Neutron Powder Investigation of the Monoclinic to Tetragonal Phase Transformation in Undoped Zirconia

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Abstract

Pure ZrO_2 powder (particle size about 60 μm) was investigated up to 1800 K by neutron diffraction. The monoclinic→tetragonal (martensitic) phase transformation is spread over more than 600 K. Anomalous behaviour of the lattice constants around 1450 K indicates a two-step transformation process. This is further supported by structural analysis with anisotropic atomic displacement parameters. Small shifts of the atoms together with highly anisotropic thermal ellipsoids indicate a displacive character at the beginning of the transition. In the second stage both structures remain almost unchanged in agreement with the martensitic character of the main transformation. Overall microstrains are present in the monoclinic and tetragonal phases with a minimum in the coexistence region of the phases around 1500 K where strong macrostrains occur.

1. Introduction

Although the monoclinic (m)←→tetragonal (t) phase transformation in pure ZrO_2 has been known for a long time (Ruff & Ebert, 1929), and undoped and doped zirconia are of exceptional importance in materials science, there are still unanswered questions concerning structural, microstructural and kinetic matters (Subbarao, Maiti & Srivastava, 1974; Subbarao, 1981; Rühle & Heuer, 1984; Schmid, 1988). Basic features of the transformation (Grain & Garvie, 1965; Patil & Subbarao, 1970; Subbarao, 1981) include (*a*) a transformation interval between 1200–1490 K (see below), (*b*) shear-type reorientation with a defined orientational relationship between mother and daughter phase, (*c*) martensitic (athermal) character with some isothermal precursor, (*d*) destructive behaviour resulting from a large difference between the unit-cell volumes, and (*e*)

thermal hysteresis. It should, however, be mentioned that for the special case of pristine (*i.e.* untreated) large and unstrained single crystals a sharp transformation temperature of 1447 K is reported (Garvie & Goss, 1986).

Based on a comparison of the structures of the monoclinic (McCollough & Trueblood, 1959; Smith & Newkirk, 1965) and tetragonal phases (Teufer, 1962) possible atomic displacements in the course of the transformation have been proposed from geometric considerations (Smith & Newkirk, 1965; Patil & Subbarao, 1970), but not proven. Some speculation concerning a dynamic origin exists [soft modes, Mitsuhashi, Fujiki, Tsukioka & Tsuda (1971), Heuer & Rühle (1985) and Negita & Takao (1989)] but again without experimental evidence.

We have investigated the $m \rightarrow t$ transformation in the coexistence range of the phases using the profile-fitting (Rietveld) method for multiphase powder data. The availability of high-resolution/high-intensity diffractometers allows the gradual changes in structure during transformation to be followed. In particular, accurate anisotropic atomic displacement parameters can be obtained, which could help in understanding the transformation mechanism. Until now this has not been attempted even in recent X-ray [Hann, Suitch & Pentecost (1985) (*m*)] or neutron refinements [Howard, Hill & Reichert (1988) (*m*), Barker, Bailey & Garrett (1973) (*t*), Aldebert & Traverse (1985) (*t*) and Schmid (1988) (*m,t*)].

We chose neutron diffraction for several reasons: (*a*) the structural parameters of the oxygens, which play the dominant role during transformation, can be refined more reliably than with X-rays; (*b*) the temperature-factor analysis is not influenced by absorption and form-factor effects; (*c*) surface effects, which play an unknown role, are negligible; and (*d*) the sample environment (furnace) is less cumbersome.

2. Experiments and data evaluation

The experiments were carried out at the high-resolution neutron powder difractometer D2B of the ILL/Grenoble (Hewat, 1986) using a wavelength of 1·595 Å from a vertically focusing Ge(335) monochromator (no $\lambda/2$!). The sample was commercially available ZrO_2 powder with a purity of 99·75%, ground and sieved to a mean diameter of about 60 μm. It was contained in an open Pt cylinder and heated in a neutron furnace developed by Lorenz (1988): the sample was placed at the common focus of two ellipsoidal mirrors with halogen lamps placed at the two other foci. The measurements were performed with increasing temperature between 1100 and 1800 K and at room temperature thereafter. The temperature stability was approximately ±5 K.

