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Reduction of Praseodymium and Terbium Higher Oxides: Chemical Reactions Similar to Diffusionless Phase Transitions

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Some solid state chemical reactions such as a change in the degree of oxidation can occur without a great displacement of the atomic positions of one kind of atom in a structure. When praseodymium and terbium oxides are reduced, the rare earth atom movement is less than the cation crystallographic distances in the fluorite-related structure. This means that the chemical transformation occurs without a great change in the framework of one kind of atom. The relative positions of these atoms are nevertheless slightly modified as in a diffusionless phase transition. In the Pr and Tb oxides the deformation changes both the volume and the shape of the structural unit. A displacement tensor can be defined for these chemical transformations. Interfaces between the two phases can be found as in ferroelastic or martensitic phase transitions by satisfying the condition of a strain-free interface. No general solution exists under these circumstances but approximate solutions exist for thin layers which give needle-like domains. The great number of glide defects in only one direction that occur in the iota phase of praseodymium thin layers obtained by reduction of the zeta phase can then be related to the chemical transformation itself. Similar results are obtained in bulk material but the transformation mechanism is not yet completely settled. © 1987 Academic Press, Inc.

Introduction

Since material transport is essential in a solid state chemical reaction large displacements of atomic positions might be expected. However, some chemical reactions occur without much change in the position of one kind of atom except for a general strain in the crystal. If, in this event, the other types of atoms are extremely mobile, such transformations can resemble a diffusionless phase transformation inside a monocrystal. Strain would then be developed between domains of different compositions due to the change in shape and volume. As the reaction proceeds a minimization of the total free energy can be expected by the formation of strain-free interfaces as in martensitic or ferroelastic phase transitions. In the Pr and Tb oxides studied here, chemical transformations occur inside a monocrystal without a great change in the atomic positions of the rare earth atoms but with a global deformation. Nucleation and growth of the new compounds with well-defined interfaces have been observed.

A search for a general solution for strain-free interfaces was undertaken. A strain tensor was defined, and possible strain-free

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interfaces that could occur during chemical transformation were sought. It was found that no general solution (for strain-free interfaces) exists, but that special solutions which are the source of the needle-like domains of Pr_7O_{12} (iota) inside Pr_9O_{16} (zeta) when the latter is reduced can occur. Finally, glide domains, usually found in Pr_7O_{12}, have been related to the chemical transformation itself. The case of terbium oxides is discussed in much less detail.

Experimental

Experimental Evidence of a Common Rare Earth Atomic Framework in the Pr and Tb Oxides

The higher oxides of the rare earths that occur in ceria, praseodymia, and terbia that can be represented as R_nO_{2n-2} are all fluorite-related as clearly indicated by their X-ray and electron diffraction patterns. The structure of Pr_7O_{12} has been determined by neutron diffraction (*1*) and Ce_7O_{12} and Tb_7O_{12} have been shown to be isostructural (*2, 3*). The structure of Pr_9O_{16} has been proposed (*4*) from high-resolution electron microscopy (HREM). The structure of Pr_7O_{12} consists of ordered vacancies of all oxygen positions along parallel strings in one $[111]_F$ direction of the fluorite subcell. The tetrahedrally coordinated cations about each vacant oxygen position move away by about 0.18 Å maintaining their tetrahedral relationship. This results in a slight rhombohedral distortion of the still fluorite-like structure. This structure can be considered as consisting of slabs of Pr_7O_{12} composition containing $\{135\}_F$ planes of six-coordinated rare earth atoms associated with contiguous parallel layers containing seven-coordinated cations. These Pr_7O_{12} slabs, when separated by parallel stoichiometric layers of RO_2 of varying thicknesses, become members of the series R_nO_{2n-2}, where n is an odd integer greater than or equal to 7. In this way Pr_9O_{16} may be represented as

$$Pr_7O_{12}(\text{slab}) + 2RO_2(\text{slab}) = Pr_9O_{16}$$

or, similarly, the delta phase in terbia ($Tb_{11}O_{20}$) would be

$$Tb_7O_{12}(\text{slab}) + 4RO_2(\text{slab}) = Tb_{11}O_{20}.$$

A consequence of this structure is that the slabs of various members of the series can intergrow coherently across these $\{135\}_F$ planes. Although the odd integer members of the series tend to have this layer-like structure the even integer members tend to twin at the unit cell level to give monoclinic unit cells that have the $\{135\}_F$ planes buckled to make a chevron-like pattern (*5*). This latter case is typical of stress–strain phenomena that usually occur in martensites. This buckling is due to different strains from the cubic-like structure that occurs for different compositions, as can be seen by the parameters of the pseudo-cubic cell of all these oxides (*6*). The strain can be rather different from one oxide to another but it is never very great (generally less than 1%).

