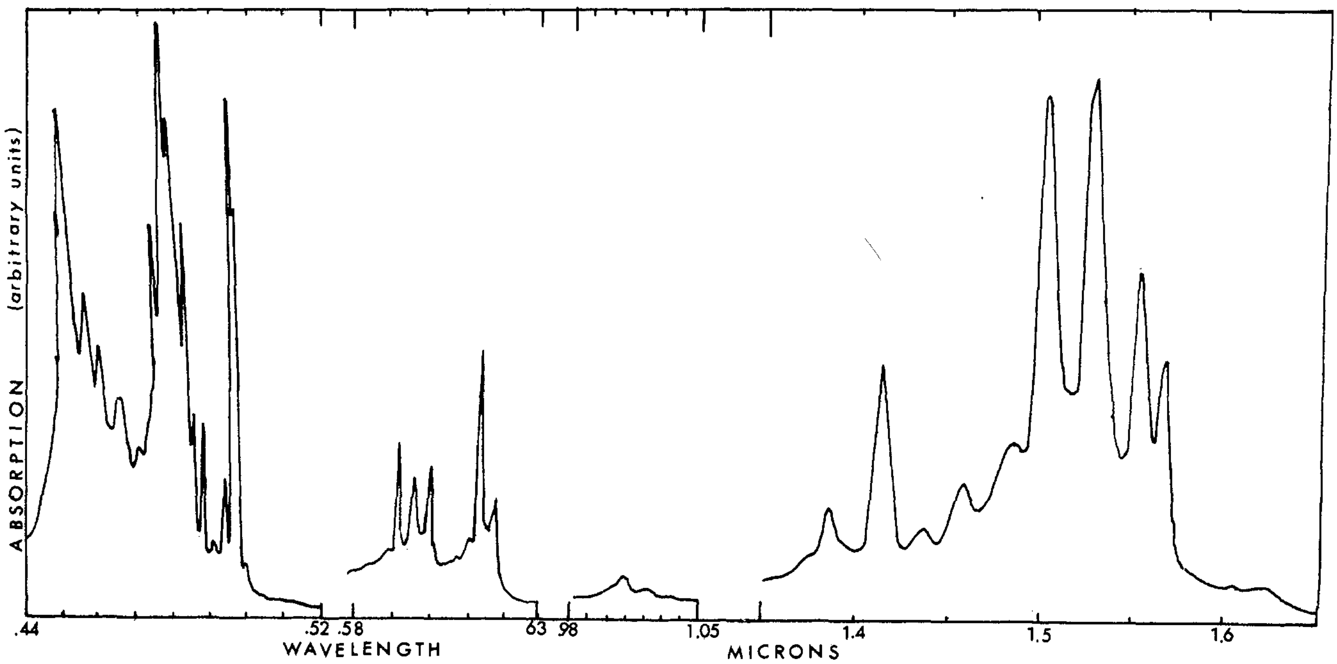

Figure 1.—Spectrum of a single crystal of A-form Pr_2O_3.

spectra of a sample of the A form taken at 95 and 40°K are shown in Figure 2. Except for the region showing transitions to the $^1D_2$ group, the mull spectrum at 95°K shows the same general features as the spectrum of the crystal. The transitions to the $^1D_2$ group in the mull spectrum have broad peaks which are not well resolved.

Table II shows the transitions in the mull spectrum of A-form sesquioxide at 40°K. A superscript a designates levels which are intensified at low temperatures. These levels are associated with transitions from the lowest level of the $^3H_4$ ground term of the free ion. Transitions to the $^3P_2$ and $^1I_6$ levels are labeled A1–A20. Lines B1 and B2 are transitions to the $^3P_1$ levels. The transitions to the $^3P_0$ levels are designated as C1 and C2. Lines D1–D9 are transitions to the $^1D_2$ levels, E1–E21 are transitions to the overlapping $^3F_4$ levels, and F1–F23 are transitions to the overlapping $^3F_2$ and $^3H_6$ levels. From Table II there appear to be levels of the ground state at about 60, 106, and 130 cm^{-1}.

The spectra of C-form sesquioxide taken at 95 and 40°K are shown in Figure 3. The peaks which are intensified at the lower temperature are indicated in Table III. The group of lines from A1 to A22 are transitions from the Stark levels of the ground state to the levels of the overlapping $^3P_2$ and $^1I_6$. Lines B1–B6 are transitions to the $^3P_1$ levels. Line C1 is the transition from the ground term of the free ion to the $^3P_0$ level. Transitions D1–D7 are those to the $^1D_2$ levels. The transitions E1–E14 are to the overlapping $^3F_4$ and $^3F_3$ levels, and F1–F23 are to the overlapping $^3F_2$ and $^3H_6$ levels. From Table III, Stark levels of the ground state lie at about 40, 70, and 155 cm^{-1}.