The data were evaluated using a multiphase Rietveld program (Wiles & Young, 1981). The peaks were fitted with a pseudo-Voigt function $\eta G(1 - \eta)L$ (with $0 \le \eta \le 1$), where G denotes a Gaussian and L a Lorentzian function. The variation of width with scattering angle 2θ is described by the formula

$$\Delta(2\theta)_i^2 = U\tan^2\theta + V\tan\theta + W. \qquad (1)$$

An asymmetry parameter P accounts for the vertical divergence effect. The background was refined by a six-parameter polynomial. Pt reflexions from the sample container caused by texture problems were excluded from the refinement. Selected observed and calculated patterns are shown in Fig. 1. Most of the refinements were carried out with anisotropic atomic displacement parameters and individual profile parameters (U, V, W, η, P) for each phase. For low minority-phase contents (monoclinic above 1700, tetragonal below 1400 K) isotropic temperature factors and constrained profile parameters had to be used.

3. Results

At all temperatures satisfactory fits were obtained within space groups $P2_1/c$ (27 structural parameters) and $P4_2/nmc$ (six parameters). No other phase was detected during the transformation. Very small extra peaks present at all temperatures are caused by the Al_2O_3 glue used to fix the Pt can. The data analysis of the minority phases was possible down to about 1 vol%. The main results are summarized in Figs. 2–7. Weighted-profile R factors $(R_{wp}\text{'s})$ were approximately 5%.* With the exception of the room-

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* Lists of atomic coordinates, cell parameters, anisotropic thermal parameters, R values and data corresponding to Fig. 1 have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53479 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
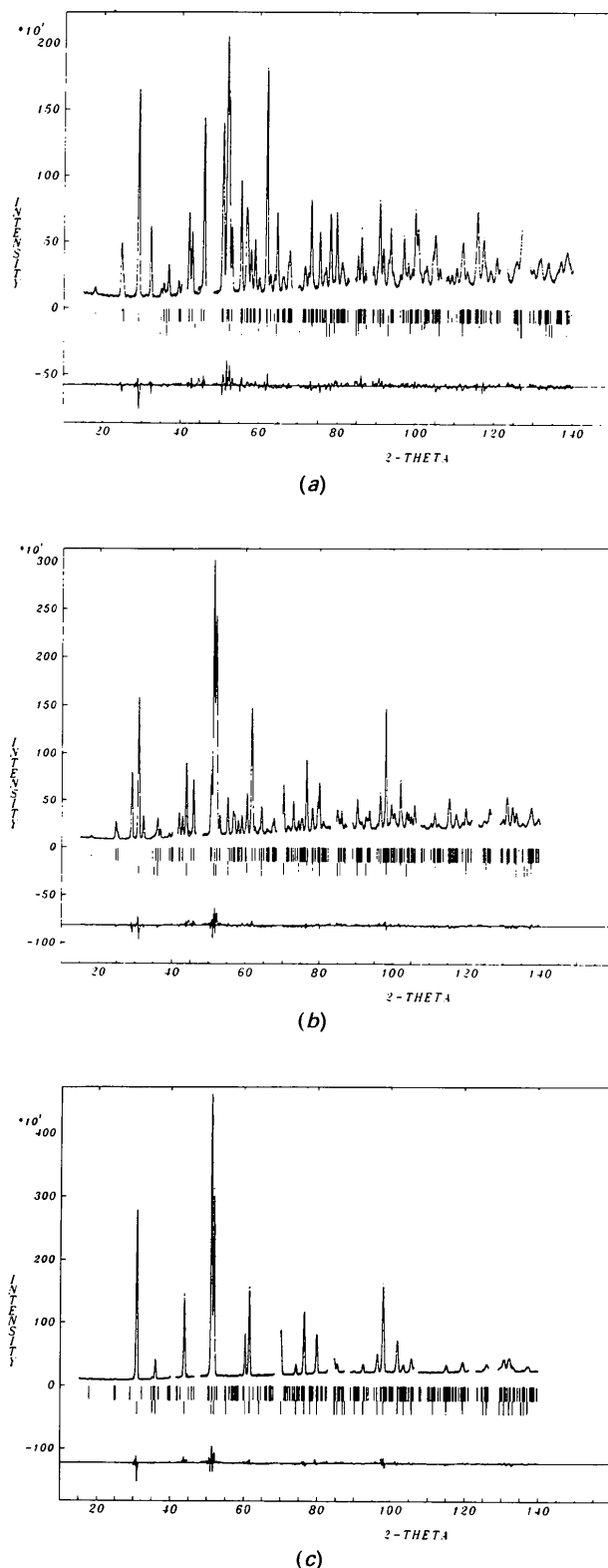