In summary, in the intermediate phases in the Tb and Pr oxides the metal atoms are essentially in a face-centered cubic arrangement with oxygens occupying the tetrahedral interstitial positions in an ordered way. In the intermediate oxides, a strain from the cubic-like structure occurs. Furthermore, and this is very important, the oxygen substructure is extremely mobile.

The Reduction of Pr_9O_{16} (Zeta) to Pr_7O_{12} (Iota)

The zeta to iota chemical transformation has been studied by HREM. Figures 1a–1c record a progressive chemical transformation of zeta crystals whose surfaces are close to their $(21\bar{1})_F$ planes which in turn are perpendicular to the a_ζ axis. The new iota structure appears as needle-shape domains. All the domains have the same ori-

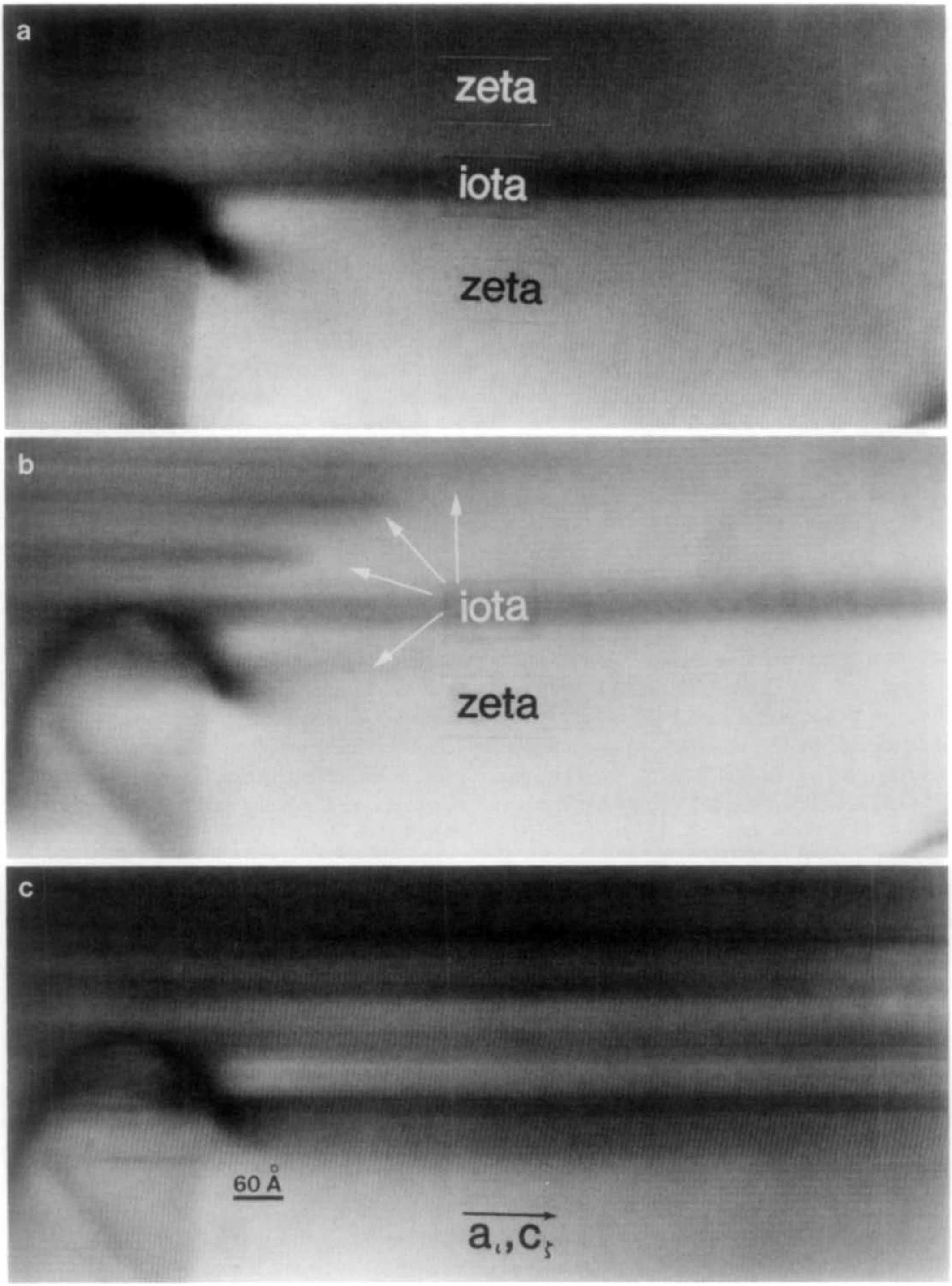

FIG. 1. (a) A needle-like domain of iota appearing by reduction of a zeta thin layer inside the electron microscope. It is only a few nanometers thick and more than 100 nm long. It has grown in epitaxy within the zeta structure. The plane of the zeta thin layer is close to the $(21\bar{1})_F$ plane. The c_ζ axis and the a_ι axis are parallel, as indicated in the figure. (b and c) The same region as (a) at intervals of a few minutes. Other similar needle-like domains of iota are formed during reduction of the zeta thin layer.

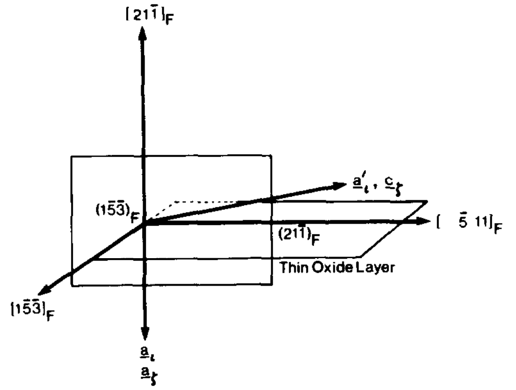

FIG. 2. The plane of the thin layer is close to the $(21\bar{1})_F$ plane and the electron beam is parallel to the $[21\bar{1}]_F$ axis. a_ι and a_ζ are parallel to this direction. a'_ι and c_ζ are in the $(1\overline{53})_F$ plane about 10° off the $[8\bar{5}11]_F$ direction in the $(21\bar{1})_F$ and $(1\overline{53})_F$ planes.

