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The Polymorphic Transformation of $Tb_{24}O_{44}$ to $Tb_{48}O_{88}$ via a Partly Ordered Incommensurate Structure

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The polymorphic transformation of $Tb_{24}O_{44}$, $\beta(2)$, to $Tb_{48}O_{88}$, $\beta(3)$, and the probable reduction to lower oxides in the thinnest regions of a crystal is followed by high-resolution electron microscopy. The mechanism by which $\beta(2)$ is observed to transform to $\beta(3)$ is via a partially disordered intermediate characterized by wavy fringes into which nuclei of the transformed polymorph, $\beta(3)$, grow. Wavy fringes of narrower spacing persist at the thin crystal edge, suggesting further reaction of this thin edge to more reduced compositions. Alternative explanations of the origin of the wavy fringes observed are considered.

Introduction

Most of the intermediate oxides of terbium can be represented as Tb_nO_{2n-2} where n is an integer, $4 \leq n \leq \infty$. These oxides have been studied by high-resolution electron microscopy (HREM). Their unit cells have been confirmed (*1*) and a structural principle proposed (*2*). All the known intermediate oxides may be considered as superstructures of a basic fluorite structure. The superstructures arise from the ordering of vacant oxygen sites. The relationships of the TbO_x phases to other anion-deficient fluorite-related oxides is considered elsewhere (*3*). The compositions are the same but the oxygen vacancy arrangements are different.

When $n = 12$ (in Tb_nO_{2n-2}) two polymorphs exist, $Tb_{24}O_{44}$ and $Tb_{48}O_{88}$, designated $\beta(2)$ and $\beta(3)$, respectively (*2*). Both of these structures have been observed repeatedly and even nucleate and grow within a specimen whose composition is changing (*3*) but until now the transformation of one into the other has not been documented.

Recently our attention has turned to transformations among the rare-earth oxides during their observation under the intense beam of the electron microscope (*4–7*). In the present work the polymorphic transformation of $Tb_{24}O_{44}$ to $Tb_{48}O_{88}$ has been observed to occur during HREM observation.

Experimental

Crystals containing the polymorphs $Tb_{24}O_{44}$ and/or $Tb_{48}O_{88}$ can be prepared by leaching the intermediate oxides with acid

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or by a hydrothermal synthesis at high oxygen pressure. The specimen used here was prepared by leaching $Tb_{11}O_{20}$. Very small crystals were mounted on a holey carbon film supported on a microscope grid.

HREM observations were made using the JEOL 200CX microscope equipped with a top-entry double-tilting specimen holder. Images were usually taken at Scherzer focus.

Results

The typical crystal from which the illustrations for this paper were obtained had a thin region that was essentially a 90° fan-shaped sector. The development of the polymorphic transformation was uneven for various reasons including the extent to which various areas were exposed to the electron beam. Figure 1a is an early $\langle 110 \rangle_F$ image of the material in which a well-ordered structure is apparent at the bottom with a region at the top exhibiting wavy fringes approximately parallel to and of approximately the same spacing as the periodic white spots in the ordered region. Figure 1b is an optical diffraction pattern from the ordered region. The diffraction pattern is identified as coming from the $[101]_{\beta(2)}$ zone parallel to the $[0\bar{1}1]_F$ fluorite zone.

Another region of the crystal, approximately at right angles to that from which Fig. 1 was made, was observed, in a series of images, to transform from $\beta(2)$ to $\beta(3)$. In Fig. 2a a rather ordered region of $\beta(2)$ is clearly discernable in the lower right-hand corner. Wavy fringes of approximately the same spacing occupy the remainder of the figure but have a different aspect below and above the platelet nucleating across the central region of the figure. In the upper, thinner edge (above the platelet) the fringes are of slightly narrower spacing and are tilted more steeply with respect to the primary fringes of $\beta(2)$.