Fig. 1. Observed and calculated powder patterns at (a) 1100, (b) 1553 and (c) 1716 K. Difference plots are shown below. Reflexion positions of monoclinic (above) and tetragonal (below) phases are indicated.

temperature measurement, η and P were nearly independent of temperature. The deviations at room temperature might be attributed to more pronounced thermal diffuse scattering at high temperatures.

Fig. 2 shows the variation of the scale factors with temperature. In this plot the scale factor of the tetragonal phase has been corrected for the ratio of the cell volumes, *i.e.* the relative portions of both phases are represented directly. The sum decreases slightly with increasing temperature possibly indicating the creation of some minor disorder. The 2θ dependence of the background shows only normal behaviour roughly proportional to $1 - \exp(-2W)$ (W is the Debye–Waller factor), *i.e.* no additional short-range-order modulations. The background increases
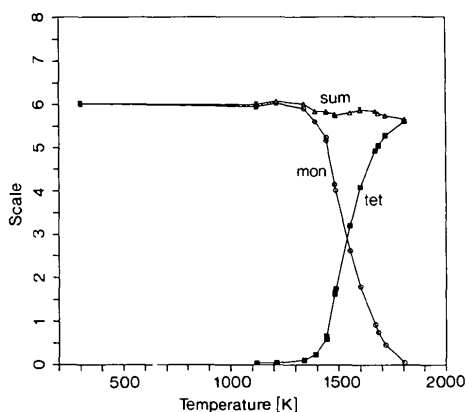
almost linearly with temperature as a result of increasing thermal diffuse (multiphonon) scattering.

Fig. 3 shows the variation of the lattice parameters. For comparison $2^{1/2}a_t$ corresponding to a *C*-centered cell of the tetragonal phase (this setting will be used throughout the paper, *t*) and $a_m\sin\beta_m$ (perpendicular to c_m and b_m) have been drawn. This suggests a relationship between c_m and c_t which is by no means proven for the whole transformation (see below). The large decrease in cell volume $V_m \rightarrow V_t$ (see Fig. 8) arises mainly because of large differences in c and b at the same temperature points.

Fig. 2. Adjusted scale factors representing fractions of monoclinic (o) and tetragonal (■) phases during the transformation (total: △).