entation such that the $(010)_\iota$ plane is parallel to the $(010)_\zeta$ plane which is the plane of the Pr_7O_{12} slabs inside Pr_9O_{16}, and moreover, the **a** and **c** axes of each structure are respectively parallel. This is possible because a_ζ is close to a_ι, c_ζ is practically the same as a_ι, and β_ζ is close to α_ι. The unit cell parameters for zeta are a = 6.70 Å, b = 8.66 Å, c = 6.73 Å, $\alpha = 97.8°$, β = 99.9°, γ = 75.9° and for iota they are a = 6.74 Å and α = 99.3° (Fig. 2). The interface observed in the thin samples that have been studied is always the $(010)_\zeta$ plane (Figs. 1 and 3). Only a small strain may occur in the common direction corresponding to a_ζ and a_ι with slightly different parameter values. This direction is generally perpendicular to the thin samples used for electron microscopy so that no long-range stress occurs in a direction parallel to the thin dimension.

All the observations clearly show that the transformation occurs from a well-ordered Pr_9O_{16} to a well-ordered Pr_7O_{12}, with a well-defined epitaxial growth pattern and yielding a well-defined interface so that this chemical transformation occurs exactly in the same way as does a cooperative phase transition between different structures of the same compound. As previously shown (7), different orientation variants of Pr_7O_{12} should occur if it were created by vacancy ordering; however, this is not the case here. The formation of only one Pr_7O_{12} variant is clearly a consequence of the direct growth of iota into zeta.

