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Features of the monoclinic-tetragonal transition in ZrO_2

© *V.P. Gorelov, S.A. Belyakov*

Institute of High-Temperature Electrochemistry, Ural Branch, Russian Academy of Sciences,
Yekaterinburg, Russia

E-mail: gorelov@ihte.ru

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A critical analysis of the features of the monoclinic-tetragonal ($m \leftrightarrow t$) phase transition in ZrO_2 has been carried out, taking into account the existence of three monoclinic forms m, m' and m'', which change one into another with increasing temperature, as well as the state of the material (single crystal, ceramics, powder). The dilatometric effects accompanying the transition on ceramic samples, namely jumps in the curve and their features, were experimentally studied and discussed. It has been shown that the jumps are a consequence of material cracking during the $m'' \leftrightarrow t$ transition and are not the transition itself.

Keywords: ZrO2, dilatometry, DTA, monoclinic polymorphs.

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1. Introduction

The remarkable properties of materials based on zirconium dioxide ZrO_2 provided them with wide and varied applications in various fields, and they continue to be actively studied [1–8].

Zirconium dioxide has a complex polymorphism, including high pressure phases. Under normal conditions, the monoclinic form of ZrO_2 (baddeleyite) with space group $P2_1/c$ (№ 14) is thermodynamically stable. As the temperature increases, the monoclinic structure (m) transforms into a tetragonal structure (t) with space group $P4_2/nmc$ (№ 137). The existence of this transition around $1000^\circ C$ was first reported by Ruff and Ebert in 1929 [9]. They were the first to study the influence of the additions of MgO, CaO, Y_2O_3 and Sc_2O_3 on the transition temperature, and also established that the high-temperature phase does not harden even from the melting point of ZrO_2.

The indicated monoclinic-tetragonal ($m \leftrightarrow t$) transition in ZrO_2 belongs to the martensitic type, as the hexagonal-cubic phase transition in metallic zirconium. The transition is accompanied by large bulk changes (the densities of the monoclinic and tetragonal phases are 5.65 and $6.10\,g/cm^3$, respectively [10]), which leads to destructive mechanical stresses and a complication of the transition pattern. In the stress field, lamellar twinning of the tetragonal phase [11–13] occurs, dislocation loops [12] appear, and high-pressure orthorhombic phases [3,14,15] can form. The most complex situation is at the junction of crystallites due to the wide variety of orientation options [16].

Considering the practical importance of zirconium dioxide, $m \leftrightarrow t$-transition was actively studied by many researchers on powders, on ceramic samples and on single crystals using various high-temperature methods [1–8]. The experimental methods presented in the literature for studying the phase transition $m \leftrightarrow t$ in ZrO_2 are divided into two groups: direct structural methods (X-ray diffraction, neutron diffraction, Raman scattering spectroscopy (RSS)) and indirect methods (dilatometry, electrical conductivity measurements, differential thermal analysis (DTA), high-temperature microscopy). The results of these two groups of methods are not just contradictory, but give directly opposite conclusions. Indirect methods showed that changes in the sample, attributed to the phase transition $m \leftrightarrow t$, occur abruptly. At the same time, direct structural methods do not detect the abrupt transition; it occurs continuously in a wide temperature range about $150-200^\circ C$.

To describe the $m \leftrightarrow t$-transition, the most developed model is the shear deformation of crystals, which describes a set of orientation relationships between the structures m and t through the habit plane [6,11,12,16–25]. The problems of such description and the complexity of the transition pattern forced some authors to accept [6,19,26,27] that $m \leftrightarrow t$-transition can occur in parallel along the martensitic and non-martensitic paths, depending on the mutual orientations of the crystallites and the resulting mechanical stresses. It was assumed that the free surface of crystallites is one of the centers of the direct martensitic transition [23,24], and at the junction of crystallites a wide variety of orientation options is possible. In this case, a favorable mutual arrangement of crystallites promotes a direct $m \leftrightarrow t$-transition [6,16,23,24], while an unfavorable arrangement can lead to the formation of high-pressure rhombic phases [14,26–28].

However, repeated attempts to construct a crystallographic model of the $m \leftrightarrow t$-transition were unsuccessful. The failure of such attempts is due to the prohibition of direct transition between the above space groups of the monoclinic and tetragonal modifications of ZrO_2. To transit between them, at least two intermediate transitions are required [29,30].

According to Evarestov *et al.* [30], $m \leftrightarrow t$-transition is regulated by three phonon modes, each individual mode induces the transition from structure to an intermediate structure with space groups $C_{2/c}$ (№ 15), $Pbcn$ (№ 60) and $Pcca$ (№ 54).

With numerous observations of the $m \leftrightarrow t$-transition the intermediate phase transitions constantly manifested themselves in experiments. Researchers noted and discussed the structural changes that precede the transition. The concept „pretransformation" was even introduced. This was the option that, in particular, Patil and Subbarao were forced to use in 1970 [22] to describe this region, since no one suggested the existence of intermediate monoclinic polymorphs. And since the „pretransition" was not observed during cooling, it was concluded that the direct and reverse transitions occur under different mechanisms: the direct transition occurs as a two-stage transition, and the reverse transition as a single-stage transition. This point of view was supported by the authors of the papers [31,32], as well as by Simeone *et al.* [21], who performed an extensive study of the $m \leftrightarrow t$-transition in ZrO_2 using high-resolution powder neutronography (Grenoble) from room temperature to 1900 K (1627°C).