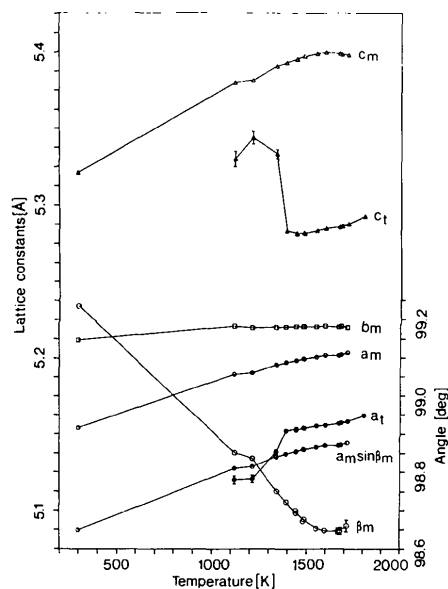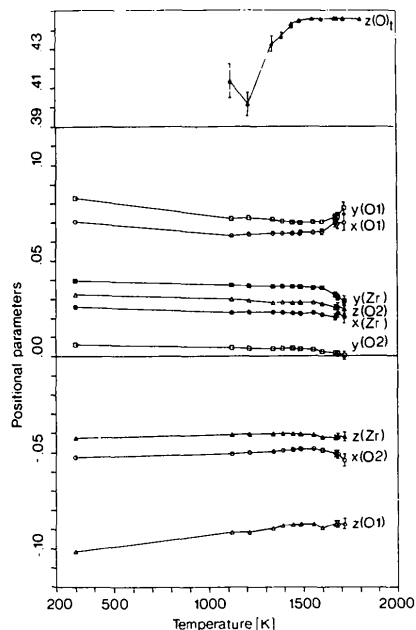Fig. 4. Fractional coordinates of monoclinic ZrO_2, given as the difference from their values in the tetragonal phase. The z parameter of O in tetragonal ZrO_2 is shown at the top of the figure.
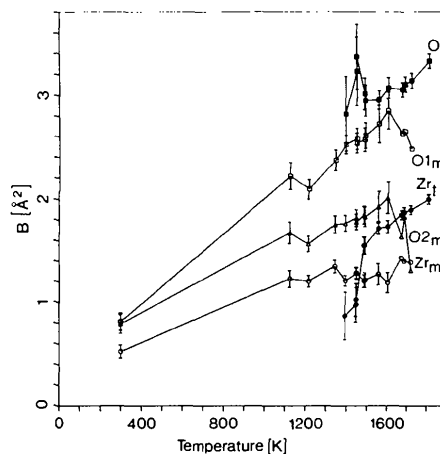

Fig. 3. Temperature dependence of the lattice constants. For convenience $2^{1/2}a_t$ and $a_m\sin\beta_m$ are shown.

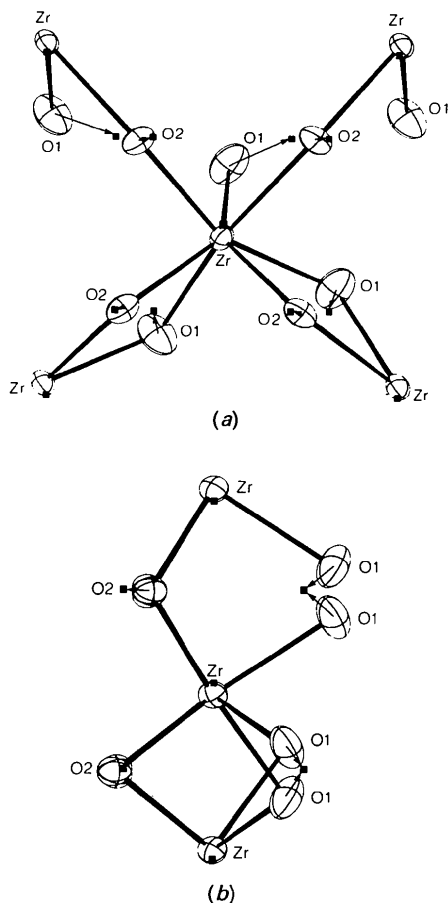Fig. 5. Temperature dependence of the isotropic temperature factors.

(a)

(b)

Fig. 6. Thermal ellipsoids at 1553 K in two projections: (a) orthogonal projection on the (100) plance (c axis horizontal, b_m corresponding to $2^{1/2}a_t$ vertical), (b) projection on the monoclinic $(a_m\sin\beta)b_m$ plane which is approximately the $(001)_m$ plane or the $(001)_t$ plane. The arrows indicate the proposed shifts from m to t.