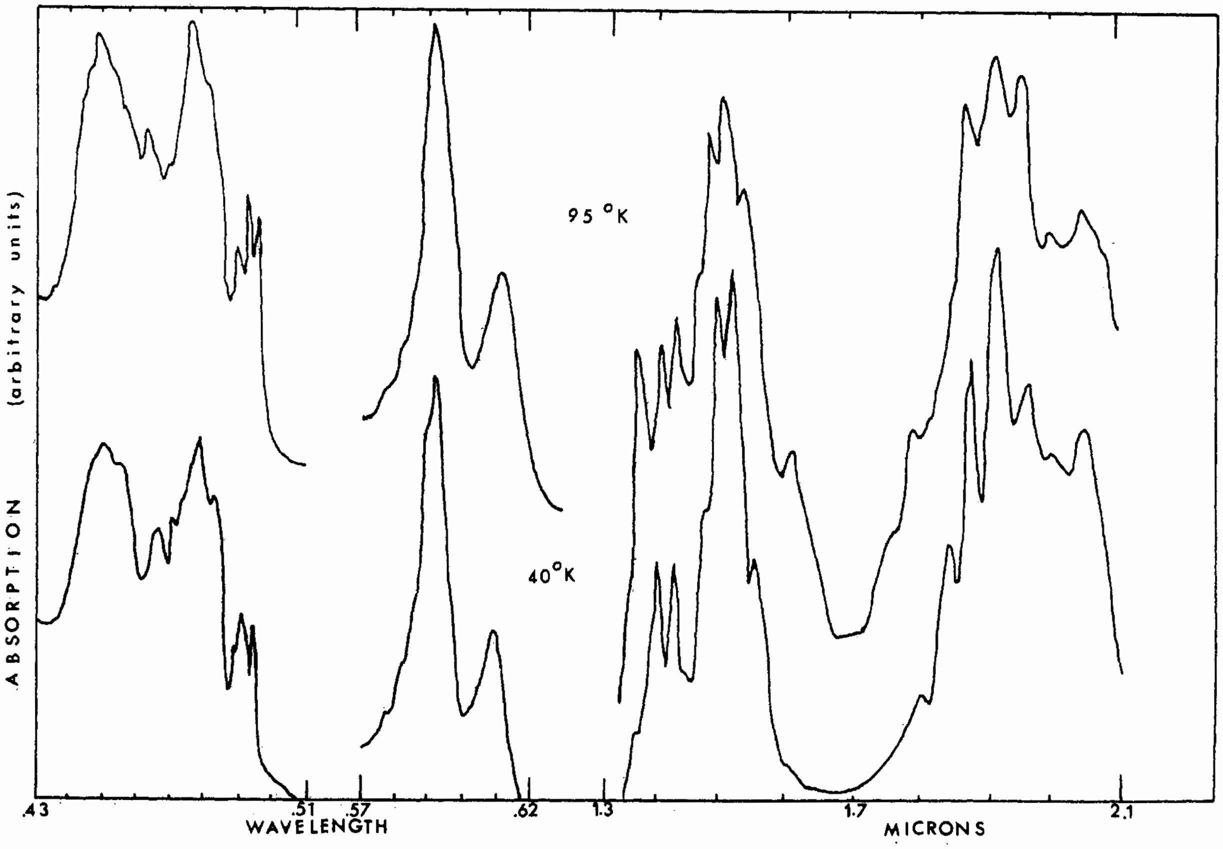

Figure 2.—Spectra of sample of A-form Pr_2O_3 at 40 and 95°K.

