β-$Be_{17}Ti_2$ is a relatively simple one, in which the $[010]_T$ direction becomes the $[0001]_H$ direction. Some titanium atoms must change from $a=0$ to $a=\frac{1}{2}$ positions, or *vice versa*, to complete the symmetry, and the removal of 7 Be atoms from the unit cell involves a small decrease in the atomic spacing in this direction, from 7·36 to about 7·30 Å. The removal of 7 atoms without disrupting the near-hexagonal symmetry displayed by the tetragonal arrangement in Fig. 2 appears difficult to accomplish. Removal of the two smaller layers is simple but results in a loss of 8 Be atoms. This raises the question of how accurately the composition of $Be_{17}Ti_2$ is known and whether a composition Be_8Ti is possible.

The other two hexagonal structures of Table 1 can be derived from this transformation. Raeuchle & Rundle's disordered hexagonal structure has the same c parameter as the β-$Be_{17}Ti_2$ structure and four times the a parameter; the α-$Be_{17}Ti_2$ structure has the same a parameter and approximately 1·5 times the c parameter. The above discussion also suggests the possibility that Raeuchle & Rundle's structure determination was carried out on crystals of $Be_{17}Ti_2$ instead of on crystals of $Be_{12}Ti$ as they believed.

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Direct high-temperature single-crystal observation of orientation relationship in zirconia phase transformation.

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Introduction

Zirconia undergoes a diffusionless phase transformation, in the neighborhood of 1000 °C, from a monoclinic structure, space group $P2_1/c$, to a tetragonal structure, space group $P4_2/nmc$.

From the data of McCullough & Trueblood (1959) for monoclinic zirconia and those of Teufer (1962) for tetragonal zirconia, one can draw the two projections of the structures shown in Figs. 1 and 2. The projections show four unit cells of the monoclinic structure. A fifth cell, indicated by dashed lines, differs only by the choice of origin in order to render it more directly comparable to the single tetragonal unit cell shown to the right. The tetragonal cell shown is not the conventional cell, but a double one that traditionally has been used for comparison

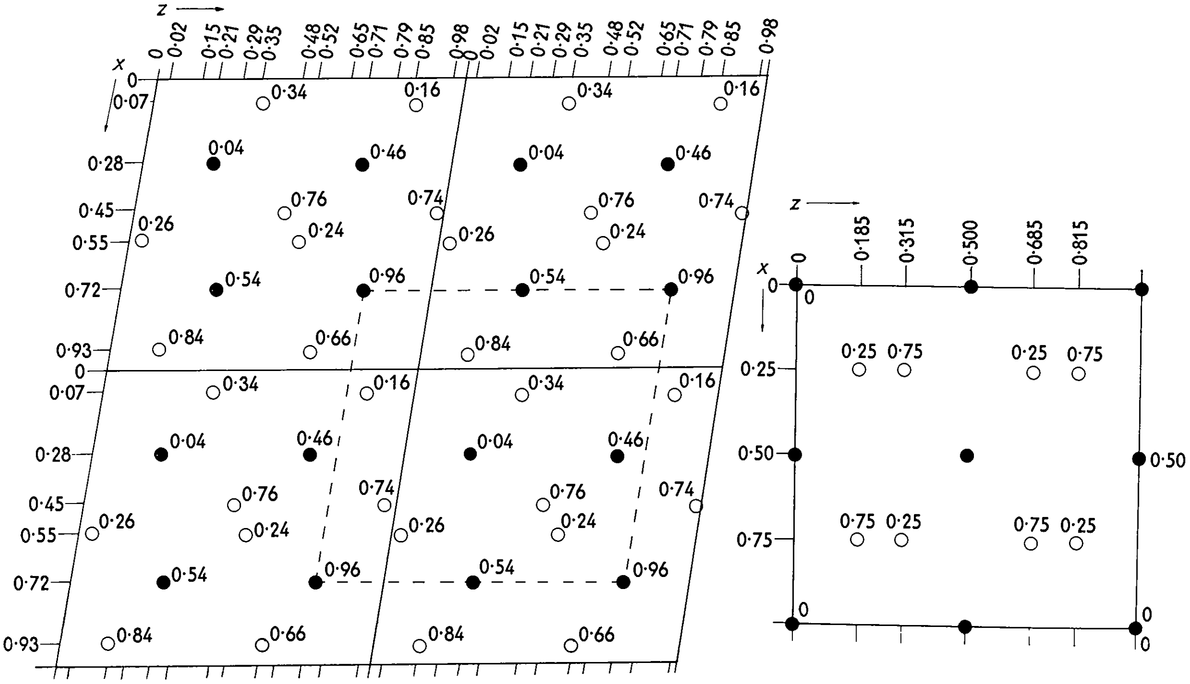

Fig. 1. Projection of ZrO_2 structure parallel to y direction onto x–z plane. Left: monoclinic. Right: Tetragonal. Parts of four monoclinic cells enclosed by broken lines become tetragonal cell after transformation. Solid circles: Zr. Open circles: O.