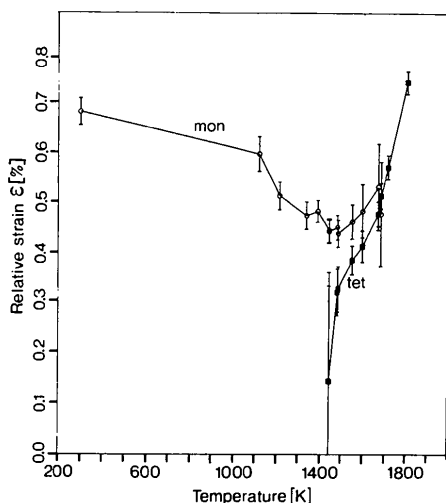The temperature dependence of the positional parameters is plotted in Fig. 4. For the monoclinic phase (Fig. 4a) they are given as deviations from their values in the tetragonal phase with $z(O)_t = 0\cdot4457$ (see Fig. 4b) for the only free positional parameter in $P4_2/nmc$. Equivalent or directly refined isotropic temperature factors are shown in Fig. 5. In this plot the rather large error bars ($\pm0\cdot20$–$\pm0\cdot55$ Å^2) in the monoclinic phase at 1670, 1693 and 1716 K have not been drawn for the sake of clarity. For the same reason the results for the tetragonal phase below 1350 K have been omitted. The thermal ellipsoids at 1553 K are shown in Fig. 6 as an illustration of the anisotropic temperature factors. The anisotropy and orientation of these ellipsoids does not change significantly with temperature. Oxygen-site occupancies have also been refined, leading to an almost constant value of $1\cdot04$ (1) for all temperatures and phases. The reason for this is not clear. Possible explanations are an uncertainty in the scattering length of Zr or the actual isotopic com-

(a)

(b)

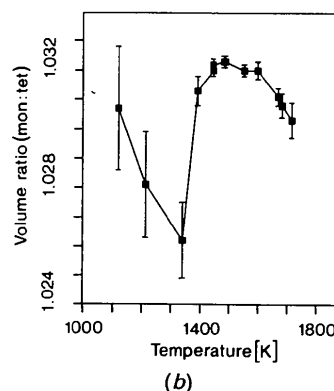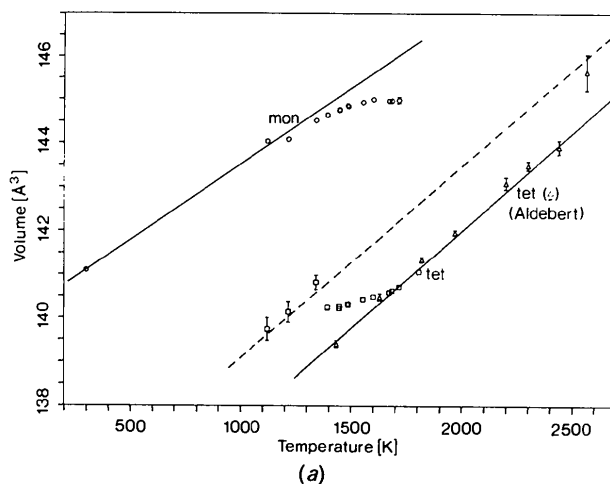Fig. 8. (a) Cell volumes [o, monoclinic; □, tetragonal; △, data published by Aldebert & Traverse (1985)]: the two points above 2500 K belong to the cubic ZrO_2 phase. (b) The ratio of the cell volumes $V_m:V_t$.

Fig. 7. Temperature dependence of microstrains ε.

position or even vacancies in the cation lattice. The values used were $b_{Zr} = 0.716 \times 10^{-12}$ cm and $b_O = 0.5805 \times 10^{-12}$ cm. In any case we observed no loss of oxygen upon heating to 1800 K.