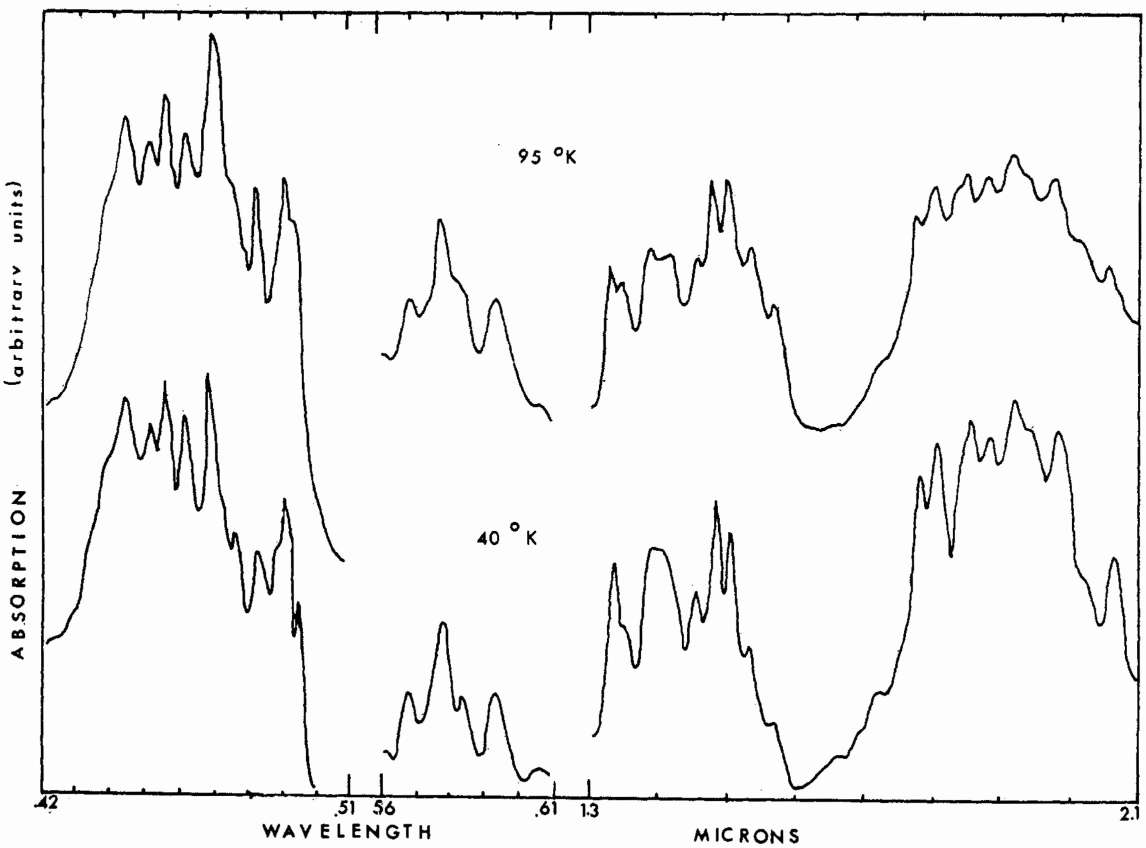

Figure 3.—Spectra of C-form Pr_2O_3 at 40 and 95°K.

TABLE II

ABSORPTION SPECTRUM OF A-FORM Pr_2O_3 (SAMPLE A-2) AT 40°K

Lines	Wave numbers, cm^{-1}	Comment
A1[a]	22,476	
A2	22,420	A1 − A2 = 56
A3[a]	22,352	
A4[a]	22,206	
A5	22,113	
A6[a]	21,952	
A7	21,771	
A8	21,634	
A9[a]	21,578	
A10	21,513	A9 − A10 = 65
A11[a]	21,458	
A12	21,393	A11 − A12 = 65
A13[a]	21,248	
A14[a]	21,131	
A15	21,007	
A16[a]	20,884	
A17[a]	20,767	
A18[a]	20,685	
A19	20,664	
A20	20,613	
B1[a]	20,457	
B2[a]	20,365	
C1[a]	20,258	$^3P_0$
C2	20,200	C1 − C2 = 58
D1	17,296	
D2	17,160	
D3	17,034	
D4[a]	16,924	
D5[a]	16,836	
D6	16,810	
D7	16,546	
D8[a]	16,389	
D9	16,351	
E1	7,601	
E2	7,500	
E3[a]	7,269	
E4	7,220	E3 − E4 = 49
E5[a]	7,064	
E6	6959	E5 − E6 = 105
E7[a]	6943	
E8[a]	6869	
E9	6847	E7 − E9 = 96
E10	6793	
E11	6760	E11 − E8 = 109
E12[a]	6733	
E13	6681	E13 − E12 = 52
E14[a]	6639	
E15	6608	E12 − E15 = 125
E16[a]	6547	
E17	6532	E14 − E17 = 107
E18	6512	E14 − E18 = 127
E19[a]	6428	
E20	6370	E19 − E20 = 58
E21	6162	
F1	5836	
F2	5662	
F3	5628	
F4[a]	5540	
F5	5402	
F6[a]	5304	
F7	5285	
F8	5252	F6 − F8 = 52
F9[a]	5191	
F10	5169	
F11	5110	
F12	5091	F9 − F12 = 100
F13	5019	
F14	4958	
F15	4870	
F16[a]	4795	
F17	4692	F17 − F16 = 103
F18[a]	4661	
F19	4444	
F20[a]	4435	
F21	4307	F20 − F21 = 128
F22[a]	4294	
F23[a]	4232	

[a] Peaks intensified at lower temperatures.

The spectra of the oxides above the sesquioxide are partially obscured by a broad, intense band which completely covers the bands of the Pr^{3+} ion in the visible region. Only transitions to the $^3F_4$, $^3F_3$, $^3F_2$, and $^3H_6$ levels can be observed. A detailed analysis of the spectra is given elsewhere.[7]

According to the phase diagram[1,3] in the composition region between $PrO_{1.5}$ and $PrO_{1.6}$, a single body-centered cubic phase or two body-centered cubic phases can be present, depending on the annealing temperature. The spectra of two samples of composition $PrO_{1.57}$ were taken. One sample was annealed at 550° and the X-ray diagram showed two body-centered cubic phases. The second sample was annealed at 605° and the X-ray diagram showed a single body-centered cubic phase. The spectra of these samples are shown in Figure 4. The difference in peak heights and noise level is due primarily to differences in the two mulls. However, the relative intensities of the peaks appear to be the same, and peak positions are identical. A physical mixture of C-form sesquioxide and $PrO_{1.714}$ gave a spectrum much like that of an annealed sample of a slightly lower composition. So at a given composition, the spectrum obtained is not critically dependent on the phases which the X-ray powder patterns show to be present. The spectra of compositions examined are shown in Figures 5–7.

