THE SOLID STATE CHEMISTRY
OF RARE EARTH OXIDES

LeRoy Eyring
Edward Summerville
A. Jerome Skarnulis

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

APPROVED:

LeRoy Eyring, Principal Investigator

Gilbert L. Cady, Vice President

Arizona State University
Tempe, Arizona
June 25, 1975
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addendum to Progress Report</td>
<td>ii</td>
</tr>
<tr>
<td>Purpose and Scope</td>
<td>iii</td>
</tr>
<tr>
<td>Abstract</td>
<td>iv</td>
</tr>
<tr>
<td>Disclaimer</td>
<td>v</td>
</tr>
<tr>
<td>I. Calculated n-Beam Lattice Images of Oxides Based on Fluorite and ReO₃ and the Interpretation of Observed Images</td>
<td>1</td>
</tr>
<tr>
<td>II. High Resolution Lattice Images of Ordered Phases in the Praseodymium Oxide System</td>
<td>36</td>
</tr>
<tr>
<td>III. Observations of Phase Transformations, Intergrowth and Disorder in Binary and Pseudobinary M₂O₃-MO₂ (Fluorite) Systems</td>
<td>71</td>
</tr>
</tbody>
</table>
ADDENDUM TO PROGRESS REPORT

(Included separately)

Submitted and In Press


Reprints

PURPOSE AND SCOPE

This research elucidates the structure (including defects) of real, nonmetallic solids. High resolution electron optical methods at 3Å resolution are utilized.

The rare earth oxides are the model systems employed because a) they exhibit the full range of structural repertory and b) they are models for nuclear fuels, power sources and solid electrolytes.
ABSTRACT

This work elucidates the structure (including defects) of real, nonmetallic solids. High resolution electron optical methods (capable of point-to-point resolution of about 3Å in the projected lattice images) are the techniques providing the greatest insights.

The rare earth oxides are the model systems of choice for three principal reasons: 1) They exhibit the full range of structural variability. 2) They are representative of the ubiquitous fluorite structure. 3) They are models for many materials needed as nuclear power sources, nuclear fuels and as fast-ion solid electrolytes.

It is demonstrated here that electron microscope images obtained at about 3Å resolution for Pr$_7$O$_{12}$ (and isomorphous Zr$_3$Sc$_4$O$_{12}$) are in excellent agreement with calculated images based upon the structure determined separately by total profile neutron powder diffraction analysis. The image calculation programs developed are described. This establishes the efficacy
of lattice image interpretation in structural terms for these types of related phases whose structures are as yet beyond conventional means to determine. Such images for several other intermediate phases are interpreted and structures proposed. Finally, images of crystals which can be made to undergo reaction within the microscope are interpreted according to the structures involved. These studies reveal the role of intergrowth and topotaxy in these systems.

DISCLAIMER

This report was prepared as an account of Government-sponsored work. Neither the United States, nor the Energy Research and Development Administration nor any person acting on behalf of the Commission

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Administration or employee of such contractor, to the extent that such employee or contractor of the Administration employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Administration, or his employment with such contractor.

CONTRACT REQUIREMENTS

The contract requirements have been fully complied with.

EFFORT OF PRINCIPAL INVESTIGATOR

The principal investigator devoted 20% of his time during the nine month academic year, September-May, and 70% of two and one-half months, June-August to Project E(11-1)-1109.
CALCULATED n-BEAM LATTICE IMAGES
OF OXIDES BASED ON FLUORITE AND ReO3
AND THE INTERPRETATION
OF OBSERVED IMAGES*

A. Jerome Skarnulis, E. Summerville***
and LeRoy Eyring†
Department of Chemistry
Arizona State University
Tempe, Arizona 85281

*Work supported by the United States Energy Research
and Development Administration.

***Present address: School of Physical Sciences, Flinders
University of South Australia, Bedford Park 5042, South
Australia.

†Author to whom inquiries should be addressed.
ABSTRACT

Dynamical n-beam calculations* are used to explore the potential of lattice imaging for investigating superstructures in fluorite-related systems. Lattice images of $M_7O_{12}$ phases are investigated under various conditions of crystal thickness and defect of focus and it is shown that under a wide variety of conditions lattice images should be directly interpretable in structural terms. Two programs, FCOEFF and DEFECT, which allow calculation of images of structures with any symmetry and in any projection, are tendered. The n-beam calculations on a number of $ReO_3$-based structures are also presented for comparative purposes.

*It has recently been found that better agreement of the experimental and calculated images can be obtained by using a smaller aperture in the calculations. It also appears that n-beam calculations are probably unnecessary for $Pr_7O_{12}$ and that better images can be calculated using the phase grating approximate. These techniques improve the accuracy of the calculated images of $Pr_7O_{12}$ but would be inapplicable for other praseodymium oxide phases.
INTRODUCTION

Many tensimetric and X-ray studies of the binary rare earth oxide systems of Ce, Pr and Tb have been carried out (Eyring, 1974) to reveal the nature of the ordering phenomena in these materials. These systems have been of considerable interest because of the presence of an homologous series of ordered phases of general formula $R_nO_{2n-2}$ with observed $n$ values of 4, 7, 9, 10, 11, 12 and \infty. Each phase is closely related structurally to fluorite and successive members of the series differ only in the proportion and arrangement of vacant fluorite anion sites. At equilibrium, each phase has a narrow range of homogeneity and a high degree of order. Since any description of the properties of these systems is impossible without taking due regard of the ordering processes in the system, detailed structural information on the intermediate phases is essential.

In a previous article, Kunzmann and Eyring (1975) described the unit cells of each of the intermediate phases and, with the aid of a lattice image of $\text{Tb}_1\text{O}_{20}$, proposed a structural model for the odd-member phases.
However, application of high resolution lattice imaging to fluorite-type structures had not been previously attempted, so its applicability and the validity of interpreting such images in terms of vacancies were uncertain.

Most previous electron microscopic studies using high resolution lattice imaging have involved block structures where the subcell is that of the ReO$_3$ structure-type (Eyring and Tai, 1973). This subcell exhibits large variations in potential when viewed down the b-axis because it consists of columns of corner-sharing MO$_6$ octahedra, within which the potential is very high and outside of which it is extremely low. The supercells of the ordered phases are then derived from this structure by crystallographic shear (CS), one result of which is a sharp increase in concentration of cations in the vicinity of the CS plane. Again large, localized variations in potential are produced parallel to the b-axis of the subcell.

In contrast, the fluorite superstructures have
little to recommend them for lattice imaging. The parent fluorite lattice has few projection directions which would exhibit large potential variations on a scale comparable to the resolution limit of an electron microscope (the most favorable direction would be \([110]_F\)). Since the supercells are formed from the parent structure by ordering of vacant anion sites with associated relaxation of the host lattice, it is likely that the potential variations within a supercell would be very similar to those existing in fluorite. A further disadvantage in imaging these phases is that any projection axis will be rather long, ranging from 6.75\(\AA\) for a \([100]_7\)-axis (the subscript refers to the value of \(n\) in the homologous series \(R_nO_{2n-2}\)) to 9.6\(\AA\) for a \([111]_7\)-axis. Such long axes strain the thin-phase-grating approximation used in calculating the images and minimize the magnitude of potential variations due to vacancy ordering. At the same time, reciprocal lattice axes perpendicular to the projection axis are also disadvantageously long, so that with reasonable aperture sizes the images were produced from the interaction of an undesirably small number of beams.
In view of these unfavorable circumstances it seemed necessary that calculations of image contrast should be made to support intuitive interpretation of lattice images. The details of such calculations have been described previously (Allpress, Hewat, Moodie and Sanders, 1972 and O'Keefe, 1973) and the most accurate method of incorporating dynamical diffraction effects, the n-beam multislice method of Cowley and Moodie (1957), was selected for this study. Since the structure of only one of the intermediate phases (n = 7, iota) is known, such calculations can only be performed on this phase, nevertheless, it is thought that the conclusions reached in this case will aid interpretation of the observed images of the other homologues. It is fortuitous that the structure is known (Von Dreеле, Eyring, Bowman and Yarnell, 1975) for that phase which appears to be the end-member of the homologous series.

EXPERIMENTAL PART

Hydrothermally grown single crystals of PrO$_2$ (Lowenstein, Khilborg, Lau, Haschke and Eyring, 1972) were ground under liquid nitrogen, placed in a loosely
closed platinum capsule which was immersed in a large bed (~ 30g) of PrOx powder and the whole sample reduced to the required composition by adjusting the ambient oxygen pressure at temperature. The sample was then isolated and cooled at constant composition. Grinding of the crystals prior to reduction had the advantages of a) allowing more rapid equilibration of the crystals with the gas phase, b) allowing strains induced during grinding to be annealed out and c) minimizing the possibility of compositional changes after annealing.

The reduced samples were mounted on a holey carbon support film via an acetone slurry and examined by means of conventional techniques on a modified JEM 100B electron microscope (Iijima, 1973).