In Fig. 2b the ordered region of $\beta(2)$ in the lower right corner is becoming somewhat wavy and fringe development is more advanced over the whole region. The platelet that appears to separate two qualitatively different regions has broadened and

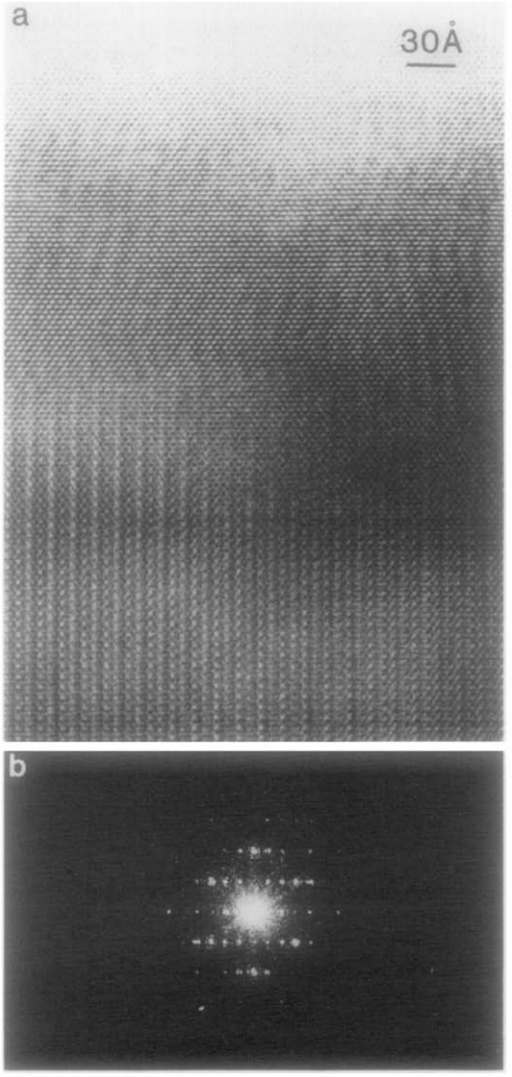

FIG. 1. (a) A $\langle 011 \rangle_F$ zone high-resolution image of a region of a crystal beginning to transform from $Tb_{24}O_{44}$ $\beta(2)$ to $Tb_{48}O_{88}$ $\beta(3)$. Note the development of wavy fringes at the thin edge. (b) An optical diffraction pattern of the ordered region of (a) confirming the $Tb_{24}O_{44}$ structure in the $[\bar{1}0\bar{1}]_{\beta(2)}$ zone.