In the region between C-form sesquioxide and $PrO_{1.71}$, the spectrum appears to be a combination of the two end members. The spectrum of $PrO_{1.71}$ shows

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(7) J. M. Warmkessel, Ph.D. Thesis, Arizona State University, Tempe, Ariz., 1968.

TABLE III

ABSORPTION SPECTRUM OF C-FORM Pr_2O_3 AT 40°K

Lines	Wave numbers, cm^{-1}	Comment
A1	23,282	
A2^a	22,971	
A3^a	22,711	
A4^a	22,552	
A5	22,516	A4 − A5 = 36
A6^a	22,455	
A7^a	22,123	
A8	22,079	A7 − A8 = 44
A9^a	21,953	
A10^a	21,895	
A11	21,733	
A12^a	21,644	
A13	21,625	
A14	21,569	
A15	21,481	
A16^a	21,339	
A17^a	21,289	
A18^a	21,100	
A19	21,029	
A20^a	20,936	
A21	20,832	
A22^a	20,677	
B1^a	20,626	
B2	20,537	
B3^a	20,427	
B4	20,382	B3 − B4 = 45
B5^a	20,336	
B6	20,209	
C1^a	20,180	$^3P_0$
C2	19,958	
D1^a	17,601	
D2^a	17,389	
D3^a	17,290	
D4	17,254	D3 − D4 = 36
D5^a	17,124	
D6^a	16,850	
D7	16,805	D6 − D7 = 45
E1	7825	
E2^a	7481	
E3	7435	E2 − E3 = 46
E4^a	7389	
E5^a	7183	
E6^a	7123	
E7^a	7034	
E8	7017	
E9^a	6853	
E10^a	6728	
E11^a	6618	
E12^a	6502	
E13	6467	E12 − E13 = 35
E14^a	6356	
F1	5997	
F2	5889	
F3	5785	
F4	5680	
F5^a	5598	
F6^a	5583	
F7	5548	F6 − F7 = 35
F8^a	5514	
F9	5419	
F10^a	5399	
F11^a	5372	
F12	5361	F10 − F12 = 38
F13	5341	F11 − F13 = 31
F14^a	5281	
F15	5275	
F16	5262	
F17^a	5226	
F18^a	5185	
F19	5141	F18 − F19 = 44
F20^a	5046	
F21^a	5019	
F22	4926	
F23^a	4823	

[a] Peaks intensified at lower temperatures.

much less splitting than that of the C form. The peaks are broad and a valley develops near 1.89 μ. The spectrum of $PrO_{1.76}$ appears to be a combination of those of $PrO_{1.71}$ and $PrO_{1.78}$. The shape of the spectrum of $PrO_{1.78}$ between 1.3 and 1.7 μ is very similar to the shape of the spectrum of $PrO_{1.71}$, but the broad peaks of $PrO_{1.71}$ are split into many components. The spectrum of $PrO_{1.80}$ seems to be a combination of those of $PrO_{1.78}$ and $PrO_{1.82}$. The spectra of $PrO_{1.82}$ and $PrO_{1.83}$ are almost identical.

Discussion

The high-temperature modification of the sesquioxide, A form, has trigonal symmetry about the Pr^{3+} ion, and the local site symmetry appears to be C_{3v}. With the exception of the A form, all of the phases of PrO_x are structurally related to fluorite. The fluorite structure can be considered as being built up of metal atoms which are cubically coordinated with oxygen. Each cube shares all its edges with similar adjacent cubes. The C form can be considered derived from fluorite in which there are oxygens missing across the body diagonal of a cube.[2] These RO_6 groups are arranged in strings which run along all four ⟨111⟩ directions in such a way that their closest approach results in oxygen vacancies on the face diagonals of all cubes which would otherwise have no vacancies. This results in all metal atoms being 6-coordinated. One-fourth of the atoms have oxygens missing across the body diagonal, and three-fourths have oxygens missing across the face diagonal of a cube.

In the actual structure of C-form sesquioxide,[8] the lattice relaxes to give rise to two types of oxygen coordination about the Pr^{3+} ion. The first is an S_6

(8) L. Pauling and M. Shappell, *Z. Krist.*, **75,** 129 (1930).