CALCULATIONS

Two FORTRAN Programs, FCOEFF and DEFECT, were written in order to calculate lattice images and to provide other information on any structures.

The Program FCOEFF is used to calculate the real, imaginary and absorption structure factors needed
for Program DEFECT. The absorption factors can be determined for particular atoms with a specified percentage of the real part used as the absorption factor. Either isotropic or anisotropic temperature factors for individual atoms may be used.

FCOEFF permits projecting the structure down any direction, [uvw], by automatically transforming the three-dimensional indices into a two-dimensional array. The input includes fractional coordinates, symmetry operators, scattering tables and lattice parameters. The output includes structure factors, three-dimensional and two-dimensional indices, a transformation matrix, new x and y axes and the plane angle of projection.

DEFECT is a program that will calculate theoretical electron micrographs by dynamical theory using the multislice method. It utilizes real, imaginary and absorption structure factors. To calculate images of dislocations, interstitials (Skarnulis, Iijima and Cowley, 1975) and overlay structures (two layers of the same structure but with different composition one on top of another).
The program could be run in various configurations: (1) utilizing all the options requires 60K (decimal) of core without overlaying the program; (2) if the absorption potential calculation is eliminated, the program requires 50K (decimal) of core, and (3) eliminating the overlay structure calculation and reducing the total number of beams would require less than 40K (decimal).

The approximate running time for a 60K (decimal) run of 12 slices, 150 beams and 257 structure factors is \( \approx 47 \text{ SUPS} \) (standard units of processing, UNIVAC 1110, approximately 4000 SUPS/hr).

The input to DEFECT is a punched deck of structure factors from FCOEFF and experimental parameters such as crystal thickness, aperture radius and the spherical aberration constant.

An excellent description of the multislice method and the relationship to other formulations is given by Goodman and Moody (1974). Program DEFECT FOURIER transforms the structure factors obtained from FCOEFF to give the crystal potential averaged among the incident direction.
\[ \varphi(x, y) = \sum_{h, k} V(h, k, 0) \exp(-2\pi i \left( \frac{hx}{a} + \frac{ky}{b} \right)). \]

The crystal potential is used to determine the transmission function (the phase change of the diffracted beams as they pass through one slice of crystal).

\[ q(x, y) = \exp(-i\sigma \varphi(x, y) \Delta z) \]

where \( \varphi(x, y) \) is the crystal potential, \( \Delta z \) is the slice thickness and

\[ \sigma = \frac{\pi}{W\lambda} \cdot \frac{2}{1+(1+\beta^2)^{\frac{1}{2}}} \]

where \( W \) is the accelerating voltage, \( \lambda \) is the relativistic wavelength of the incident electrons with velocity \( v \) and

\[ \beta = \frac{v}{c}. \]

The diffraction of the electron beam between the slices is calculated by convoluting the wave equation with the propagation function

\[ p(r, \Delta z) = \frac{i}{\Delta z \lambda} \exp\left( \frac{-i\pi r^2}{\lambda \Delta z} \right) \]

so that the wave equation in real space is represented by

\[ \psi(r, z_{n+1}) = q(r) \cdot [\psi(r, z_n) \ast p(r, \Delta z)]. \]

The equivalent equation in reciprocal space becomes

\[ \psi_{n+1}(h) = Q(h) \ast [\psi_n(h) \ast P_{\Delta z}(h)]. \]
where the capital letters are the FOURIER transforms of their lower case counterparts.

\[ P_{\Delta z} = \exp(i\pi \Delta z u^2) \quad \text{where} \quad u^2 = \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} \right). \]

In reciprocal space the convolutions become simple summations instead of integrations yielding

\[ \psi_{n+1}(h) = \sum_{h'} Q(h-h') P_{\Delta z}(h') \psi_n(h') \]

which can be represented physically as a diffracted beam with wave equation \( \psi_n(h') \) entering a slice of crystal and having its phase changed by the effect of the potential encountered in that slice and by the distance it has moved through space. This calculation is repeated until the number of slices equal the crystal thickness.

The program simulates an objective aperture and determines which of the diffracted beams pass through and contribute to the intensity of the image.

The phase change due to defocus

\[ \psi_R(h, k) = \psi(h, k) \exp(i\pi \lambda R u^2) = \psi(h, k) \exp(i\pi \lambda R \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} \right)) \]

where \( R \) is the amount of defocus and to spherical aberration.
\[ \psi_I(h,k) = \psi_R(h,k) \exp\left(i \frac{\pi}{2} \lambda^3 C_S u^4 \right) \]
\[ = \psi_R(h,k) \exp\left(i \frac{\pi}{2} \lambda^3 C_S \left(\frac{b^2}{a^2} + \frac{k^2}{b^2}\right)^2 \right) \]

where \( C_S \) is the spherical aberration coefficient applied to the diffracted beams that contribute to the image. Once the amplitudes and phases of all the diffracted beams have been calculated for a particular thickness, a series of corrections corresponding to different degrees of underfocus can be applied and the images can be obtained with little additional computation.

The effect of chromatic aberration is determined by averaging the intensity of the image over a range of defocus (not the amplitudes since electrons of different energies will not interfere coherently) (Fejes, 1973).

In practice it is possible to perform one multislice calculation for a thick crystal and to punch out the amplitudes and the phases of the diffracted beams at selected intermediate thicknesses. These can be input to DEFECT and images calculated without the need for repeating the multislice calculations.

The final image is then displayed either on a line-printer with overprinting or on a graphics terminal. The output of the program includes an overprinted
image of the projected potential, an alphanumeric
phase map (showing areas of maximum phase change),
a convolution test, a normalization parameter, inte-
grated intensities and the calculated images at different
values of defocus. Plots of amplitudes and phases
of diffracted beams versus crystal thickness can also
be obtained.

RESULTS OF CALCULATIONS

1. \[ \langle 211 \rangle_F = \langle 100 \rangle_7 \] Images
   
   a. Iota (Pr\(_7\)O\(_{12}\)). The differences in potential
distribution of this phase and of the parent fluorite struc-
ture arise because of the presence of anion vacancies (V)
and the attendant dilation of the cations of the VM\(_4\)
coordination tetrahedra. These two effects result in a
significant (though not major) decrease in electrostatic
potential in the vicinity of an anion vacancy. If, there-
fore, a lattice image reproduces the variations of
potential across a unit cell, one could hope to see
evidence of these "vacancies." Figure 1 shows pro-
jections of the ideal atom positions of Pr\(_7\)O\(_{12}\) when
viewed down the \([111]_F\) and \([211]_F\) axes. An MO\(_8\)
coordination cube is also outlined in each case to facilitate interpretation of the geometry.

Two series of calculated n-beam lattice images are shown in Figure 2; variation of the images with defect of focus is shown across and variation with thickness down the figure. The conditions used to calculate these images were: number of beams = 300; aperture radius = 0.263Å⁻¹; spherical aberration constant = 1.8 mm; depth of focus = 250.0Å. In both cases the origin is situated at the top left-hand corner of the figure with two of the axes (a ≡ b ≡ c) along the edges of the figure. In each case a six-coordinate cation is located at the origin.

A number of comments can be made about these calculated images. For example, there are two general types of recurrent images—one with an array of spots which is similar to the arrangement of vacancies, the other in which the arrangement of spots is similar to the arrangement of six-coordinate cations. The former image type is observed only in very thin crystals (less than 100Å for ionic scattering factors and less than 75Å for atomic scattering factors). In some cases the
spot arrangement corresponds directly to that of the vacancies, whereas in others the spots are displaced from the vacancy positions by a shift of $a/2$ along either of the axes. The true images are delineated in Figure II where it can be seem that as the thickness of the crystal increases the defocal range over which the true image is observed steadily decreases. In an experimental situation there would be no way of deciding whether an image of this type was real or whether the origin was shifted. It is interesting to note that this image, unlike those of many of the block structures, does not repeat with thickness.

The second type of image generally has one spot per unit cell located at the origin provided the under-focus is close to 900Å. This spot can therefore be regarded as representing a six-coordinated cation. There is no obvious correlation between projected potential and this particular image, and, since these images are observed in thicker crystals it is doubtful whether they are valid lattice images in the conventional sense. However, images such as these seem
to be as potentially useful in interpreting this system as conventional thin-crystal lattice images would be. In cases where the defect of focus is not close to -900Å the spots often shift, again by a/2 along one of the axes.