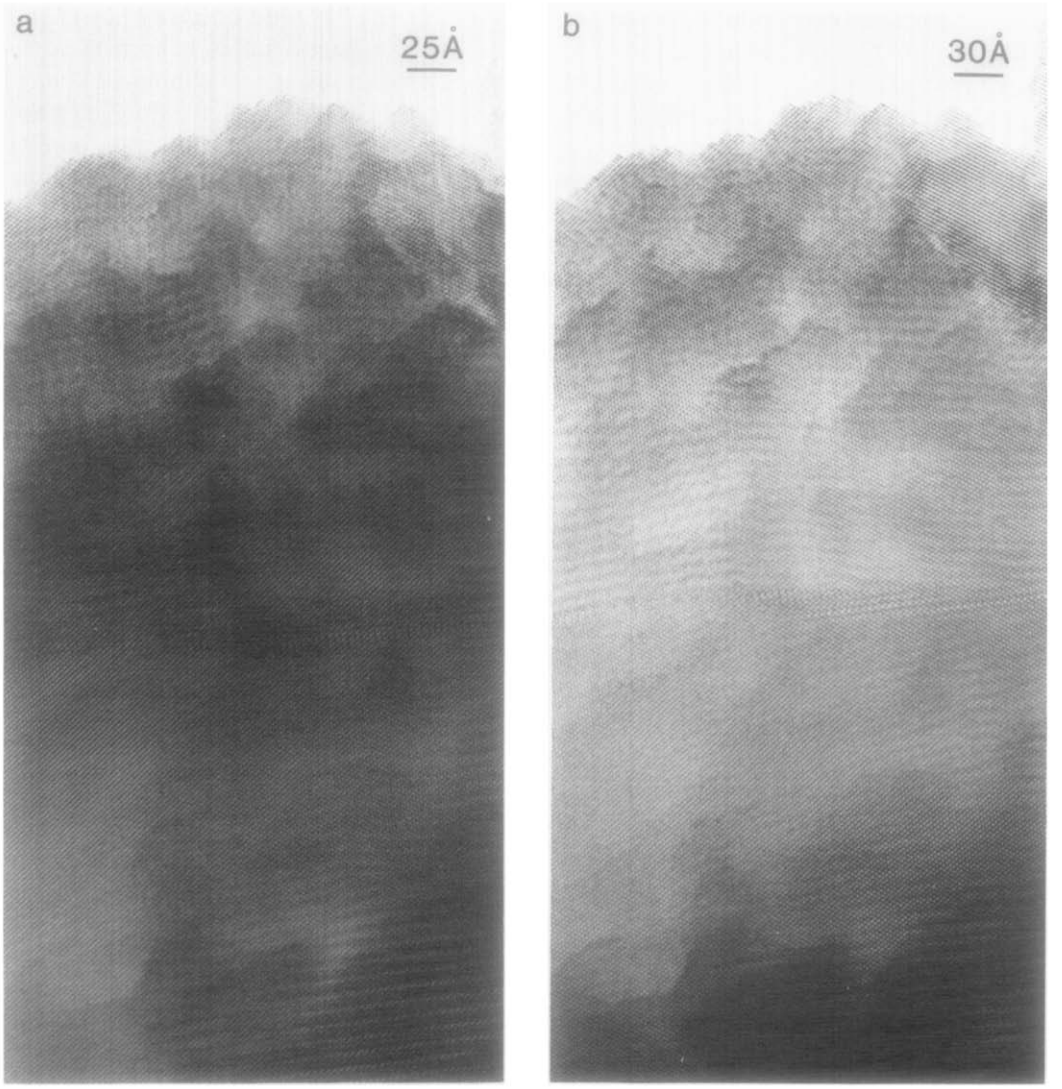

FIG. 2. (a) Early stages of the transformation of $\beta(2)$ to $\beta(3)$. Below the platelets at the central region the wavy fringes correlate with $\beta(2)$ in spacing and direction but above the platelets the fringes have a different aspect and general direction. (b) The transformation underway in (a) has progressed showing further deterioration of the order in $\beta(2)$ at the bottom right with a significant development of the central platelets. (c) At a later time $\beta(2)$ in the thicker regions has transformed to $\beta(3)$ as is apparent in the image and the corresponding $[\bar{6}1\bar{3}]_{\beta(3)}$ optical diffraction pattern.

is altered in appearance. Finally in Fig. 2c well-ordered $\beta(3)$ has crystallized and transformed the entire thicker region from $\beta(2)$ including the region of the platelet. The optical diffraction pattern corresponds to the $[\bar{6}1\bar{3}]$ zone of $\beta(3)$ or the $[\bar{1}0\bar{1}]$ zone of fluorite. Wavy fringes remain in the thinnest regions near the edge of the crystal.

During early observation of the crystal and before Fig. 2a was recorded the platelet nucleus was not apparent but it is clearly seen in the middle of 2a. The development