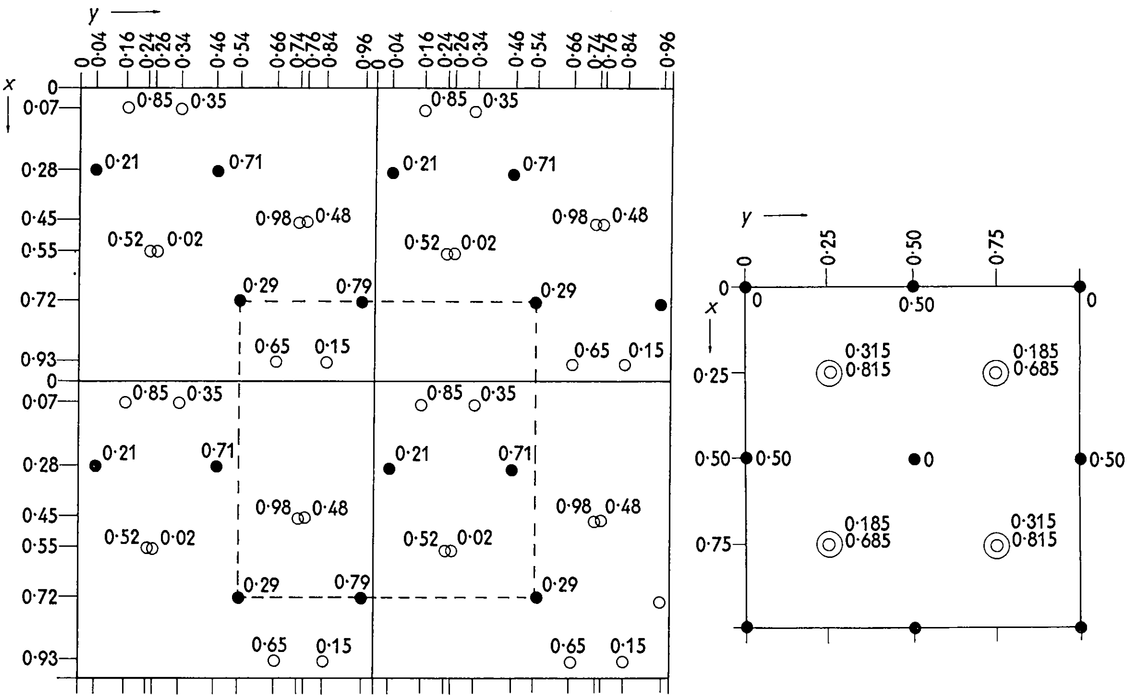

Fig. 2. Projection of ZrO_2 structure parallel to z direction onto x–y plane. Left: monoclinic. Right: tetragonal. Parts of four monoclinic cells enclosed by broken lines become tetragonal cell after transformation. Solid circles: Zr. Open circles: O.

with the monoclinic structure. The conventional cell is very nearly body-centered, and the larger one is nearly face-centered. The relationship between these cells with respect to size, orientation, and transformation matrices is the same that prevails between a truly body-centered tetragonal cell and its related, larger face-centered cell.

The atom movements incident to the phase transformation are immediately obvious from the projections. Furthermore, if a single crystal could be kept intact through the transformation, one might postulate that the tetragonal *c* axis would remain parallel to the monoclinic *c* axis, one tetragonal *a* axis parallel to the monoclinic *b* axis, and the remaining *a* axis necessarily inclined 9·2° to the monoclinic *a* axis.

The work reported here was undertaken to examine the validity of these predictions.

Materials

Single crystals of zirconia were difficult to obtain in the past, but recently the author's colleague, Dr. W. S. Ginell (private communication, to be published), has grown a large number of small monoclinic zirconia crystals by a variety of methods. To date, those crystals that have been examined were twinned by a 180° rotation about the *c* axis[*]. In many cases, including the crystals used for this work, the relative intensities of X-ray reflections indicated that the volume fractions of the two individuals were quite unequal. Using a similar crystal, Dr. Ginell obtained a photomicrograph under crossed polaroids which showed two thin lamellae of one orientation traversing a much larger bulk of the other orientation. Thus the bulk of the crystals used here had a single orientation, and the small amount of twinning is not likely to have affected the results. The twinning was examined by observing the appropriate duplicate reflections with a single-crystal orienter.

Experimental

The crystals were mounted on the end of a small aluminum oxide thermocouple insulator on a eucentric goniometer head, which, in turn, was placed on a General Electric single-crystal orienter. The crystals were attached in one case with Zircoset ceramic cement, and in another case tied with 38-gauge platinum wire. The crystals were oriented with the a^* and c^* axes in the plane of the diffractometer, and the b^* axis vertical. In order to heat the crystal, an oxy-gas torch was lowered over it, with the flame adjusted to a size that just enveloped the crystal alone. The crystals were approximately 1·5 × 1·0 × 0·5 mm, in the directions parallel to c_0, parallel to b_0 and normal to (100), respectively.