A large variation in the widths of the peaks was found: with increasing temperature they become narrower in the monoclinic phase and broader in the tetragonal phase. Unfortunately, a reliable quantitative analysis in terms of particle sizes S and relative strains $\varepsilon = [(\overline{\Delta d/d})^2]^{1/2}$ according to the relation:

$$(\Delta 2\theta)^n = [K(\lambda/S)(1/\cos\theta)]^n \oplus (\varepsilon\tan\theta)^n \oplus (\Delta 2\theta)_i^n \quad (2)$$

was not possible because of ambiguities in the correct instrumental broadening $(\Delta 2\theta)_i$. The line profiles for a perfect powder standard are not purely Gaussian $(\eta \neq 1)$ and the correct kind of superposition of the individual terms in (2) depends on the peak shape produced by each broadening effect (convolution). This is indicated by the symbol $\oplus$ and the exponent n in (2). Simple sums $(\oplus = +)$ can be derived only if all contributions are exclusively Gaussian $(n = 2)$ or Lorentzian $(n = 1)$. Fits of $(\Delta 2\theta)$ versus θ for these two cases were only moderately satisfactory, but indicated that the main broadening is caused by strains only. This is further supported by the fact that there is no additional broadening at $2\theta = 0°$ [see (2)] within the limits of resolution. This leads to a lower limit for the particle size of about 1000 Å. Moreover, in the half-width formula (1) the refined U's are found to be the predominantly varying parameter [compare with (2)!]. The refined ε values obtained by quadratic superposition $(n = 2)$ are shown in Fig. 7. Similar curves with slightly different absolute values are obtained from a linear superposition. Hence, although the absolute numbers should not be taken too seriously, the striking general behaviour is definitely correct. In the following we will denote the strains discussed here, which cause the peak broadening and arise from fluctuations in the lattice constants, as microstrains. These will be distinguished from macrostrains which are the result of shifts in the average lattice constants from 'ideal' values (see below).

4. Discussion of the monoclinic→tetragonal transformation

We cannot, at least for our sample, define a sharp transformation point for the $m \rightarrow t$ transformation. From Fig. 2 we see a broad range of coexistence covering more than 600 K centered roughly around 1550 K. This is considerably larger than reported elsewhere [cf. Table 1 in Subbarao et al. (1974)].

Lattice parameters (macrostrains)

Concerning the lattice changes during transformation we found a normal expansion of the mono-

clinic lattice parameters only up to 1500 K [in agreement with data of Patil & Subbarao (1969) and Ruh, Hollenberg, Skaggs, Stoddard, Gac & Charles (1981)], but a kind of saturation of c_m and β, and even a slight decrease in c_m and increase in β at temperatures above 1650 K. Striking features are the considerable decrease in c_t at the very beginning of the transformation, i.e. below 1400 K, accompanied by a marked discontinuity in the shape of the a_t curve. The temperature dependence of the cell volumes also reflects this anomalous behaviour around 1500 K. Far from this temperature, on either side, both V_m and V_t show a linear dependence on T (Fig. 8a). Values of V_t obtained by Aldebert & Traverse (1985) are given in this figure and show good agreement above 1500 K. The deviations of both $V_m(T)$ and $V_t(T)$ from this linear dependence around 1500 K are obvious and indicate that strong macrostrains are present in the proper transformation range. The similarities of c_m and c_t and of $a_m\sin\beta_m$ and a_t at temperatures below 1400 K suggest a mutual relation between the corresponding planes and, possibly, an accommodation of the lattices via common interfaces roughly parallel to these planes. Therefore, the $V_m(T)$ and $V_t(T)$ behaviour could be explained in this temperature range as a consequence of some macrostrain. Unfortunately, thorough discussion is hampered by a lack of detailed knowledge concerning the orientational relationship. For example, Smith & Newkirk (1965) propose a parallelism of $(100)_m$ to $(100)_t$ and an alignment of the c axes $[001]_m\|[001]_t$, whereas Bansal & Heuer (1974) propose $(100)_m\|\sim(100)_t$, $[001]_m\|[001]_t$, and $[010]_m\|[001]_t$ below and above 1273 K, respectively. Other observations are listed in Table 3 of Subbarao et al. (1974). Apart from the possibility that the orientational relationship depends on differences in the sample material, there is obviously a dependence on temperature (change of the habit plane).