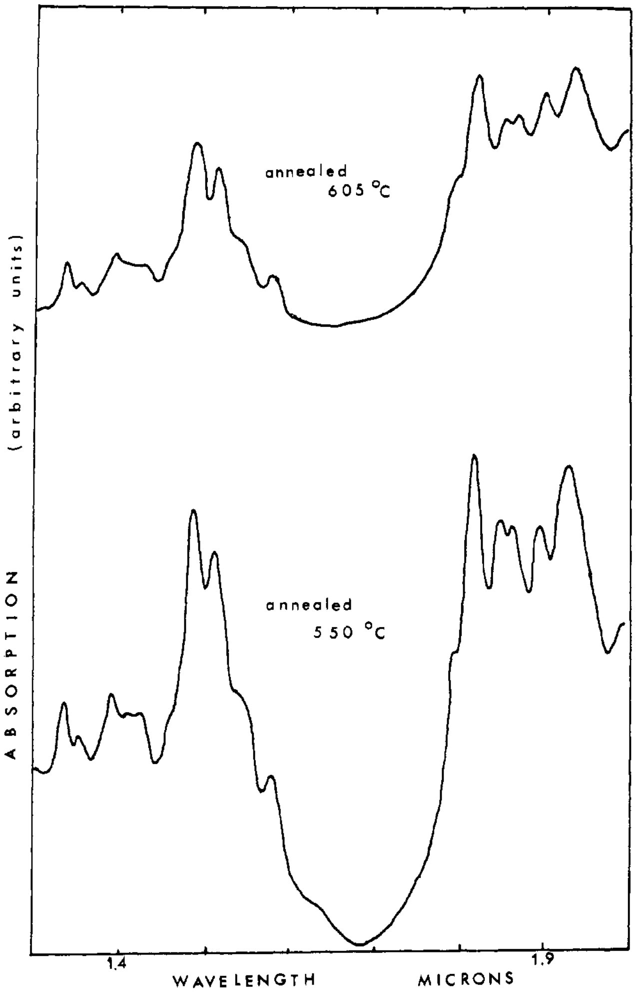

Figure 4.—Spectra of $PrO_{1.57}$ annealed at 605 and 550°.

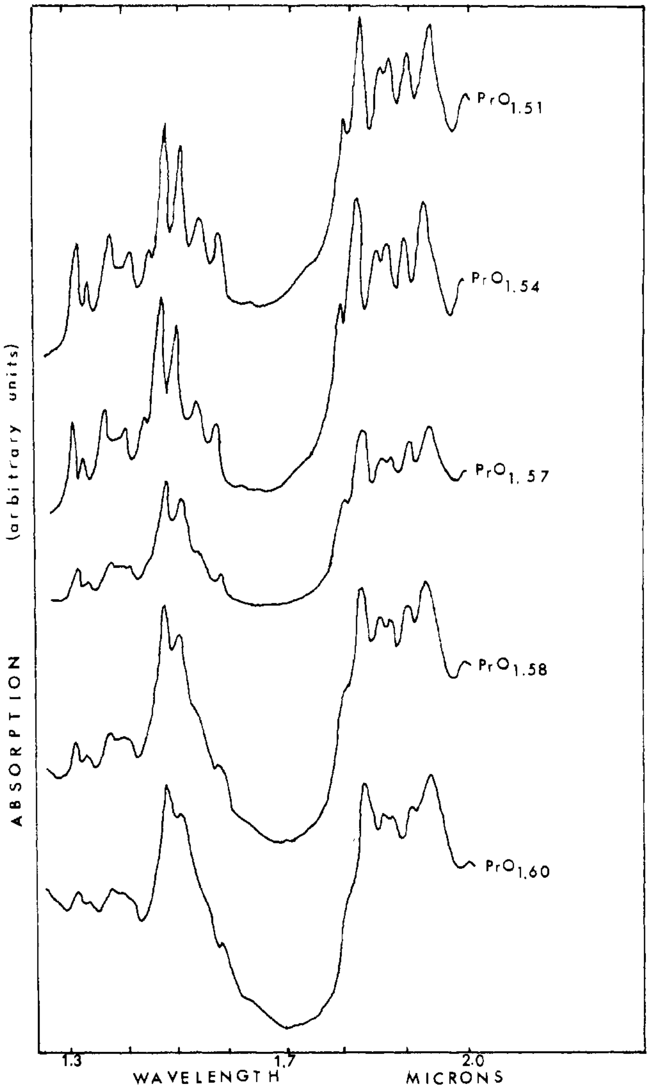

Figure 5.—Spectra of $PrO_{1.51}$, $PrO_{1.54}$, $PrO_{1.57}$, $Pr_{1.58}$, and $PrO_{1.60}$.

site which is derived from the cube with oxygens missing across a body diagonal. The second type is a C_2 site which is derived from the cube with oxygens missing across face diagonals. Since the S_6 site contains a center of inversion, "forced" electric dipole transitions should not be observed. Thus, the spectrum of C-form sesquioxide is due to transitions of the Pr^{3+} ion in C_2 sites.