Figure 3 shows plots of amplitudes and phases of three beams--one the direct beam, another a subcell reflection and the third a supercell reflection. The figure shows that the amplitudes of the diffracted beams are essentially out of phase with the direct beam, which is to be expected, but that the phases are uncorrelated. Also evident in the figure is the variation in extinction distance with scattering factor--from 200Å (peak-to-peak) for ionic f's to 133Å for atomic f's. It seems that the nature of the lattice images can be correlated with the extinction distance--that a true lattice image showing anion vacancies is observed in thicknesses up to that of the first extinction contour (Region A in Figure 3), that no interpretable image is seen in samples with thicknesses corresponding to region B in Figure 3, and that beyond that thickness lattice images showing six-coordinated cation are observed.
It is interesting that the extinction distance is so dependent on ionicity. Anstis, Lynch, Moodie and O'Keefe (1973) have previously refined the ionicity of W in W₄Nb₂₆O₇₇ to W⁺⁰·⁶, basing the refinement on diffracted intensities. It now seems that a fairly direct measure can be obtained by measuring the extinction thickness and comparing it to calculated values—for shear-plane structures (in which planar faults are relatively common) this could be a relatively easy method of determining form-factors of constituent atoms.

b. Zr₃Sc⁴O₁₂. This phase is isostructural with Pr₇O₁₂ and hence any difference in the images would be largely due to the different form-factors of the cations. The results in Figure 4 were calculated using atomic scattering factors. It can be seen that the features in this figure are qualitatively very similar to those of Pr₇O₁₂, the chief difference being in the greater extinction thickness for Zr₃Sc⁴O₁₂ which results from the low scattering factor of scandium. One consequence of the increased extinction thickness is that the thickness region, over which any image-type is identifiable, is extended. The calculated lattice images also show how the true
anion vacancy image fades out as an equivalent array
(with an origin shift of $b/2$) appears.

2. $\langle 111 \rangle$, Images of Pr$_7$O$_{12}$

In general these calculated images (Figure 5) usually show one spot per unit cell as before. However, the images suffer from the same problem as those from a $\langle 100 \rangle$, zone—that there are two arrays of spots both of which correlate with the iota phase structure. The first image type has spots located over the columns of six-coordinated cations and anion vacancies, the second type has an identical array but shifted by $b/2 + c/2$ to the center of the projected unit cell. With any real image it would not be possible to determine which array was being observed. However, in many cases this would not raise an insuperable barrier to intuitive interpretation of an image.

3. Calculated Images of Other Structures

A series of more familiar images are shown in Figure 6 for comparison with previously observed and calculated images. These structures cover a variety of space groups and demonstrate the versatility of the FCOEFF-DEFECT combination.
4. **Observed Lattice Images**

a. \(\langle 100 \rangle_7\) Images of \(M_7O_{12}\) Phases. All observed images of \(Pr_7O_{12}\) exhibit only one spot per unit cell, so that in no case was a crystal thin enough for observation of anion vacancies imaged. Since this phase is highly isotropic and since its cleavage is conchoidal it is quite likely that edges were never thinner than 100 Å. Most images show only circular spots although a few thicker specimens showed either elliptical spots or streaking. Images showing these features are presented in Figure 7 along with a very-thin-crystal lattice image of \(Zr_3Sc_4O_{12}\) which shows the two spots per unit cell with the same arrangement as the vacancy array.

b. \(\langle 111 \rangle_F = \langle 111 \rangle_7\) Images. These images (Figure 8) are quite comparable to the calculated images. There seems to be no reason why the white spots should not be directly interpreted in terms of columns of six-coordinated cations and anion vacancies, since, even though the actual columns may be shifted by \(b/2 + c/2\) from the white spots. In Figure 8(b), two twin orientations of \(Zr_3Sc_4O_{12}\) are shown, their
orientations are exactly as expected from the diffraction pattern. In the center there is a region of overlap of the two phases.

Figure 8(c) shows a direct interpretation of this overlay image which, interestingly enough, is the only possible way that these two twin orientations can overlay; i.e., regardless of choice of origin of either twin the same epitorial relationship holds--this results in columns of six-coordinated cations continuous through both twins surrounded by a hexagonal array of columns that penetrate only one twin. It should be noted that the thickness of the twin on the right is very much less than that of the left-hand twin.

CONCLUSIONS

Comparison of observed and calculated images of Pr$_7$O$_{12}$ and Zr$_3$Sc$_4$O$_{12}$ has shown that the technique of lattice imaging may be successfully applied to fluorite oxides provided certain limitations are appreciated. The usefulness of lattice image calculations with the programs FCOEFF and DEFECT has been demonstrated and copies of these programs are available from the
authors. The apparent correlation between structure and lattice images in these phases of known structure leads us to attempt to interpret lattice images of phases of unknown structure. These results will be presented elsewhere.

ACKNOWLEDGEMENT. We appreciate helpful discussions with J. M. Cowley. S. Iijima generously provided observed lattice images for Figure 6. We are grateful to K. H. Lau who grew the PrO₂ single crystals from which the specimens of Pr₇O₁₂ were prepared.
REFERENCES


New York, pp. 565-634.


FIGURE CAPTIONS

Fig. 1  Projections of the ideal atom positions of Pr$_7$O$_{12}$ down a) the [111]$_F$ axis and b) the [211]$_F$ axis. MO$_8$ cubes are also outlined to facilitate interpretation.

Fig. 2  Calculated n-beam lattice images for the $\langle 100 \rangle_7$ zone of Pr$_7$O$_{12}$ as functions of sample thickness ($H$) and defocus ($\varepsilon$). Calculations were made with atomic scattering factors in a) and ionic scattering factors in b).

Fig. 3  Plots of intensities and relative phases of a number of beams in a $\langle 100 \rangle_7$ zone as a function of crystal thickness; a) and b) were calculated with atomic scattering factors, c) and d) with ionic scattering factors. 000 is the direct beam, 132 a subcell reflection and 100 a supercell reflection.

Fig. 4  a) Calculated $\langle 100 \rangle_7$ lattice images for Zr$_3$Sc$_4$O$_{12}$ as functions of sample thickness ($H$) and defocus of focus ($\varepsilon$). b) Calculated intensities and phases of several diffracted
beams from the \langle 100 \rangle_7 zone as a function of crystal thickness.

Fig. 5 Calculated \langle 111 \rangle_7 lattice images of Pr\textsubscript{7}O\textsubscript{12} showing variation with crystal thickness (H) and defect of focus (\varepsilon).

Fig. 6 Experimental and computed lattice images of some ReO\textsubscript{3}-based superstructures: a) H-Nb\textsubscript{2}O\textsubscript{5}, b) TiNb\textsubscript{2}4O\textsubscript{6}2, c) Ti\textsubscript{2}Nb\textsubscript{1}0O\textsubscript{2}9 and d) GeNb\textsubscript{9}O\textsubscript{2}5. The experimental images were kindly supplied by S. Iijima. Calculated images were generally made for crystals about 50\,Å thick using 100 beams.

Fig. 7 Observed \langle 100 \rangle_7 lattice images of Pr\textsubscript{7}O\textsubscript{12} and Zr\textsubscript{3}Sc\textsubscript{4}O\textsubscript{12}: a) typical image of Pr\textsubscript{7}O\textsubscript{12}, b) thick-crystal image of Pr\textsubscript{7}O\textsubscript{12} and c) thin-crystal image of Zr\textsubscript{3}Sc\textsubscript{4}O\textsubscript{12} showing vacancy arrangement.

Fig. 8 Observed \langle 111 \rangle_7 images of Pr\textsubscript{7}O\textsubscript{12} and Zr\textsubscript{3}Sc\textsubscript{4}O\textsubscript{12}: a) typical image, b) two twin orientations of Zr\textsubscript{3}Sc\textsubscript{4}O\textsubscript{12} separated by a region of overlay and c) diagrammatic representation of the overlay region in b).
Fig. 1. Projections of the ideal atom positions of Pr$_7$O$_{12}$ down a) the [111]$_F$ axis and b) the [211]$_F$ axis. MO$_8$ cubes are also outlined to facilitate interpretation.
Fig. 2. Calculated n-beam lattice images for the ⟨100⟩7 zone of Pr₇O₁₂ as functions of sample thickness (H) and defocus (ε). Calculations were made with atomic scattering factors in a) and ionic scattering factors in b).
Fig. 3. Plots of intensities and relative phases of a number of beams in a (100) zone as a function of crystal thickness; a) and b) were calculated with atomic scattering factors, c) and d) with ionic scattering factors. 000 is the direct beam, 132 a subcell reflection and 100 a supercell reflection.
Fig. 4. a) Calculated \langle 100 \rangle _7 lattice images for Zr₁Sc₄O₁₂ as functions of sample thickness (H) and defect of focus (e). b) Calculated intensities and phases of several diffracted beams from the \langle 100 \rangle _7 zone as a function of crystal thickness.
Fig. 5. Calculated $\langle 111 \rangle_7$ lattice images of Pr-O$_{12}$ showing variation with crystal thickness ($H$) and defect of focus ($\epsilon$).
Fig. 6. Experimental and computed lattice images of some ReO$_3$-based superstructures: a) H-Nb$_2$O$_5$, b) TiNb$_{24}$O$_{62}$, c) Ti$_2$Nb$_{17}$O$_{29}$ and d) GeNb$_9$O$_{25}$. The experimental images were kindly supplied by S. Iijima. Calculated images were generally made for crystals about 50Å thick using 100 beams.
Fig. 7. Observed (100)$_7$ lattice images of Pr$_7$O$_{12}$ and Zr$_3$Sc$_4$O$_{12}$: a) typical image of Pr$_7$O$_{12}$, b) thick-crystal image of Pr$_7$O$_{12}$ and c) thin-crystal image of Zr$_3$Sc$_4$O$_{12}$ showing vacancy arrangement.
Fig 8. Observed (111) images of Pr$_7$O$_3$ and Zr$_3$Sc$_4$O$_{12}$: a) typical image, b) two twin orientations of Zr$_3$Sc$_4$O$_{12}$ separated by a region of overlay.
Fig. 8(c). Diagrammatic representation of the overlay region in b).
HIGH RESOLUTION LATTICE IMAGES
OF
ORDERED PHASES IN THE
PRASEODYMIUM OXIDE SYSTEM*

by

E. Summerville** and LeRoy Eyring†
Department of Chemistry
Arizona State University
Tempe, Arizona 85281

*Work supported by the United States Energy Research
and Development Administration.