Below 1400 K the three lowest temperature points within the tetragonal modification show exceptional behaviour. In agreement with Patil & Subbarao (1970) who found a 'pretransformational regime' below 1380 K, we interpret this as a clear division between the two different stages of the $m \rightarrow t$ transformation (their observation of the variation of some d spacings is probably a consequence of the anomalous temperature dependence of c_m and c_t in this temperature region). Considering the ratio of V_m to V_t which plays an essential role in ZrO_2-based ceramics, we find (Fig. 8b) a sharp increase in $\Delta V/V$ from 2.6% at 1320 K to 3.2% at 1480 K. This ratio remains constant above 200 K and decreases at higher temperatures owing to expansion of V_t and the nearly constant value of V_m (Fig. 8a). The dashed line in Fig. 8(a) is drawn through the three tetragonal

points discussed above and two points measured by Aldebert & Traverse (1985) in the cubic phase: this 'fitting' could indicate an 'ideal' volume of ZrO_2 from which both polymorphs deviate strongly.

Structural changes

All our refinements were only successful with the monoclinic and tetragonal phases. Patil & Subbarao (1970) discuss the existence of a new 'hybrid' crystal structure. We feel that the arguments given by these authors in favour of this idea are not convincing since: (a) the variation of some interplanar spacings (see above) is no indication of a new structure; (b) intensity variations of some monoclinic reflections may be the result of variations of the static parameters (Fig. 4); (c) the observation that in an early stage of the transformation the $(101)_t$ reflexion is the only observable one is not unusual (it is the strongest reflexion at low scattering angles). If some disorder occurs during the rearrangement a static Debye–Waller factor would prevent the observation of more reflexions.

Monoclinic phase. The temperature dependence of the static parameters of Zr, O1, O2 in the monoclinic phase (Fig. 4) does not confirm the transformation mechanism proposed by Smith & Newkirk (1965) and similarly by Patil & Subbaraoo (1970) for the whole transformation range. These authors modelled possible atomic pathways, in particular for the O1 atoms, on the seven- to eightfold coordination of Zr. However, it is only between room temperature and 1100 K that there are slight shifts of all atoms towards their positions in the tetragonal phase: ~ 0.1 Å for O1 and ~ 0.02 Å for O2 and Zr (Fig. 4). This is also reflected in the bond distance between Zr and the O atom, which completes the eightfold coordination in the tetragonal phase (top left O1 in Fig. 6a). This distance, which is not even the smallest in the second coordination shell at room temperature, decreases from 3.74 (1) to 3.63 (1) Å. The thermal ellipsoids show a marked anisotropy roughly along the proposed displacement vectors (Fig. 6), which is again most pronounced for the O1 atoms which have to perform the largest shifts. In consequence, there are shallow potentials along these distinct directions which might facilitate atomic movements and initialize the transformation process. The inherent assumption of a displacive character of the transformation is also guided by the group–supergroup relation: $P2_1/c \rightarrow P2_1/c$ $2/c$ $2/a \rightarrow C2/c$ $2/c$ $2/a \rightarrow P4_2/n$ $2_1/n$ $2/c$.

The mean isotropic B factors (Fig. 5) of Zr and O2 also show saturation within the transformation region, while O1 exhibits a more or less 'normal' behaviour. The absolute values of the r.m.s. displacements even for O1 are, however, not remark-

ably large (~ 0.2 Å), in contrast to Grain & Garvie (1965) who reported a maximum mean amplitude of 0.4 Å within the (100) planes at 1339 K. This analysis of atomic displacement parameters does not support any dynamic mechanism as proposed elsewhere (Patil & Subbarao, 1970; Mitsuhashi, Fujiki, Tsukioka & Tsuda, 1971; Garvie & Chan, 1989; Negita & Takao, 1989). Linear extrapolation of the $B(T)$ curves down to 0 K (Fig. 5) reveals a small but distinct part at least for Zr and O2. We relate these phenomena to a static disordering within the monoclinic phase, which decreases in the course of the transformation. .