As indicated before, the basic framework of rare earth atoms is unchanged in the zeta to iota reaction, but their position is slightly altered because of a slight strain resulting from the chemical reaction. This change in position consists of (i) a global deformation and (ii) a small atomic rearrangement. Both of these changes in position occur with very small cationic movement, a distance much less than interatomic distances. In this re-

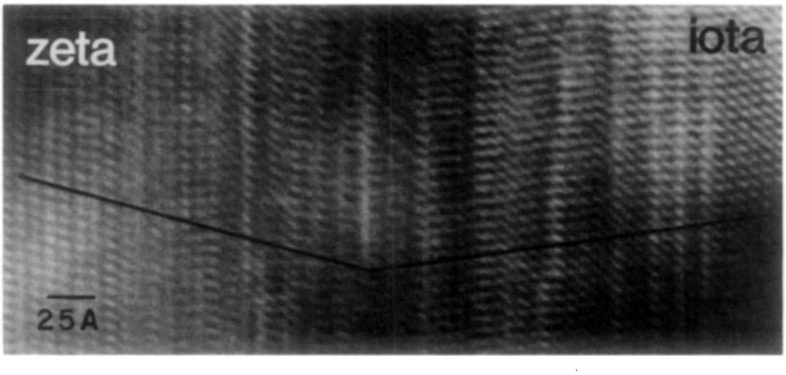

FIG. 3. Faulted structure of iota obtained by reduction of a zeta thin layer. Straight lines mark the projection of the (010) planes of zeta and iota. Layers of Pr_8O_{14} occur between the P_7O_{12} slabs.

spect they are similar to the general class of cooperative (diffusionless) phase transitions. The distinction is that in this oxide system, (i) we deal with a chemical reaction and not simply a phase transition, and (ii) only one of two kinds of atoms moves small distances and the other is very mobile. Such chemical reactions can be said to be partly diffusionless. A framework exists where one kind of atom, although strained, is conserved in the transformation. Therefore, most of the properties of cooperative phase transitions must be expected, especially the existence of strain-free interfaces between domains of different compositions. We will see that in the present case we are close to these conditions. A strain tensor can be defined for such transformations and one can search for strain-free interfaces just as in the case of diffusionless transformations.

The Strain Tensor from Iota to Zeta and the Search for Strain-Free Interfaces

For crystal deformation, diffusionless phase transformations, and also for the present case of a chemical reaction occurring in a partly diffusionless way, a strain tensor can be defined as

$$\begin{bmatrix} \partial u_1/\partial x_1 & \partial u_1/\partial x_2 & \partial u_1/\partial x_3 \\ \partial u_2/\partial x_1 & \partial u_2/\partial x_2 & \partial u_2/\partial x_3 \\ \partial u_3/\partial x_1 & \partial u_3/\partial x_2 & \partial u_3/\partial x_3 \end{bmatrix},$$

where u is a small displacement of a point M having the coordinates $x_1x_2x_3$.

This tensor (*8*) corresponds to a pure rotation represented by an antisymmetrical part plus a pure deformation represented by the symmetrical part. We will consider only the symmetrical part of the tensor which represents the pure deformation. It can be named the "pure deformation tensor" (PDT) such that

$$(\mathrm{PDT}) = \begin{bmatrix} e_{11} & e_{12} & e_{13} \\ e_{21} & e_{22} & e_{23} \\ e_{31} & e_{32} & e_{33} \end{bmatrix}$$

with $e_{ab} = \partial u_a/\partial x_b + \partial u_b/\partial x_a$. The expression of this tensor must be given in a Cartesian coordinate system. It can easily be deduced from the parameters of the iota and zeta pseudo-cubic cells (*6*). Considering the iota to zeta transformation (for iota $a_c = 5.51$ Å, $\alpha = 89.63°$, and for zeta $a_c = 5.48$ Å, $b_c = 5.48$ Å, $c_c = 5.50$ Å, $\alpha = 90.15°$, $\beta = 90.50°$, $\gamma = 90.91°$) the strain tensor deduced from the pseudo-cubic coordinates of each structure is

$$\begin{bmatrix} -5.7 \times 10^{-3} & -11 \times 10^{-3} & -7.6 \times 10^{-3} \\ -11 \times 10^{-3} & -5 \times 10^{-3} & -4.5 \times 10^{-3} \\ -7.6 \times 10^{-3} & -4.5 \times 10^{-3} & -2.5 \times 10^{-3} \end{bmatrix}.$$

This tensor is rather similar to the deformation tensor used for ferroelastic phase transitions but the change in volume at the transition cannot be eliminated in this case because it is as important as the change in shape itself. From this it is deduced that the strain tensor is not traceless. It is well known that in all diffusionless transformations such as martensitic transformations, interfaces between different structures occur so as to be strain-free. Recent results show that a similar situation exists in ferroelastic phase transformations (*9*). All previous results indicate the importance of strain energy in the vicinity of the interface in effecting diffusionless phase transitions. Since the reduction considered here occurs in a similar way the same phenomenon should be expected.