**Present address: School of Physical Sciences, Flinders
University of South Australia, Bedford
Park 5042, South Australia

†Author to whom inquiries should be addressed.
ABSTRACT

Lattice images of three of the ordered phases in praseodymium oxide (Pr$_7$O$_{16}$, Pr$_{40}$O$_{72}$ and Pr$_{24}$O$_{44}$) are presented. A structural model for Pr$_{24}$O$_{44}$ is developed which involves chemical twinning of a primitive triclinic unit cell (Pr$_{12}$O$_{22}$) in either of two possible ways, resulting in two possible polymorphs. Lattice images of the beta phase are compared with calculated images of one of the possible polymorphs and diffraction effects from this polymorph are shown to be compatible with those observed from the beta phase. A general structural principle is suggested which may relate all intermediate phases in the binary rare earth oxide systems.
INTRODUCTION

In a previous article\(^1\) it was shown that under a wide
variety of conditions it was possible to obtain lattice images
of a fluorite-related phase and to interpret these images
directly in structural terms. While direct interpretation
of such images is not yet as unambiguous as in some other
systems (i.e., ReO\(_3\)-related block structures) it was
decided to attempt to use this technique to study the crystal
chemistry of the rest of the \(R_n O_{2n-2}\) homologous series
of intermediate oxide phases. Here lattice images of
three of the remaining intermediate phases of the praseodymium oxide system—the beta (\(Pr_{12}O_{22}\)), epsilon (\(Pr_{10}O_{18}\))
and zeta (\(Pr_9O_{16}\)) phases are presented and interpreted.

The unit cells of these phases have been described by
Kunzmann and Eyring\(^2\) and a structural model proposed
which would apply to the zeta phase. This principle also
appears to be operative in the structure of the \(\psi\) phase
\(Ca_2Hf_7O_{16}\) reported by Allpress, Rossell and Scott (1974)\(^3\)
and it will be shown in this paper that it may also apply
in the even-membered phases of the rare earth oxide systems.
EXPERIMENTAL PART

All relevant experimental techniques have been described previously.¹

RESULTS AND DISCUSSION

Beta Phase (Pr₁₂O₂₃).--The most convenient (though nonreduced) unit cell of this phase has been described⁴ as being monoclinic, space group P2₁/n and having axial relationships equivalent to

\[
\begin{align*}
\mathbf{a} &= a_1 + \frac{2}{3}a_2 - \frac{1}{3}a_3, \\
\mathbf{b} &= +\frac{3}{2}a_2 + \frac{3}{2}a_3, \\
\mathbf{c} &= -2a_2 + 2a_3
\end{align*}
\]

and these axial relationships will be retained in this discussion. The systematic absences of this space group are:

\[
\begin{align*}
0k0 & \quad k = 2n+1 \quad 2_1 \text{-axis} \\
h0l & \quad h+1 = 2n+1 \quad n \text{-glide}
\end{align*}
\]

The existence of the screw-axis cannot be verified by electron diffraction because of dynamical diffraction effects. However, the existence of the glide plane would be evident in an \langle 010 \rangle_{12} diffraction pattern. Examination of many \langle 010 \rangle_{12} diffraction patterns showed absences resulting from the glide plane occurred
in some instances, however, in many other cases sharp, very weak reflections were present. These additional reflections could have resulted from the presence of a very small proportion of a twin orientation or they may indicate that the glide plane is only approximate.

Reexamination of the single-crystal X-ray data referred to by Kunzmann and Eyring (1975)2 showed the occurrence of many more absences of the form

\[ h + \frac{k}{3} + 1 = 2n + 1. \]

About 72% of 360 such reflections were absent and only about 12 were of moderate intensity. These absences are important for two reasons: 1) when \( k = 0 \) the rule predicts the same absences as would result from an \( n \)-glide, and 2) if the rule were strictly obeyed it would indicate that the unit cell would be "one-third body-centered along the \( \bar{b} \)-axis." Consequently, if the unit cell is subdivided into three units such that for each \( \bar{a} = a_\beta \), \( \bar{b} = \frac{2}{3} b_\beta \), \( \bar{c} = c_\beta \), these units would be body-centered. As can be seen from Figure 1, in the ideal beta phase unit cell (i.e., ignoring the existence of anion vacancies) each of these
units is body-centered. This raises the possibility that the "systemmatic absences," attributed to the n-glide, are accidental "absences" resulting from the high pseudosymmetry of the fluorite subcell. Since the ideal beta phase cell has both the n-glide and the twofold screw-axis, and since it is appropriately one-third body-centered, the observed set of absences would result if these symmetry elements are not significantly destroyed during the ordering process. If this is the case the absences imply nothing about the time space group of this phase.

Figures 2 and 3 show \((100)_{12} \langle 211 \rangle_F\) images of the beta phase from a number of crystals of undetermined thickness. Despite the variation in the images, it appears that they can be described as variations upon two fundamental themes, both of which can be interpreted directly in structural terms. Each theme represents a structural model involving octahedral cations (the term octahedral cation will hereafter be used as an abbreviation for "octahedrally coordinated metal atom;" the terms cation and anion are used for convenience and imply nothing about the changes on
these atomic species) and each model may produce images which represent either the array of octahedral cations or the array of anion vacancies. The spot arrays corresponding to both of these models are shown in Figure 4. The structure illustrated in Figure 4(a) belongs to space group Pm and that in Figure 4(b) to space group P1, however, despite the apparent contradiction between the observed space group of beta and those of these models, the lattice images suggest that these structures may be those of the beta "phase." It is also important that the projection symmetry is always P1 or Pm, results that are compatible with the proposed models but not with any structure in space group P21/n. It therefore appears that the beta phase may be dimorphic, that some unit cells may be monoclinic (space group Pm) and that others are triclinic (space group P1).

The structure of the phase shown in Figure 4(b) has been studied in some detail. It consists of octahedral cations located at the origin and at \( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \). The anion vacancies are arranged as shown and occur
across the body diagonal of an MO₈ cube (as in iota).
The vectors from the octahedral cations on all four of
the origins at the bottom of the figure to the octahedral
cation at \( \frac{1}{8}, \frac{1}{6}, \frac{1}{3} \) are all \( \frac{2}{8}[211]_F \) vectors. Thus the
unit cell can be divided into two halves, each of which
is an \( n = 12 \) version of the odd-membered series
described by Kunzmann and Eyring. Alternatively,
if the precise locations of the anion vacancies are
ignored, the true unit cell can be obtained by chemically
twinning the \( n = 12 \) unit cell defined above about the
(110)\(_F\). Yet another description of this structure is
that it consists of slabs of fluorite (PrO₂) alternating
with slabs which are structurally closely related to
iota (Pr₇O₁₂), the slabs being arranged perpendicular
to a \([110]_F\) axis (the \( b \)-axis of the beta phase).

The second proposed model, Figure 4(a), is
structurally very similar. It consists of octahedral
cations at the origin and at \( \frac{1}{8}, \frac{1}{6}, \frac{1}{3} \). The anion vacancies
again occur across the body diagonal of an MO₈ cube and
again the vectors from all four left-hand origins to the
\( \frac{1}{8}, \frac{1}{6}, \frac{1}{3} \) site are all \( \frac{2}{8}[211]_F \) vectors. Furthermore,
the structure can again be described in terms of chemical twinning (literally in this case) of an \( n = 12 \) triclinic unit cell, or as slabs of iota-like material separated by slabs of fluorite, but in this latter case the slabs are perpendicular to a \([110]_F\) axis which is now the \( c\)-axis of beta. The axial relationships of these two \( n = 12 \) triclinic cells and of the \( n = 24 \) "monoclinic" cell are given in Table I.