There is every indication that the structure of $PrO_{1.71}$ (Pr_7O_{12}) is the same as other R_7O_{12} compounds such as $UO_3 \cdot 3Y_2O_3$.[4,9] In the structure of this compound, the rhombohedral primitive cell is a supercell of the fluorite lattice, but the two anion sites along the threefold axis (the ⟨111⟩ direction) are vacant. A projection along the ⟨111⟩ direction of the ideal stacking arrangements of the metals[2] is shown in Figure 8. The cations at the centers of the circles have RO_6 coordination with the vacant anion sites, V, in the RO_6V_2 cubes directly above and below the cations concerned. It follows that the cations on the circumference of the circles have RO_7 or RO_7V coordination. All anion sites projecting onto circle centers are unoccupied. Thus, the R_7O_{12} structure consists of parallel infinite strings of 6-coordination cations surrounded by contiguous sheaths of 7-coordinated cations.

It has been proposed[10] that the strings of RO_6V_2 coordinated octahedra with the vacancies along the ⟨111⟩ direction are the structural entity which generates the series R_nO_{2n-2} from the parent RO_2. If $1/n$ of the cations are in the strings and each original RO_8 unit is missing two anions, the composition becomes $RO_{2(1-(1/n))}$ or R_nO_{2n-2} as required. Using the idea of strings, structures for Pr_9O_{16} and $Pr_{12}O_{22}$ have been proposed[2] which are consistent with the X-ray diffraction data.

The actual structure[9] of R_7O_{12} belongs to space group $R\bar{3}$ with 6-coordinated ions at (0, 0, 0), $(^1/_3, ^2/_3, ^2/_3)$, and $(^2/_3, ^1/_3, ^1/_3)$. The stacking arrangement is

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[9] S. F. Bartram, *Inorg. Chem.*, **5**, 749 (1966).

[10] B. G. Hyde, D. J. M. Bevan, and L. Eyring, "I. Electron Diffraction, II. The Nature of Defects in Crystals," Pergamon Press Ltd., London, 1966, p II C-4.

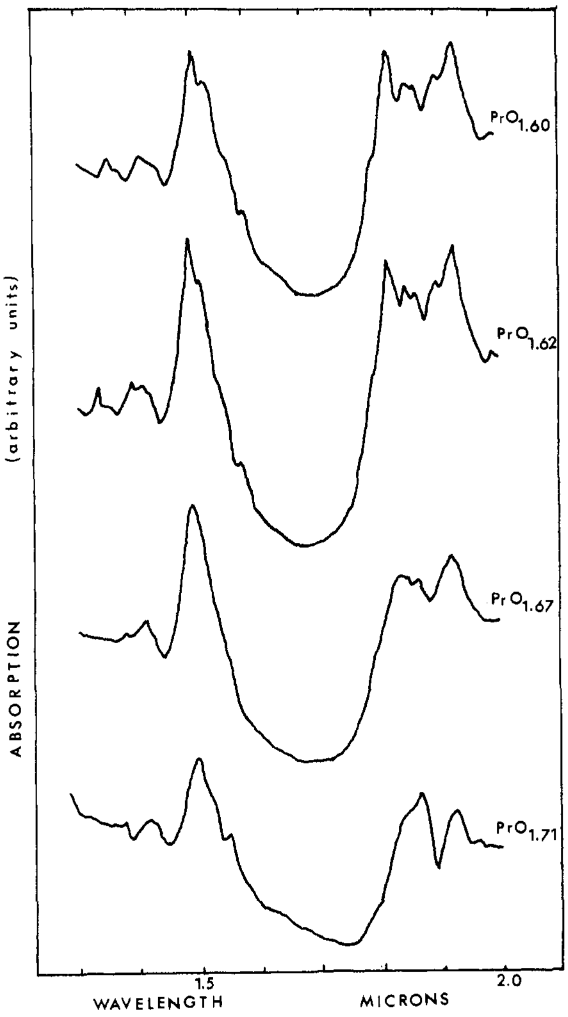

Figure 6.—Spectra of $PrO_{1.60}$, $PrO_{1.62}$, $PrO_{1.67}$, and $PrO_{1.71}$.