Results and discussion

In the case of the crystal attached with Zircoset, the cement reacted with the crystal and stabilized the tetragonal phase; therefore, the results could not be considered reliable. For this reason, the experiment was repeated with a crystal tied into place with platinum wire. The

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[*] The *c* axis is thus the twin axis. Alternatively, this twinning can be described as a 180° rotation about the normal to (100), the latter being the twin plane. This type of twinning is common in the mineral baddeleyite, where it is described as 100 twinning, or loosely as a reflection in (100). Other types of twinning, observed occasionally, were absent from the crystals used for this work.

nature and orientation of the tetragonal crystal while hot turned out to be exactly the same as in the first case. However, in this second case, since the crystal reverted to the monoclinic structure on cooling, it was possible to obtain some information on the reverse transformation.

As soon as a crystal was heated above ~1200 °C, tetragonal reflections could be observed. There were, of course, three orthogonal axes, and one of these, as predicted, was parallel to the original monoclinic b axis. However, instead of one axis being parallel to monoclinic c and one 9·2° from a, the two tetragonal axes split the difference, *i.e.* the 90° tetragonal angle was inscribed, approximately symmetrically, within the larger monoclinic angle, β. Although somewhat unexpected, this becomes plausible when one considers the next result. The tetragonal crystal was a triplet, and each axial direction gave a reflection both for a^* and for c^*.

Removal of the flame resulted in quenching of the crystal, and the one that was tied with wire reverted to the monoclinic structure. Its reflections were now broad and of low peak height. The extent of twinning was considerably enhanced, and in addition the crystal now consisted of a number of slightly misoriented blocks, still parallel along the original $\mathbf{b}$ direction but rotated out of register in the $a-c$ plane over a range of about 10°. Since the tetragonal axes must rotate 4 to 5° in the a–c plane to become the monoclinic a and c axes, the various partners of the tetragonal trilling must have rotated their respective axes in opposite senses, thus giving rise to the 10° spread in orientation.

The observational evidence does not furnish a clear decision as to whether the transformation is of the brittle martensitic or the true martensitic type (Wolten 1963), but favors the latter point of view.

If the transformation is martensitic, it should be possible, in principle, to apply the theory of zero average strain by Wechsler, Lieberman & Read (1953) for the calculation of the habit plane. The term 'habit plane', as used here, does not refer to the crystal habit but denotes a crystallographic plane which, in a martensitic phase transformation, is common to both lattices and remains undistorted and unrotated through the transformation. The calculation cannot, at present, be carried out for lack of certain additional data. However, the observations plainly suggest that the habit plane is the monoclinic (101) which becomes (101), (110), and (011) of the tetragonal trilling, indexed on the double cell. The misfit of the attice parameters is relieved by twinning.

The data that are lacking for the application of the theory are the lattice parameters of the monoclinic phase at the temperature of the transformation. The tetragonal parameters were measured directly by Teufer (1962) at 1250 °C, a little above the transformation range. The lattice parameters of the monoclinic phase are accurately known only at room temperature*. A mean (bulk) coefficient of thermal expansion for zirconia is known (Fulkerson, 1960), but if this is applied to the room temperature cell volume and extrapolated to 1250 °C, a volume difference of about 1% between the phases is obtained, which is inconsistent with the observed bulk volume change of the transformation of about 7% (Geller & Yavorsky, 1945). It is clear, therefore, that the coefficient of expansion of the monoclinic phase must change rapidly above 1000 °C. This effect would distort dilatometric curves of the transformation and explain the discrepancy between dilatometric and X-ray transformation temperatures noted by Duwez & Odel (1950).

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* Lattice parameters for monoclinic zirconia were determined by McCullough & Trueblood (1959) using a single crystal of baddeleyite and by Adam & Rogers (1959) using synthetic ZrO_2 powder. The discrepancy between the two sets of data is very slight but results in significant differences in calculated interplanar spacings at low diffraction angles. The spacings observed by the author on many occasions, as well as those reported by Ferguson (1960), for synthetic ZrO_2 consistently agreed with those calculated from the lattice parameters of Adam & Rogers.

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Determination of particle size and strain in a distorted polycrystalline aggregate by the method of variance.

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Recent work by Tournarie (1956 *a*, *b*) and Wilson (1962 *a*, *b*, *c*; 1963) has clearly established the usefulness of the variance of an X-ray diffraction line profile due to an aggregate of distorted crystallites as a measure of the particle size and strain of the aggregate. Langford & Wilson (1963) and Halder & Mitra (1963) have described practical methods of determining particle size and strain from the study of variances of the line profiles. Both the methods are extremely dependent on the choice of the range over which the variance has been determined. The present work describes a graphical method in which this difficulty has been removed.

Wilson (1962 *b*) has shown that, if the entire line broadening is due to particle size effect, the variance of the line profile in 2θ,