Strain-free interfaces will be defined such that a point M taken on the interface of coordinate $\mathbf{r}$ (xyz) will be in M′ of coordinate $\mathbf{r}' = \mathbf{r} + \Delta\mathbf{r}$ ($x + \Delta x$, $y + \Delta y$, $z + \Delta z$) at the same distance from the origin, O, after the transformation (as we deal with small deformations so that $\Delta\mathbf{r}$ is small compared to $\mathbf{r}$); i.e.,

$$\Delta\mathbf{r} \cdot \mathbf{r} = 0 \qquad (1)$$

for a small $\Delta\mathbf{r}$, where $\Delta\mathbf{r}$ is the displacement due to the pure deformation. A rotation of $\Delta\mathbf{r}/\mathbf{r}$ will then occur to superimpose $\mathbf{r}$ and $\mathbf{r} + \Delta\mathbf{r}$. Relation (1) can also be written

$$(xyz)\begin{pmatrix}\Delta x\\ \Delta y\\ \Delta z\end{pmatrix} = 0.$$

But $(\Delta x \Delta y \Delta z)$ and (xyz) are related, not taking rotations into account, by the relation $(\Delta x \Delta y \Delta z) = (\mathrm{PDT})\,(xyz)$ where (PDT) represents the pure deformation tensor. Equation (1) can then be written

$$(xyz)\,(\mathrm{PDT})\begin{pmatrix}x\\ y\\ z\end{pmatrix} = 0. \qquad (2)$$

Equation (2) being homogeneous of the second degree is the equation of a cone with the apex at O. Not only must M($\mathbf{r}$) or or M′($\mathbf{r}'$) be equidistant from the origin, O, taken on the interface after transformation, but also the same restriction applies to M and M′ to make the interface strain-free. This last condition is not satisfied by (2) in the general case, but it is satisfied when no special point like the cone apex occurs, i.e., when the cone has degenerated into a pair of planes. This degeneration occurs for

$$\Delta = 0, \qquad (3)$$

where Δ is the determinant associated with the strain tensor. Condition (3) gives a general solution for strain-free interfaces. In the present case condition (3) is not satisfied and no general solutions occur.

In the reduction reaction being considered we deal with crystals for which the $[21\bar{1}]_F$ axis is parallel to the electron beam (except for tilting possible up to about 10°) so that such thin crystals have surface directions close to the $(21\bar{1})_F$ plane. An approximate solution (9) can exist if the cone and the $(21\bar{1})_F$ plane intersect. This gives, for solutions, two directions:

$$\mathbf{A}\text{: } [1, -0.92, 1.08]$$
$$\mathbf{B}\text{: } [1, -3.03, -1.03].$$

The angle between **A** and **B** is 65°. **B** is far from any important crystallographic direction of zeta or iota, **A** is close (13°) to the $[8, -5, 11]_F$ direction which, in the fluorite notation, is the projection on the $(21\bar{1})_F$ plane of both **c** directions of iota and zeta which are experimentally found to superimpose. From this we conclude (i) that only one of the possible strain-free directions is found experimentally to give a real interface and (ii) the direction experimentally found is 13° off the strain-free direction and is a very important crystallographic direction for both structures. Moreover, it is the intersection of the plane of the Pr_7O_{12} slabs inside Pr_9O_{16} with the plane of the thin layer. If strain-free conditions were the only important consideration both strain-free directions would be expected to occur. It is significant that only the one corresponding to an important crystallographic direction occurs and 13° off the real strain-free direction. This is different from ferroelastic phase transitions for which only the condition of strain-free interfaces is important. This can be explained in the present case by the rather small strain existing at the transformation so that the lowering of interface energies is obtained as much by common dense atomic rows which fit with important crystallographic axes as by strain-free interfaces.