A lattice image from a \( \langle 010 \rangle_I \) (\( \equiv \langle 110 \rangle_F \)) zone of beta is shown in Figure 5(a). The spot array corresponds precisely to the projection of the octahedral cation sites of the \( P_1 \) structure down this direction as shown in Figure 5(b). The projection symmetry of this image is \( P_2 \) which places very little restriction on the possible space group of the unit cell.

In order to test the acceptability of the proposed \( P_1 \) model, it was decided to predict atomic positions by comparison with \( Pr_7O_{12} \) and then calculate the diffraction pattern, and lattice images of the structure using the programs FCOEFF and DEFECT written by A. J. Skarnulis. To do this a transformation matrix was derived to convert iota-phase cation positions to
those of beta. This matrix was then applied to each of the six seven-coordinated cations surrounding every vacancy pair. These seven-coordinated cations are indicated in Figure 4. Anion positions were unaltered since their positions in iota probably do not correlate well with their positions in beta (due to the absence of strings of six-coordinated cations in the latter structure). Proposed vacancy sites were of course left vacant. The resulting parameters (Table II) when input to FCOEFF and DEFECT produced the results shown in Figure 6 and Table III.

It can be seen that there is a reasonable correlation between the observed and some of the calculated images. The diffraction pattern shows "absences" consistent with one-third body-centering (and also of an n-glide) despite the fact that the unit-cell and atomic positions have no symmetry. This effect is partly due to the fact that twelve of the cations and the forty-four anions are still on normal fluorite sites, but twelve cations have been significantly shifted and four anions have been removed without producing diffraction effects.
in gross disagreement with the observed pattern.
Provided the real shifts of the remaining atoms are small, it seems quite possible that this structure could completely satisfy the diffraction pattern of the beta phase.

A very similar structure to the above Pl structure but with the anion vacancies near $\frac{1}{2}, \frac{1}{4}, \frac{1}{2}$ rotated 180° about an axis parallel to the $b$-axis has Pn symmetry. However images calculated for this model show almost no correlation with the observed images.

Any disagreement between observed and calculated images can be readily rationalized as resulting from inaccuracies in the predicted atomic positions. Not only are many atoms on ideal fluorite sites but those shifts which have been made to atomic positions are unlikely to be correct even if the models are correct. In particular the atom shifts along the $c$-axis which should have been made to Pl model are probably greater than those which were derived from the iota phase structure because the vacancy planes are further apart in beta than in iota. It could similarly be predicted that the atom shifts along the $b$-axis in the Pm model would be
greater than those derived from the iota structure. No calculations have been performed utilizing these larger shifts because it is quite obvious that with so many variables it would be possible to obtain any desired result without the model necessarily being correct. In other words, with no knowledge of real atom positions within the unit cell, structure refinement of the type suggested above is probably no more reliable than direct interpretation of the images in structural terms. No calculations have as yet been performed on the Pm model of beta.

On the Possibility of Disorder in Beta (Pr₁₂O₂₂).

Since beta is effectively the end member of the homologous series of ordered phases, it seems reasonable to conclude that the ordering forces decrease as the composition increases towards beta. In terms of the above structural principle this is tantamount to stating that the farther apart the planes of six-coordinated cations are the smaller their interaction will be. If this is so then beta should be substantially less-ordered than the other homologues. However, if the ordering forces in this phase are weak there will be no great tendency for defects to agglomerate
into complete columns or planes as in the block structures and defects may only be evidenced by slight contrast changes in the electron micrographs. Such changes are apparent in most images of beta, but Figure 7 shows two well-defined cases of stacking faults in this phase. In both cases there appears to be a shift in the positions of the six-coordinated cations along the b-axis, but by different amounts.

One other defect is shown in Figure 8 which is not interpretable in terms of the origins of the unit cells. There is some indication that both polymorphs are imaged in this crystal and that the outlined boundary separates domains of each of these polymorphs.

If the proposed model of beta and the postulated disorder are real then the lack of success in refining the X-ray data is to be expected. Apart from conventional problems of mechanical twinning and multiple nucleation, the above forms of disorder would result in crystallites whose diffraction patterns would completely overlay those of each other.

The Zeta (Pr$_9$O$_{14}$) and Epsilon (Pr$_{10}$O$_{18}$) Phases.

Lattice images of these phases are shown in Figure 9.
Those of epsilon are again variable, in one case the image appears to be interpretable, in part, in terms of anion vacancies, in the other case interpretation appears impossible. As in the beta phase, it appears that epsilon has a zig-zag array of octahedral cations related by \( \langle 211 \rangle_F \) axes, although not all of the vacancies within the unit cell can be located.

The image of zeta appears to be completely compatible with the proposed structural model.\(^2\) However, there is an almost identical array of anion vacancies to the proposed structure in which the vacancies are arranged along a \([111]\)_\(F\) axis included at 84.4° to the \((135)\)_\(F\) plane instead of being at 73.0° as in iota. These two structures are shown in Figure 10. The observed lattice image corresponds to the structure in Figure 10(b) projected down the a-axis, so that the correct structure is that derived directly from iota with the vacancy \([111]\)_\(F\) axis inclined at 73.0° to the \((135)\)_\(F\) plane. It is interesting that the other structure is not favored, even though it not only has the \((135)\)_\(F\) planes of octahedral cations but also the \([111]\)_\(F\) strings of six-coordinated cations and anion vacancies, as in iota. The
lattice image unambiguously indicates the existence of the structure with (135)$_F$ planes identical to those of iota.

Similarly there are two possible structures for the delta phase, the proposed one which is derived directly from iota and another with the vacancy-pairs inclined at 84.4° to the b-face of the unit cell. These structures appear in Figure 11 and it can be seen that the vacancy arrays in Figure 11(b) correspond most closely to the observed image. This is not the structure derived directly from the iota phase and described by Kunzmann and Eyring. However, it is not known whether this slight structural change has really occurred or whether lattice relaxations have been sufficient to shift the "vacancies" from their ideal sites to their observed positions in the lattice images. The increasing resolution of the vacancies, going from iota to zeta to delta is clearly noticeable in the images. This may be due in part to increasing lattice relaxation as the planes of six-coordinated cations get further apart and in part to diffraction effects from the nonequivalent structures.
CONCLUSIONS

On the basis of the proposed structures for the intermediate phases in the praseodymium oxide system it seems possible to extend the structural model proposed by Kunzmann and Eyring. In each of the odd-membered phases one set of $[135]_F$ type planes of cations has every nth plane composed entirely of six-coordinated cations. This plane contains the two $\langle 211\rangle_F$ a- and c- axes (e.g., $[135]_F$ contains $[1\bar{2}1]_F$ and $[21\bar{1}]_F$).

To be specific, in zeta ($\text{Mg}_9\text{O}_{16}$) every ninth $(135)_F$ plane of cations consists only of six-coordinated cations, in delta the same is true of every eleventh $(135)_F$ plane. The same principle apparently applies to the even-membered phases, however, the $(135)_F$ planes are puckered so that on average the six-coordinated cations lie on planes parallel to $(110)_F$. Again to be more specific, in the case of beta there are alternate segments of $(135)_F$ and $(5\bar{3}1)_F$ planes of six-coordinated cations which make up the b-face of the "monoclinic" unit cell. These average out to be the $(101)_F$ plane.
The structure of the low temperature zeta phase is important because, of the two possible structures, one not only had the (135)\textsubscript{F} planes of six-coordinated cations but also the [111]\textsubscript{F} strings of six-coordinated cations and anion vacancies. However, the latter is not the structure observed implying that such strings have no real crystallographic significance.

While the above appears to be a consistent, coherent description of the crystallography of much of the praseodymium oxide system, verification from structure refinement of intensity data will be required for definite proof.
REFERENCES


TABLE I
Axial Relationships for the Real and Primitive Unit-Cells of Beta (Pr$_{24}$O$_{44}$)

<table>
<thead>
<tr>
<th></th>
<th>&quot;Monoclinic&quot;(n=24)</th>
<th>P1(n=12)</th>
<th>Pm(n=12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}aF$</td>
<td>$\frac{1}{2}bF$</td>
<td>$\frac{1}{2}cF$</td>
<td>$\frac{1}{2}aF$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>0</td>
<td>3</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>4</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>
TABLE II

Atom Positions for the P1 Model of Beta ($Pr_{1.2}O_{2.2}$)