Tetragonal phase. In the tetragonal phase the only free positional parameter $z(O)$ shows a pronounced temperature dependence (Fig. 4). The initial shift from 0.40 to higher values seems to approach the 'cubic' value of 0.5, but saturates at 0.44. Together with the variation of the $c{:}a$ ratio the coordination polyhedron around Zr is considerably more distorted in the initial stage of the transformation where the two Zr—O bond lengths are 2.57 (1) and 2.00 (1) Å. At higher temperatures they become almost constant: 2.43 (1) and 2.09 (1) Å. The B-factor analysis reveals some remarkable features. Around 1480 K there is an increase in $B(O)$ (Fig. 5). This might reflect some static displacement disorder of the oxygens in the first transformed tetragonal grains. Above 1600 K the temperature dependence of the $B(O)_t$ factor follows closely that of the O1 atoms in the monoclinic phase. A quite analogous continuation holds for the Zr atoms. The anisotropy of the thermal ellipsoids is very small in this case.

Microstrains

As discussed in §3, microstrains which vary with temperature are present in both phases. Obviously there is a relevant contribution to the free energy from microstrains in the monoclinic phase which diminishes approaching the temperature range around 1400 K (Fig. 7). On the other hand, the first tetragonal particles occur nearly unstrained, but after completing the transformation (at about 1800 K) the tetragonal phase has an overall strain component comparable with that of the monoclinic phase at room temperature. The minimum miocrostrain in both phases at about 1500 K corresponds to the maximum macrostrain as discussed above (Fig. 8). Possibly 'domains' occur in a temperature interval around 1500 K where both phases coexist with coherent interfaces of small extension accounting for the minimum microstrain. This 'domain' model was proposed by Garvie (1965) and Patil & Subbarao (1970) to explain the changeover from a precursor (isothermal = diffusional) part of the transformation at $T \leq 1400$ K to the martensitic (athermal) part.

According to this model the character of the transformation is related to non-equilibrium conditions (kinetics). Further discussion of this point would require a knowledge of the whole strain tensor, i.e. its anisotropy as well as reliable results for the minority phases at the beginning and end of the transformation. Both cannot be deduced from the present data.

5. Concluding remarks

From a detailed analysis of positions, intensities and profiles of powder reflections we were able to verify some of the assumptions made earlier concerning the $m \rightarrow t$ transformation in pure ZrO_2. In particular, our results support a two-step transformation process: a precursor regime of displacive character and the martensitic part. The most surprising feature is the changeover from micro- to macro- to microstrains, especially the large microstrains present in the pure phases. We have no conclusive explanation for this behaviour. It might be caused by an 'ideal' (volume) packing of ZrO_2 from which both the monoclinic and tetragonal arrangements deviate. During transformation the volumes approach these values thus allowing release of the microstrains. Adopting this idea the relevant free energy includes strain terms which vary with temperature, as also reported by Chan, Li & Nevitt (1989). On the other hand microstrains might be caused by an intimate intergrowth of domains (twinning, microstructure) in each powder particle. The smaller volume of the first transformed tetragonal domains allows for their initial unstrained appearance which is observed until the intergrowth is recovered when the whole particle is transformed. The deviation of the tetragonal volume found by Aldebert & Traverse (1985) at 1420 K (see Fig. 8) might then be due to different samples. A domain model with internal interfaces was also discussed by Chan, Epperson, Fang & Li (1989).

Important structural questions still remain concerning: (a) the true orientational relationship between m and t ZrO_2 phases (this demands single-crystal work); (b) a detailed consideration of the strain tensors (see above); (c) the static or dynamic character of the displacement of the oxygens, which should be studied in more detail although a static component is obviously present; (d) the degree of disorder at any stage during the transformation, which demands a careful analysis of diffuse-scattering parts; (e) the time dependence, which must be studied in order to obtain a clear insight into the kinetics of the transformation. Note, that the reverse transformation $t \rightarrow m$, which was not investigated in our experiment, should show a remarkably different behaviour [see, for example, Subbarao (1981)].

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