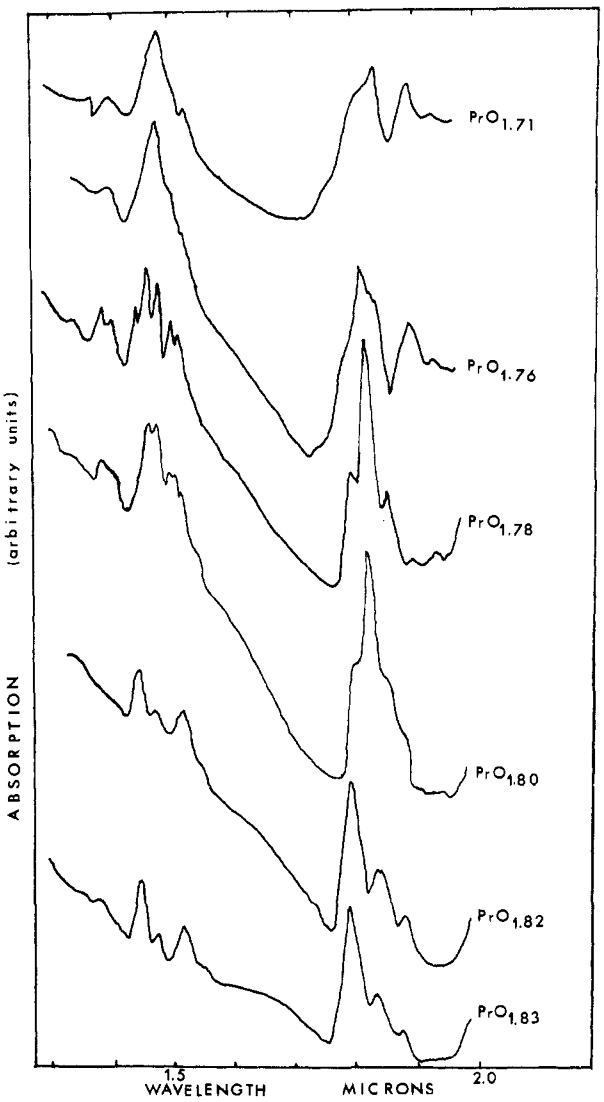

Figure 7.—Spectra of $PrO_{1.71}$, $PrO_{1.76}$, $PrO_{1.78}$, $PrO_{1.80}$, $PrO_{1.82}$, and $PrO_{1.83}$.

essentially the same as the ideal arrangement shown in Figure 8. However, 7-coordinated cations are displaced slightly out of the (111) planes. The oxygens shift toward the vacant sites, resulting in S_6 symmetry about the 6-coordinated cations and C_1 symmetry about the 7-coordinated cations.

In terms of valence, Pr_7O_{12} can be written $(Pr^{4+})_3(Pr^{3+})_4O_{12}$. The space group $R\bar{3}$ requires either only one type of metal ion to be at the origin of the cell or a statistical occupation of these sites if more than one type is present. Because of the large difference in size between the Pr^{3+} and Pr^{4+} ions and other considerations, it is believed that there is only one type of 6-coordinated metal atom in the strings, either Pr^{3+} or Pr^{4+}. As a result, the other metallic positions, which are also equivalent, must be filled statistically by a mixture of Pr^{3+} and Pr^{4+} ions. However, the unusual stability of Pr_7O_{12} suggests electronic shifts which make the ions in the 7-coordinated sites equivalent. Structurally the formula would be either $Pr^{4+}(2Pr^{4+},4Pr^{3+})O_{12}$ or $Pr^{3+}(3Pr^{4+},3Pr^{3+})O_{12}$. By analogy[9] with $UO_3 \cdot 3Y_2O_3$, the Pr^{4+} might be expected to be at the origin of the cell with equivalence obtained between the two Pr^{4+} and four Pr^{3+} ions. Thus the stable composition Pr_9O_{16} ($PrO_{1.78}$) could be written as $Pr^{4+}(3Pr^{4+},3Pr^{3+})O_{12.5}$.

Continuing to fill the vacant oxygen positions in the strings, the following structural formulas might be expected to produce the stable compositions $Pr^{4+}(4Pr^{4+},2Pr^{3+})O_{13}$ ($PrO_{1.86}$) and $Pr^{4+}(5Pr^{4+},1Pr^{3+})O_{13.5}$ ($PrO_{1.93}$); however, neither of these stoichiometries is found in the pure praseodymium oxides.

Putting Pr^{3+} at the origin of the cell and allowing the extra oxygen to form MO_8 polyhedra in an ordered way in the structure, the next composition could be written $Pr^{3+}(3Pr^{4+},3Pr^{3+})Pr^{4+}O_{14}$. However, the oxide Pr_8O_{14} has not been found, but the stable phase with stoichiometry Pr_9O_{16} can be written $Pr^{3+}(3Pr^{4+},3Pr^{3+})2Pr^{4+}O_{16}$. Continuing in the same manner one can write $Pr^{3+}(3Pr^{4+},3Pr^{3+})3Pr^{4+}O_{18}$ ($PrO_{1.80}$), $Pr^{3+}(3Pr^{4+},3Pr^{3+})4Pr^{4+}O_{20}$ ($PrO_{1.818}$), and $Pr^{3+}(3Pr^{4+},3Pr^{3+})5Pr^{4+}O_{22}$ ($PrO_{1.83}$) which are stoichiometries that give stable phases. These formulas are also consistent with the idea of strings of 6-coordinated ions which are carried over from C-form sesquioxide. These arguments are