<table>
<thead>
<tr>
<th>Pr No.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Pr No.</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>13.</td>
<td>0.500</td>
<td>0.500</td>
<td>0.000</td>
</tr>
<tr>
<td>2.</td>
<td>0.969</td>
<td>0.996</td>
<td>0.234</td>
<td>14.</td>
<td>0.500</td>
<td>0.500</td>
<td>0.750</td>
</tr>
<tr>
<td>3.</td>
<td>0.978</td>
<td>0.993</td>
<td>0.505</td>
<td>15.</td>
<td>0.490</td>
<td>0.518</td>
<td>0.500</td>
</tr>
<tr>
<td>4.</td>
<td>0.000</td>
<td>0.000</td>
<td>0.750</td>
<td>16.</td>
<td>0.500</td>
<td>0.500</td>
<td>0.250</td>
</tr>
<tr>
<td>5.</td>
<td>0.522</td>
<td>0.174</td>
<td>0.995</td>
<td>17.</td>
<td>0.010</td>
<td>0.648</td>
<td>0.000</td>
</tr>
<tr>
<td>6.</td>
<td>0.500</td>
<td>0.167</td>
<td>0.750</td>
<td>18.</td>
<td>0.000</td>
<td>0.667</td>
<td>0.250</td>
</tr>
<tr>
<td>7.</td>
<td>0.500</td>
<td>0.167</td>
<td>0.500</td>
<td>19.</td>
<td>0.000</td>
<td>0.667</td>
<td>0.500</td>
</tr>
<tr>
<td>8.</td>
<td>0.531</td>
<td>0.171</td>
<td>0.266</td>
<td>20.</td>
<td>0.000</td>
<td>0.667</td>
<td>0.750</td>
</tr>
<tr>
<td>9.</td>
<td>0.990</td>
<td>0.351</td>
<td>0.000</td>
<td>21.</td>
<td>0.478</td>
<td>0.826</td>
<td>0.005</td>
</tr>
<tr>
<td>10.</td>
<td>0.000</td>
<td>0.333</td>
<td>0.250</td>
<td>22.</td>
<td>0.469</td>
<td>0.829</td>
<td>0.734</td>
</tr>
<tr>
<td>11.</td>
<td>0.022</td>
<td>0.341</td>
<td>0.495</td>
<td>23.</td>
<td>0.510</td>
<td>0.815</td>
<td>0.500</td>
</tr>
<tr>
<td>12.</td>
<td>0.031</td>
<td>0.338</td>
<td>0.766</td>
<td>24.</td>
<td>0.500</td>
<td>0.833</td>
<td>0.250</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vacancy No.</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.250</td>
<td>0.167</td>
<td>0.063</td>
</tr>
<tr>
<td>2.</td>
<td>0.250</td>
<td>0.000</td>
<td>0.438</td>
</tr>
<tr>
<td>3.</td>
<td>0.750</td>
<td>0.833</td>
<td>0.938</td>
</tr>
<tr>
<td>4.</td>
<td>0.750</td>
<td>0.333</td>
<td>0.563</td>
</tr>
</tbody>
</table>

Anion positions used were all ideal fluorite positions
### TABLE III

Calculated Diffraction Pattern for the P1 Model of Beta
\((\Pr_{1.2}O_{2.2})\) \(\langle 100\rangle_{1.2}\) Zone

<table>
<thead>
<tr>
<th>&quot;Absences&quot;</th>
<th>Reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>hkl</strong></td>
<td><strong>F^2</strong></td>
</tr>
<tr>
<td>001</td>
<td>.003*</td>
</tr>
<tr>
<td>003</td>
<td>.024*</td>
</tr>
<tr>
<td>030</td>
<td>.034†</td>
</tr>
<tr>
<td>032</td>
<td>.013†</td>
</tr>
<tr>
<td>034</td>
<td>.035†</td>
</tr>
<tr>
<td>061</td>
<td>.155†</td>
</tr>
<tr>
<td>063</td>
<td>.246†</td>
</tr>
</tbody>
</table>

\(\langle 010\rangle_{1.2}\) Zone

<table>
<thead>
<tr>
<th>&quot;Absences&quot;*</th>
<th>Reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>hkl</strong></td>
<td><strong>F^2</strong></td>
</tr>
<tr>
<td>001</td>
<td>.003</td>
</tr>
<tr>
<td>003</td>
<td>.024</td>
</tr>
<tr>
<td>005</td>
<td>.043</td>
</tr>
<tr>
<td>100</td>
<td>.000</td>
</tr>
<tr>
<td>102</td>
<td>.009</td>
</tr>
<tr>
<td>104</td>
<td>.023</td>
</tr>
<tr>
<td>106</td>
<td>.031</td>
</tr>
<tr>
<td>201</td>
<td>.002</td>
</tr>
<tr>
<td>203</td>
<td>.010</td>
</tr>
<tr>
<td>205</td>
<td>.016</td>
</tr>
</tbody>
</table>

*Expected from an n-glide or one-third body centering.
†Expected only from one-third body centering.
FIGURE LEGENDS

1. Ideal atom positions of beta projected down the $a$-axis ($[211]_F$).

2. $<100>_1 \bar{2}$ lattice images of beta.

3. Lattice images of beta from a $<100>_1 \bar{2} \equiv <211>_F$ zone.

4. Diagrammatic representations of the proposed structures of the beta phase. (a) Model with symmetry $Pm$. (b) Model with symmetry $P1$.

5. (a) $<010>_1 \bar{2}$ lattice image of beta. (b) Diagram of the arrangement of octahedral cations corresponding to the lattice image in Figure 5(a).

6. Calculated $<100>_1 \bar{2}$ lattice images of the $P1$ model of the beta phase.

7. Lattice image of beta from a $<100>_1 \bar{2}$ zone showing apparent stacking faults.

8. Lattice images from $<100>_1 \bar{2}$ showing image variations which may correspond to domains of each of the proposed polymorphs of beta.

9. (a) Lattice image from a $<100>_1 0$ zone of
epsilon. (b) \((211)_F\) lattice images of the zeta phase.

10. The possible structures of zeta \((\text{Pr}_9\text{O}_{16})\) projected down \([211]_F\).

11. The possible structures of delta \((\text{Pr}_{11}\text{O}_{20})\) projected down \([211]_F\).
Fig. 1. Ideal atom positions of beta projected down the $a$-axis ([211]$_F$).
Fig. 2. $\langle 100 \rangle_1$ lattice images of beta.
Fig. 3. Lattice images of beta from a $\langle 100 \rangle_{12} \equiv \langle 211 \rangle_F$ zone.
Fig. 4. Diagrammatic representations of the proposed structures of the beta phase. (a) Model with symmetry \( \text{Pm} \). (b) Model with symmetry \( \text{Pl} \).
Fig. 5. (a) \(\langle01\rangle_2\) lattice image of beta. (b) Diagram of the arrangement of octahedral cations corresponding to the lattice image in Figure 5(a).
### Fig. 6. Calculated $\langle 100 \rangle_{12}$ lattice images of the $P1$ model of the beta phase.
Fig. 7. Lattice image of beta from a $\langle 100 \rangle_{1/2}$ zone showing apparent stacking faults.
Fig. 8. Lattice image from \((100)\)_2 showing image variations which may correspond to domains of each of the proposed polymorphs of beta.
Fig. 9(a). Lattice image from a (100)$_0$ zone of epsilon.
Fig. 9(b). \(\langle 211\rangle_F\) lattice images of the zeta phase
Fig. 10. The possible structures of zeta (Pr$_9$O$_{16}$) projected down [211]$_F$.
Fig. 11. The possible structures of delta (Pr\textsubscript{1.1}O\textsubscript{2.0}) projected down [211]\textsubscript{F}. 
OBSERVATIONS OF PHASE TRANSFORMATIONS,
INTERGROWTH AND DISORDER IN BINARY
AND PSEUDOBINARY.
M₂O₃-MO₂ (FLUORITE) SYSTEMS*

E. Summerville** and LeRoy Eyring†
Department of Chemistry
Arizona State University
Tempe, Arizona 85281

*Work supported by the United States Energy Research
and Development Administration.

** Present address: School of Physical Sciences, Flinders
University of South Australia,
Bedford Park 5042, South Australia.

† Author to whom inquiries should be addressed.
ABSTRACT

The technique of lattice imaging has been applied to the study of disorder in the PrO$_x$ system and a number of samples in the ZrO$_2$-Sc$_2$O$_3$ system. Disorder and intergrowth in the latter system are easily interpreted from the lattice images. Observations of transformations, intergrowth and disorder in the PrO$_x$ system are much more difficult to interpret in detail but they have thrown considerable light on the nature of ordering processes in the system.
INTRODUCTION

The nature of observed and calculated images of some fluorite-related oxides and the structural principle relating member-phases of the homologous series \( \text{R}_n\text{O}_{2n-2} \) (\( n = \text{integer}, \ 7 \leq n \leq 12 \)) have been discussed in the two previous papers.\(^1\), \(^2\) The use of lattice images for studying phase transformations between homologues and samples which are either disordered or polyphasic will be discussed in this paper.

METHOD

All standard techniques have been discussed previously. Beam heating to induce phase reaction was achieved either by concentrating the beam with the second condenser current control (mild heating) or by removing the condenser aperture briefly (intense heating)

RESULTS AND DISCUSSION

A. Transformations

Under an oxygen partial presence of \( 10^{-7} \) Torr it is not surprising that all of the phases with oxygen-to-
metal ratios greater than 1.70 can be easily reduced by beam heating. In fact such reduction was more often a curse than a blessing. It was therefore a little surprising to find that in some cases samples actually oxidized when beam heated and many such cases have been well documented, with studies being done both in diffraction and imaging mode.