What predictions can be made from these results for bulk materials for which there are no experimental data? No two-dimensional strain-free interfaces can occur in bulk since for this case Eq. (2) has no general solution. Planes of the Pr_7O_{12} slabs could be interfaces between Pr_7O_{12} and Pr_9O_{16} but with an important strain at the interface along the common **a** direction or with the formation of interfacial dislocations. A priori, in the case of three-dimensional crystals, it is impossible to be sure of the existence of such a planar interface, the more so as needle-like domains of iota with the c_ι axis parallel to the c_ζ axis could also occur with less strain energy but with larger interface energy. Iota obtained from three-dimensional zeta crystals and crushed in thin layers has been examined inside the electron microscope (Fig. 4). A great number of defects occur parallel to only one of the **a** axes of iota but this could be due to planar interfaces parallel to the Pr_7O_{12} slabs as well as to needle-like domains of Pr_7O_{12} so that it is not possible to come to a conclusion in the case of bulk material. Finally, when iota is obtained by reduction of zeta a very highly faulted structure is obtained in only one direction in the case of bulk material as well as in the case of the reduction of a thin layer. In both cases, stacking faults that can exist throughout the thin layer as planar interfaces appear and, as previously shown, they fit imperfectly together causing regions of a different composition (7), but this does not completely settle the question of what occurs in the bulk material.

The analogous reaction, when the delta phase is reduced to iota in terbium oxide, is sometimes observed with a well-defined interface between iota and delta. However, more often the delta–iota boundary is incoherent indicating that the condition of low-energy interfaces is not satisfied as well in this case as in that for praseodymium oxide. With no exact values of the unit cell parameters available, it has not been possible to make an exact calculation of the strain-free directions.

Conclusions

In thin layers of praseodymium oxide, the iota phase grows from zeta with very well-defined interfaces in one direction, growing needle-like domains. The boundaries of these thin domains are effectively stacking faults that are accompanied by a compositional change. The origin of these needle-like domains is the near coincidence of dense atomic rows parallel to the Pr_7O_{12} slabs in Pr_9O_{16} and strain-free directions along the interface of iota and zeta. Con-

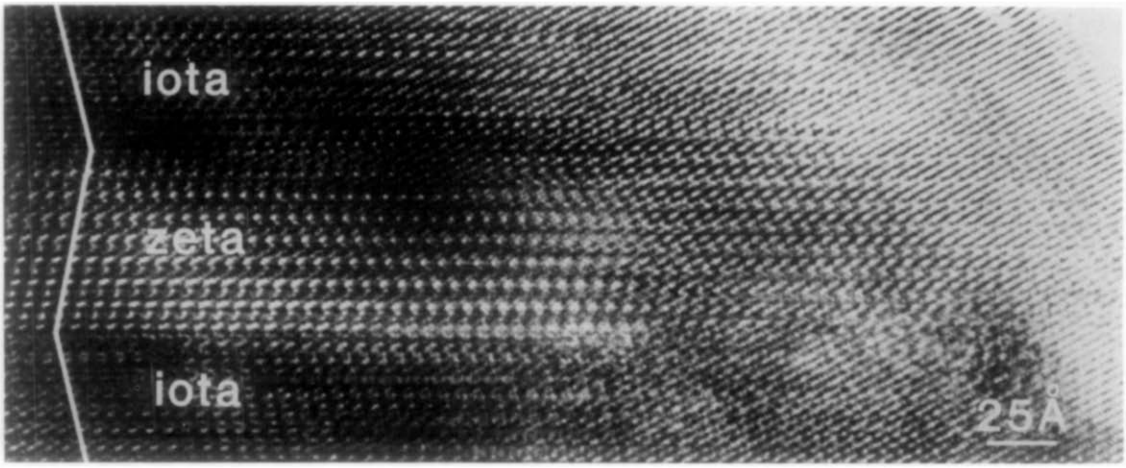

FIG. 4. A faulted structure of bulk iota obtained by reduction of zeta crystals, then crushed for observation. Note the well-ordered remnant of zeta imbedded in iota. The faulted structure is similar to that obtained in the case of a thin layer (see Fig. 3). (Image taken by D. J. Smith on the JEOL 400 kV 4000 EX microscope.)

trary to what is observed in ferroelastic transformations, the direction of the needle axis is determined as much by preferred dense atomic rows as by strain-free directions. A possible strain-free direction that is far from any dense atomic row direction does not result in a viable interface. Similar intergrowth forms have been found to occur in fragments obtained from crushed, partially reduced crystals, but this does not completely settle the problem of the transformation in the case of bulk material, and it is not clear whether planar interfaces parallel to the Pr_7O_{12} slabs in Pr_9O_{16} really occur.

Acknowledgment

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