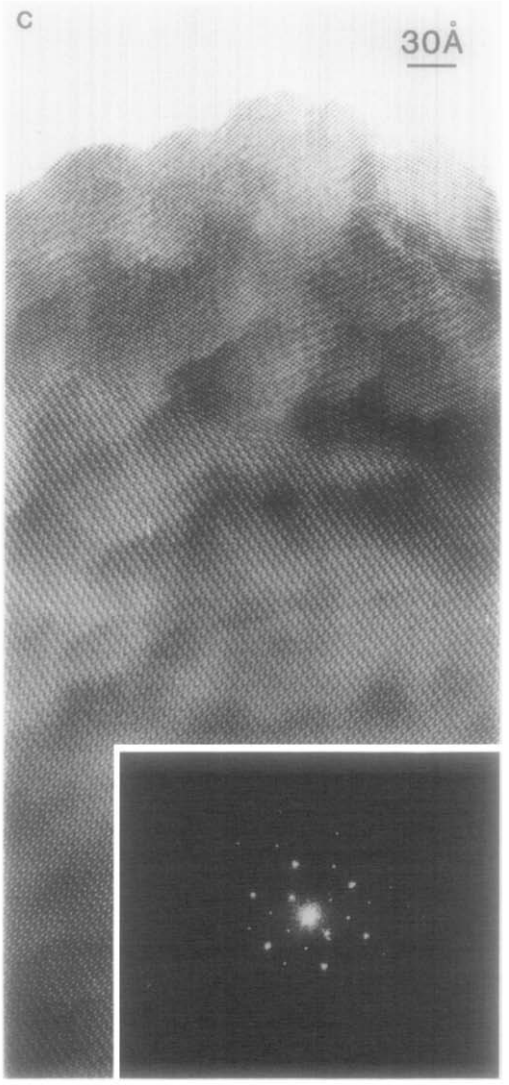

FIG. 2—*Continued*

of the platelet may be observed more clearly in the slightly enlarged images of Figs. 3a–3c. In Fig. 3a the features are clearly related to the $\beta(2)$ image in Fig. 2a. The general directions and spacing of the fringes are different above and below the platelet. The width of the nucleated region has increased in Fig. 3b without changing its general appearance. In Fig. 3c the spot pattern has altered somewhat to conform more nearly to the pattern of $\beta(3)$ in the same region of Fig. 2(c).

The evolution of the wavy fringes are shown more clearly in Figs. 4a–4c taken from the general region of Fig. 1. In this instance the wider fringes at the top give way to the narrower ones at the bottom. The optical diffraction pattern (Fig. 4b) shows streaked and not quite linear superstructure spots that correspond to the wavy fringes and are quite reminiscent of the $\beta(2)$ diffraction pattern of Fig. 1b. The diffraction pattern of Fig. 4c emphasizes the narrower and incommensurate fringe spacing in the same direction as in Fig. 4b. The fluorite substructure persists in both regions.

Discussion

From the images and optical diffraction patterns shown a mechanism for the transformation of $\beta(2)$ to $\beta(3)$ TbO_x can be proposed. The direction of the decomposition is itself of interest. Under the conditions of the experiment, $\beta(3)$ would appear to be more stable. This is not inconsistent with the frequency of observation of these two polymorphs produced thermally (*1*, *2*).

The wavy fringes themselves appear to chart the course of the transformation. In Fig. 2 the areas not occupied by two-dimensional patterns of ordered $\beta(2)$ or $\beta(3)$ are occupied by wavy fringes. These fringes persist, usually with a narrower spacing, in the thin regions of the crystal. It is within these wavy fringes that a nucleus of an ordered superstructure appears and spreads by a rapid transformation of $\beta(2)$ to $\beta(3)$ (Fig. 2c).

The origins of the fringes could be moiré patterns. However, they are judged not to be from the following observations. (i) They are everywhere nearly parallel to the image features of the $\beta(2)$ structure. Elsewhere in the TbO_x images are patterns that are clearly moiré fringes. (ii) The wavy fringes