It now appears that this apparent oxidation is a local effect produced by pumping oxygen from a thicker, hotter part of the crystal. Presumably beam heating is greatest near an extinction contour so that this part of a crystal becomes hottest; the equilibrium oxygen pressure is therefore lowest and oxygen is pumped out to the cooler edges of the crystal. Since the edges are the regions from which both diffraction patterns and images are obtained it is only the localized oxidation which is observed, although the sample overall is undergoing reduction. One such sample (edge) was seen to undergo the following series of transformations

\[ \nu(7) \rightarrow \beta(12) \rightarrow \epsilon(10) \rightarrow \epsilon \& \beta \]

\[ \rightarrow \text{LPSS} \rightarrow \zeta(9) \rightarrow \epsilon(10) \]
(where LPSS is a long period superstructure with the spots always present as satellite-pairs, the number in parentheses is n in RₙO₂ₙ₋₂). On successive heatings the oxygen content of the crystal edge obviously fluctuated erratically, indicating that oxygen was sometimes pumped into the edge faster than it was expelled and sometimes the reverse. Following each composition change the crystal reordered.

Although the environment of the microscope is hostile to any of the higher oxides being studied these compositional changes occurred under rather more severe conditions than were generally used in these studies. However, such processes were probably occurring to some extent in all crystals examined.

Specimen behavior generally fell into two categories: those samples which showed no disorder were extremely unreactive, virtually independent of their constitution, whereas those which were initially disordered were extremely reactive. The only phase which readily reacted was beta which appeared on several occasions to reorder in the electron beam. In each such case a
(211)\textsubscript{F} zone was under observation and the superstructure reflections were replaced by a new set which was invariably a \langle 100 \rangle_1 \textsubscript{2} (still (211)\textsubscript{F}) diffraction pattern. Whether or not these samples were initially nonstoichiometric beta phase is not known, although it seems likely that they were hyperstoichiometric and that reordering occurred during reduction.

**Diffraction Effects.** -- In all cases of disorder diffuse scatter in the form of weak continuous streaking was observed along \textit{b}*. Before the diffuse scatter becomes substantial it is replaced by a set of spots corresponding to the new phase. It therefore appears that the transformations occur in two stages--the first corresponding to the introduction of a substantial degree of disorder into the host phase, the second to the formation of domains of the new phase which grow at the expense of the host phase. In view of the previous comments on the stability of ordered samples, it appears that the first stage has a large activation energy so that disordering a sample is relatively difficult. However, once this has been achieved transformation is then
relatively easy.

The streaking observed in the praseodymium oxides is characteristically continuous and diffuse although directional, implying that while the transformations are essentially planar in nature the initial stage is one of disorder in the spacing of these planes. For example, in the transformation of iota to zeta where the spacing of the \( (135)_F \) planes of six-coordinated cations has to increase from every seventh plane to every ninth, the initial stage (probably resulting from oxidation of parts of some planes of six-coordinated cations) appears to involve a random spacing of many of these planes.

In no case has the delta phase \( (\text{Pr}_1\text{O}_{20}) \) been observed in the praseodymium oxide system. Gentle reduction of beta always results in the direct formation of epsilon and oxidation of epsilon produces beta. The early stages in the transformation again result in diffuse scatter along \( b^* \) (now \( (110)_F \)) followed by the appearance of discrete reflections due to the product phase. If the structural model of these phases is correct, transformation of beta to delta could be
expected to be extremely difficult since the $(110)_F$ planes of six-coordinated cations (consisting of alternate segments of $(135)_F$ and $(531)_F$ planes) would have to be converted entirely to $(135)_F$ planes and concurrently the spacing of the planes would have to decrease appropriately. This transformation is shown in Figure 1 and it is obvious that a complete reorganization of the crystal is required. Figure 1 also shows part of the rearrangement required for reduction of beta to epsilon (not all of the six-coordinated cations are shown for epsilon) and it is obvious that this is a relatively minor structural change. It is therefore not surprising that the $(110)_F$ planes retain their integrity and that beta and epsilon are formed directly from each other without delta being an intermediary.

**Lattice Images.** --Figure 2 shows a series of images taken as epsilon reduces to iota. The initial image can be compared to those of epsilon published earlier. While the degree of disorder appears extremely high it probably is not as extensive as it appears, since in principle one stacking fault perpendicular to the beam
could completely destroy an image. Nevertheless, the sample is clearly disordered to some extent. The succeeding images show the appearance of iota in an epsilon matrix. Early in the transformation the image appears as a set of fringes which separate into discrete images of octahedral cations, eventually becoming circular spots. This rounding-off of the image of the octahedral cations is most evident in the vicinity of the planar defects where the streaks become ellipsoidal and finally circular. The orientation of the streaks appears to be directly related to the orientation of vacancies in an overlay of iota and epsilon as shown in Figure 3. The sequence of images shows the formation of twin domains of iota and a number of regions of iota in the same orientation which may have incompatible unit cell origins. These appear to be the result of multiple nucleation as do the defects where it appears that the untwinned (135)F planes of iota have nucleated with the spacing of the epsilon unit cell, a not surprising phenomenon. The resultant crystal is remarkably disordered although much of the apparent disorder could
again result from overlaying regions of iota that are either twinned or have their origins shifted in relation to each other. The planar nature of the transformation is evident despite the fact that in this transformation the octahedral cations about the (110)\textsubscript{F} planes have to reorder onto (135)\textsubscript{F} planes. Even in this case a classical nucleation and growth process, in terms of spheroidal domains of one phase growing in a matrix of the other does not appear to occur.

Figure 4 shows a series of lattice images of a beta phase sample reducing to epsilon. In any one print a variety of images can be seen, the same images appeared in all photographs although the images shifted across the sample as the reduction proceeded. It is believed that the sample contained a number of reaction fronts (as shown in Figure 5) which traversed the sample. Each image region would therefore result from an overlay of beta and epsilon and the variation in the image with time would result from the changing proportions of each phase. The planar nature of the transformation is again very apparent.

B. **Intergrowth of Phases**

Although coherent intergrowth of various homologues
could be expected, few well-defined cases were actually observed. Figure 6(a) shows one case of intergrowth of zeta with iota. Here the planes of six-coordinated cations are randomly seven or nine cation planes apart. Figure 6(b) shows another case where a domain of iota phase occurs in a crystal which is very largely C-type. This is the only case in the praseodymium oxide system in which a classical domain of one phase was observed in a matrix of another phase. This type of intergrowth probably occurs in this composition region because of the structural dissimilarity of the two phases and the fact that either phase must completely reorder to form the other phase. On the other hand, intergrowth of two phases which differ only in the spacing of planes of structural elements could be expected to retain this planarity in intergrowths, as in Figure 6(a).

Figure 7 shows a series of images from \( \langle 111 \rangle _{F} \) zone of crystals from an arc-melted sample with a composition of approximately \( \text{Zr}_{0.29} \text{Sc}_{0.71} \text{O}_{1.64} \). At this composition the sample should consist of about one-third C-type sesquioxide and two-thirds \( \text{Zr}_{3} \text{Sc}_{4} \text{O}_{12} \).
As shown in Figure 7 the sample consists of domains of C-type embedded in an iota phase matrix. The images can again be directly interpreted even in the overlay regions and regardless of the location of the domain within the sample (i.e., whether the C-type occurs superficially or internally). Figure 8(a) shows a typical diffraction pattern from such a sample with many unallowed reflections resulting from dynamical interaction of iota phase reflections with those of C-type. Figure 8(b) shows the construction of an overlay image of the two phases from their individual images. This image, like that of an overlay of the two twin orientations of iota\(^1\) is independent of choice of origin. Figure 7(b) has inverted contrast relative to Figure 7(a) due to a change of defocus and in Figure 7(c) there is a triple overlay composed of two overlapping C-type regions (whose origins are not superimposed) in a matrix of iota phase. It is interesting that even such a potentially complex image has good contrast and can be directly interpreted. Many of the images show ill-defined regions which appear to show the presence of a trace of C-type, as if incipient phase separation had resulted in a
thin layer of C-type material within the iota phase.

Probably all stages from small (100Å diameter) crystallites to single unit cells of Sc$_2$O$_3$ in a matrix of Zr$_3$Sc$_4$O$_{12}$ are present in the sample. On annealing the preceding sample at 1600°C for 28 hrs macroscopic phase separation occurred and few iota C-type boundaries were observed. Figure 9 shows one of the few observed boundaries. This image is of a $\langle 211 \rangle_F$ zone and shows Sc$_2$O$_3$ on the left, iota on the right with a diffuse, inclined boundary region separating them which results in an overlay image of iota and C-type.