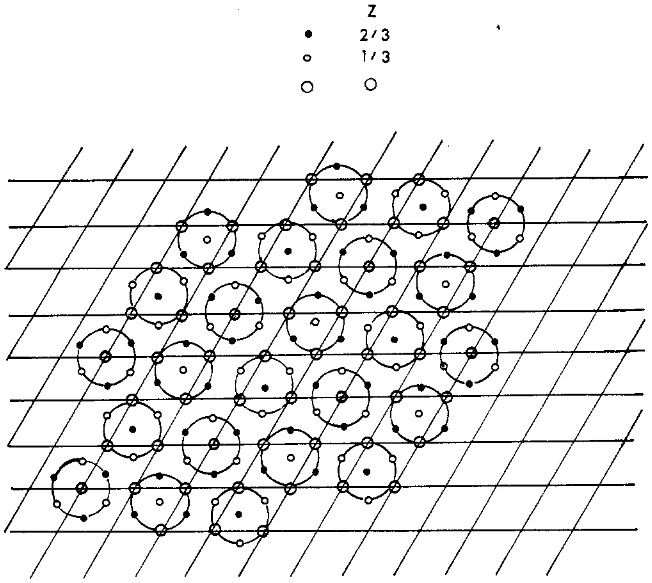

Figure 8.—Projection of the metal positions in $PrO_{1.71}$.

mild support for the contention that the 6-coordinated ions in the fluorite-related phases should be Pr^{3+} ions.

Recently, Asprey, *et al.*,[11] have reported a band near 2800 cm^{-1}, which is due to the f^1 transitions in compounds of the types PrF_4, Na_2PrF_6, and $Na_7Pr_6F_{31}$. The structure of PrF_4 contains a center of inversion, and the f^1 transitions would not be expected to be observed. It was found, however, although it was much weaker and more difficult to detect than in the other compounds.[12]

Several compositions of PrO_x were examined in the region around 2800 cm^{-1}. In no case was any transition observed. It is possible that in some compositions Pr^{4+} ions would be located in sites with inversion symmetry, but in Pr_7O_{12} if Pr^{4+} ions were present, at least two-thirds of them must be located in unsymmetric 7-coordinated sites.

A possible explanation for the apparent absence of Pr^{4+} ions in the 7-coordinated sites may lie in the fact that the oxides turn black with even a small amount of oxidation above the sesquioxide. In d-group complexes, intense absorption bands, which correspond to an electron transfer from a filled molecular orbital concentrated mainly on the ligand to a molecular orbital on the metal, are found in complexes with oxidizing metal ions and oxidizable ligands.[13] Since Pr^{4+} is a very powerful oxidizing agent, it is conceivable that there is a transfer of an electron from adjacent oxide ligands to Pr^{4+} ions. Jørgensen[14] has observed a broad absorption band in $Pr_{0.0005}Th_{0.9995}O_2$ which has a maximum at about 0.41 μ. This band is attributed to a charge transfer to the metal from an electron nearer the oxygen. It is this charge transfer that could account for the equivalence of the Pr^{3+} and Pr^{4+} ions in the 7-coordinated sites.

The spectrum of compositions above the sesquioxide in the near-infrared region is characteristic of transitions of the $4f^2$ configuration. Since transitions from cations in sites with inversion symmetry are weak, the spectrum obtained is primarily due to transitions from cations in 7-coordinated sites.

Since the 7-coordinated sites do not contain any elements of symmetry except the identity element, the spectrum of $PrO_{1.71}$ might be expected to look like that of C-form sesquioxide. In C form all of the degeneracies are lifted and all transitions are allowed. However, $PrO_{1.71}$ has broad peaks which show little splitting. The fact that the shape of the spectrum is similar to that of the spectrum of $PrO_{1.78}$, which shows a great deal of splitting, suggests that the broad peaks are due to poor resolution of overlapping transitions.

The apparent simplification at $PrO_{1.78}$ could be due to the increase in symmetry in the arrangement of the strings which would result in a more symmetric arrangement of oxygen about the metallic ion. In $PrO_{1.71}$ the 6-coordinated cations are located in the three (111) planes in which metal can be found. This results in a misalignment of the strings. In the proposed structure of $PrO_{1.78}$, the 6-coordinated cations are only found in (111) planes with $z = 0$. Here the strings are all aligned in the same way. Thus in $PrO_{1.71}$ it is possible that the lattice can relax, resulting in more than one type of field about the 7-coordinated cations which give rise to levels which are so close together that the transitions overlap.

The spectrum of $PrO_{1.76}$ is much more like that of $PrO_{1.71}$ than might be expected on the basis of composition alone. This suggests that there are more 7-coordinated sites in $PrO_{1.71}$ than in $PrO_{1.78}$ since some have become 8-coordinated in oxidation. This is in agreement with the structures proposed.

The spectra of $PrO_{1.82}$ and $PrO_{1.83}$ are almost identical yet are different from those of $PrO_{1.78}$ or $PrO_{1.71}$. The peaks in the spectrum of $PrO_{1.82}$ and $PrO_{1.83}$ are not extremely broad, which indicates that an increase in symmetry has occurred.

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