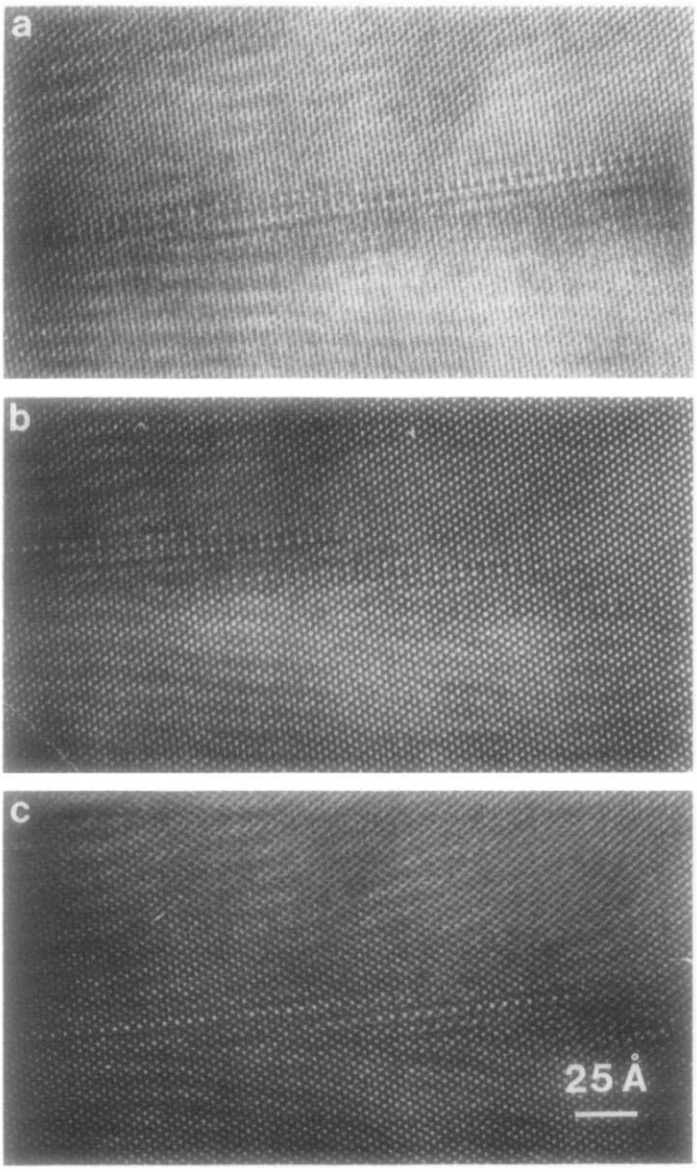

FIG. 3. (a–c) Images showing the development of the platelets of Fig. 2 from being closely related in direction and spacing to $\beta(2)$ in (a) to being more apparently related to $\beta(3)$ in (c).

occur in the thinnest regions also where moiré fringes would not be expected. (iii) The spacing is small for moiré patterns. (iv) The spacing of the wavy fringes adjacent to the $\beta(2)$ structure is similar to the repeat distance of the ordered pattern.

The most likely cause of the wavy fringes seems to be the partial and imperfect ordering of vacant oxygen sites within the fluorite substructure corresponding to the change when $\beta(2)$ in the $[\bar{1}0\bar{1}]_{\beta 2} \equiv [0\bar{1}1]_F$ orientation transforms to $[\bar{6}1\bar{3}]_{\beta 3} \equiv [\bar{1}01]_F$.