In both systems studied the iota and C-type (sigma) phases show no tendency to intergrow. As mentioned above, in the ZrO$_2$-Sc$_2$O$_3$ system if the samples are given the opportunity phase separation occurs on a macroscopic scale. In the PrO$_x$ system attempts were made to produce and observe diphasic samples in this composition region. While powder X-ray patterns of these samples were always polyphasic, individual crystallites were almost invariably monophasic, usually either iota or sigma. From only two crystals of the many observed were diphasic diffraction patterns obtained.
Figure 10 shows a $<111>_P$ lattice image of a sigma-phase sample with an obvious fault. More importantly, the banded appearance perpendicular to the crystal edge is believed to result from intergrowth of two sigma-type phases. It is not yet clear whether these two phases are structurally slightly different or whether their lattice parameters differ slightly, however, this is the only case of intergrowth of two phases observed in the composition interval $\text{PrO}_{1.5} - \text{PrO}_{1.714}$. The lack of intergrowth of iota and sigma praseodymium oxides is apparent evidence of their structural dissimilarity, underlining the fact that $\text{Pr}_2\text{O}_3$ is not $n = 4$ of the homologous series $\text{R}_n\text{O}_{2n-2}$.

The fact that each $\text{PrO}_x$ crystal in this composition interval was either iota or sigma but very rarely both was extremely surprising. It seems that each crystal-lite has its own free energy surface and transforms under conditions suitable to it and that once transformation of one phase to another commences it proceeds essentially to completion. This argument would also account for the lack of intergrowth observed in other
composition regions. If the same situation applies to powder particles, this implies that the data of any tensimetric run simply reflect the overall properties of a very large number of microscopic systems, no two of which are necessarily identical. In fact it is likely that each particle's behavior is un reproducible on successive runs; but that on successive cycles the average properties of the sample are retained. This approach is comparable to the description of the properties of gases, that while the motions of no particular molecule are known or reproducible, the overall properties of a sample can be described exactly.

C. The Occurrence of Disorder in Lattice Images

Apparent disorder is probably the rule rather than the exception in lattice images. Figure 11 shows examples of disorder in Zr$_3$Sc$_4$O$_{12}$ arc-melted samples. Considering their thermal history, the occurrence of disorder in these samples is only to be expected. It appears almost certain that this disorder results from a nonuniform distribution of Zr$^{4+}$ and Sc$^{3+}$ ions which result in structural elements of adjacent phases being
included in the sample. However, since this situation is highly metastable and an artifact of the preparation technique it could obviously be removed by annealing the sample.

Several other examples of disorder in the PrO\textsubscript{x} system are presented in Figure 12. Part of this disorder is probably a result of the examination techniques. As was previously mentioned, it is both possible to reduce and oxidize different parts of the sample at the same time so there is little doubt that the observed extent of disorder is considerably greater than that of the equilibrium condition.

One recurrent problem, particularly with iota, was reduction of the surface to (probably) the sesqui-oxide. However, the resulting microstructure was so characteristic (Figure 12(b)) that its occurrence was never a source of confusion. Perhaps the most important aspect of the other defects in Figure 12 is their planar nature despite the fact that the defect planes do not extend entirely through the crystal. It is also significant that, again, the defect planes do not appear to be related directly to intergrowth of two phases. For
example, across such a defect the overall spacing of (135)ₚ planes of octahedral cations is always that of pure iota--the planes never separate to accommodate the unit cell of a larger homologue. Again, it is believed that this stage of disorder is probably a necessary prerequisite to any transformation in the system.

CONCLUSIONS

From a structural viewpoint all the data on transformations, intergrowth and disorder are quite compatible with the structural model of the homologous series presented in Section II. This study has considerably extended understanding of the structural arrangements within samples of the binary rare earth oxides and the processes of phase reaction between them. While none of the results are structurally detailed they have further proven the usefulness of lattice imaging in studies of such complex systems.
REFERENCES


FIGURE CAPTIONS

1. Diagram of the cation sublattice of a $\langle 211 \rangle_F$ zone showing the projected shifts required for the octahedrally coordinated cations as beta transforms to (a) delta and (b) epsilon (not all vacancy sites are implied in (b)).

2. Lattice images from $\langle 211 \rangle_F$ showing sequential stages in the transformation of epsilon to iota.

3. Model of the "vacancy streaks" observed in the transformation of epsilon to iota.

4. Sequential stages in the reduction of beta to epsilon as observed in $\langle 211 \rangle_F$ lattice images.

5. Model of the possible production of many image types from superposition of two basic images.

6. (a) Lattice image from $\langle 100 \rangle_9$ showing intergrowth with iota. (b) $\langle 111 \rangle_F$ lattice image showing a domain of Pr$_7$O$_{12}$ in a crystal which is largely sigma phase.

7. Domains of Sc$_2$O$_3$ in a matrix of Zr$_3$Sc$_4$O$_{12}$ as seen in $\langle 111 \rangle_F$ images.

8. (a) Diffraction pattern from a sample imaged
in Figure 7 showing double-diffraction effects.

(b) Diagram showing the structural basis of an overlay image of C-type and iota from a $\langle 111 \rangle_F$ zone.

9. Regions of C-type and iota in an annealed sample of Zr$_{0.29}$Sc$_{0.71}$O$_{1.64}$ as seen in a $\langle 211 \rangle_F$ image.

10. $\langle 111 \rangle_F$ lattice image of a sigma phase crystal showing faulting and banding due to the presence of two very similar phases.

11. Disorder evident in $\langle 111 \rangle_7$ images of Zr$_3$Sc$_4$O$_{1.2}$.

12. Examples of disorder in $\langle 211 \rangle_7$ images of Pr$_7$O$_{1.2}$. 
Fig. 1. Diagram of the cation sublattice of a $\langle 211 \rangle_F$ zone showing the projected shifts required for the octahedrally coordinated cations as beta transforms to (a) delta and (b) epsilon (not all vacancy sites are implied in (b)).
Fig. 2. Lattice images from $\langle 211 \rangle_F$ showing sequential stages in the transformation of epsilon to iota.
Fig. 2 (Cont.) Lattice images from \( \langle 211 \rangle_F \) showing sequential stages in the transformation of epsilon to iota.
Fig. 2 (Cont.) Lattice images from \( \langle 211 \rangle_F \) showing sequential stages in the transformation of epsilon to iota.
Fig. 3. Model of the "vacancy streaks" observed in the transformation of epsilon to iota.
Fig. 4. Sequential stages in the reduction of beta to epsilon as observed in $\langle 211 \rangle_F$ lattice images.
Fig. 4 (Cont.) Sequential stages in the reduction of beta to epsilon as observed in \( \langle 211 \rangle_F \) lattice images.
Fig. 4 (Cont.) Sequential stages in the reduction of beta to epsilon as observed in (211)\textsubscript{F} lattice images.
Fig. 4 (Cont.) Sequential stages in the reduction of beta to epsilon as observed in $\langle 211 \rangle_F$ lattice images.
Fig. 5. Model of the possible production of many image types from superposition of two basic images.
Fig. 6. (a) Lattice image from $\langle 100 \rangle$ showing intergrowth with iota. (b) $\langle 111 \rangle_F$ lattice image showing a domain of Pr-O$_{12}$ in a crystal which is largely sigma phase.
Fig. 7. Domains of Sc₂O₃ in a matrix of Zr₃Sc₄O₁₂ as seen in (111)_F images.
Fig. 7 (Cont.) Domains of $\text{Sc}_2\text{O}_3$ in a matrix of $\text{Zr}_3\text{Sc}_4\text{O}_{12}$ as seen in $\langle 111 \rangle_F$ images.
Fig. 7 (Cont.) Domains of Sc₂O₃ in a matrix of Zr₃Sc₄O₁₂ as seen in ⟨111⟩ₚ images.
Fig. 7 (Cont.) Domains of Sc$_2$O$_3$ in a matrix of Zr$_3$Sc$_4$O$_{12}$ as seen in $<111>_F$ images.
Fig. 8(a) Diffraction pattern from a sample imaged in Fig. 7 showing double-diffraction effects.
Fig. 8(b) Diagram showing the structural basis of an overlay image of C-type and iota from a \(\langle 111 \rangle_F\) zone.
Fig. 9. Regions of C-type and iota in an annealed sample of Zr$_{0.29}$Sc$_{0.71}$O$_{1.64}$ as seen in a (211)$_F$ image.
Fig. 10. (111) \textsubscript{f} lattice image of a sigma phase crystal showing faulting and banding due to the presence of two very similar phases.
Fig. 11. Disorder evident in \( \langle 111 \rangle \) images of \( \text{Zr}_3\text{Sc}_4\text{O}_{12} \).
Fig. 11 (Cont.) Disorder evident in \langle 111 \rangle_7 images of Zr$_3$Sc$_4$O$_{12}$. 
Fig. 12. Examples of disorder in $\langle 211 \rangle_7$ images of Pr$_7$O$_{12}$. 
Fig. 12 (Cont.) Examples of disorder in \(\langle 211\rangle_7\) images of \(\text{Pr}_7\text{O}_{12}\).