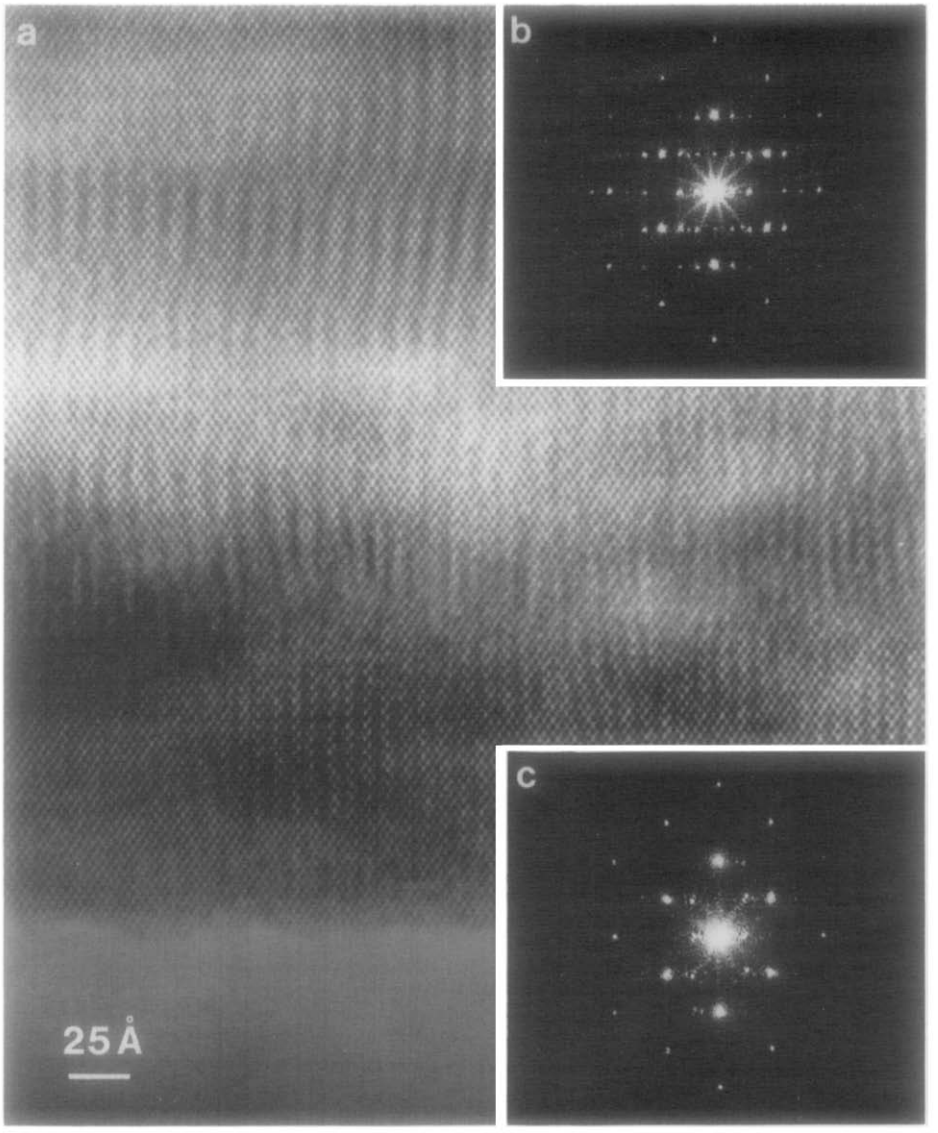

FIG. 4. (a) An image showing the development of the fringes in the region of the crystal shown in Fig. 1. The shift in the spacing of the fringes top and bottom is apparent, and is further confirmed by the optical diffraction patterns (b) and (c). (b) An optical diffraction pattern similar to that in Fig. 1b. (c) An optical diffraction pattern where the narrower incommensurate spacings and misalignment with the substructure are apparent.

There is no change in composition, hence there is a very small driving force for the reaction that is not inconsistent with a very slow ordering of the vacancies that must occur before the transition is complete.

In the ⟨110⟩ zone of the fluorite structure the metal and nonmetal atoms are aligned separately. The pattern observed in the thin region is the net of metal columns. The contribution of the oxygen atoms to the pro-

jected potential is relatively small. However, a partial ordering of the vacant oxygen sites is accompanied by a partial disordering of the metal atom positions from their fluorite positions. It is this partial disorder that is mainly responsible for the contrast fluctuations in the wavy fringes. This would be entirely consistent also with the more or less parallel alignment of the wavy fringes near the ordered $\beta(2)$.

The fringe spacings vary from about $4d_{220F}$ to about $5.5d_{220F}$ and are narrowest in the thinnest regions. The spacing could also correlate with the vacancy concentration and would suggest a more reduced composition in the thinnest regions. Furthermore, the directions of the ordered vacancy planes would be different in the reduced material and this could explain the apparent swinging of the wavy fringes in the thinnest region.

The incommensurability of the pseudostructures of the wavy fringes and the basic fluorite structure shown in the optical diffraction patterns of Fig. 4 (especially Fig. 4c) strongly suggests compositional heterogeneities and reduction in the thin edge with a composition $TbO_{2-\delta}$ where δ could vary continuously from about 0.7 (β-phase).

Somewhat similar modulations are observed when the vernier structures $MnSi_{2-x}$ (*8, 9*) and $Ba_{1+x}Fe_2S_4$ (*10–12*) are studied under the electron microscope. In these compounds a compositional variation exists where none is present in this study. A consideration of these possibly related phenomena is a matter of continuing study.

Summary

It is proposed that the transformation of $\beta(2)$ ($Tb_{24}O_{44}$) to $\beta(3)$ ($Tb_{48}O_{88}$) occurs via a partially disordered structure that gives rise to wavy fringes corresponding to local compositional heterogeneities approximating the projected structure of $\beta(2)$. Within the regions of the wavy fringes and parallel to them platelet nuclei form that evolve and grow to produce the $\beta(3)$ structure. The wavy fringes that persist at the thinnest edge have a narrower spacing and their direction is altered suggesting reduction to a lower intermediate phase is occurring.

Acknowledgment

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