A focused study conducted by us [33] using high-temperature dilatometry (up to 1500°C), electrical conductivity and RSS (up to 900°C) with analysis of experimental curves using Suzuki method clearly revealed kinks in the temperature dependences of expansion and electrical conductivity. These kinks indicate phase transitions at 350 ± 20°C and at 730 ± 20°C — hence, the existence of two intermediate ZrO_2 polymorphs in the monoclinic region predicted in works [29,30]. RSS spectra taken after 50°C in the range up to 900°C confirmed that the detected transitions occur within the monoclinic system.

Taking into account the results of the papers [29–30,33,34] it can be stated that at normal pressure in the temperature range from room temperature to melting point ZrO_2 has 6 stable polymorphic modifications, transforming into one another with temperature increasing: three monoclinic, two tetragonal and one cubic. By analogy with the accepted designations t and t' for tetragonal polymorphs of ZrO_2 [34], we designated monoclinic polymorphs as m, m' and m''. Then the complete $m \leftrightarrow t$-transition proceeds according to the scheme $m \leftrightarrow m' \leftrightarrow m'' \leftrightarrow t$, and the „pretransition", as the intermediate hybrid structure, is excluded.

The discovery of transitional monoclinic polymorphs m' and m'' forces us to more carefully analyze the $m \leftrightarrow t$-transition itself — in particular, the features of the jumps that we noted on the dilatometric curves accompanying transition. At the same time, the authors did not set the task to write a review, but only to draw correct conclusions using reliably performed experimental results available in the literature.

2. Experimental part

Ceramic samples in the form of bars 40 mm long and with cross-section 4×4 mm were made from zirconium dioxide of special purity 99.999% [35]. To avoid the oxide contamination the powder was not ground before pressing. The compacts were sintered in air at temperatures of 1300 and 1500°C (3 h) with heating and cooling rates of 3°C/min. The geometric density of the samples sintered at 1500°C was $75 \pm 2\%$ of the theoretical, equal to 5.65 g/cm^3 [10]. Note that the measured density was obtained after sample cracking as a result of the transition and is not a correct characteristic of its density.

Thermal expansion was studied by optical dilatometry on the ODP-868 platform (TA Instruments, USA) in horizontal mode in cycles of heating–cooling to 1500°C, as well as to 1300°C, with heating and cooling rates 1°C/min [33].

Scanning electron microscopy (SEM) was performed using a MIRA 3 LMU microscope (TESCAN, Czech Republic).

3. Results and discussion

3.1. Transition $m'' \leftrightarrow t$ in single-crystals ZrO_2

Single crystals cannot be defect-free, but nevertheless they are more perfect objects than ceramics or powders, so it is advisable to discuss the features of the $m'' \leftrightarrow t$-transition coarse first in them, based on literature data.

A unique study of thermal effects accompanying the $m \leftrightarrow t$-transition in ZrO_2 was carried out in the paper of Mitsuhashi and Fujiki [35] on ~ 60 single-crystals. The single-crystals were grown by the flux method, as well as by the hydrothermal method, and had dimensions of 1–3 and 0.4–0.7 mm, respectively. During heating DTA detected a sharp endothermic peak with a vertical front. In this case, the verticality of the front did not depend on the heating rate in the rate range from 0.625 to 10°C/min, and the half-width of the peak was 0.04°C, which indicates a very high rate of the process, as it should be during a diffusionless martensitic transition. The statistics collected in the paper showed that even for single-crystals the temperature of the DTA peaks is not constant, but during heating lies in the range 1160–1190°C with a distribution maximum at 1175°C, and in the range 1100–1070°C when cooling. When measuring crystalline aggregates, the number of DTA peaks corresponded to the number of crystals in the aggregate, confirming that for different crystals, even under strictly identical conditions, the peak temperatures are different.

It is clear that if DTA measurements are carried out on a statistically significant ensemble of such single-crystals, then an integral diffuse peak with a length of 30°C will be observed, and the X-ray diffraction method will record a phase transition extended by the same amount. Polycrystals in the form of powders and ceramics make up such ensembles. But, due to the greater scattering in defectiveness, the width of the DTA peaks for them will be greater. For example, even for a monomodal powder of ZrO_2 with rounded particles of the same size 80 nm, the width of the DTA peaks exceeded 60°C [15], and for nanopowder with an average size 50 nm obtained through hydroxides, the DTA peak during the reverse transition had length of about 170°C [36].

Let's return to single-crystals [35]. Microscopy showed that after DTA the single-crystals cracked, transforming into polycrystals. The fact of cracking indicates a significant defectiveness of single-crystals. To rearrange the structure during the $m'' \leftrightarrow t$-transition, some overheating (or overcooling during the reverse transition) is required, its magnitude depends on the concentration of defects and the strength of the sample (we use the term „strength" in the generally accepted sense, as the ability of the material resist destruction).

This model is confirmed by high-temperature optical microscopy of single-crystals ZrO_2 [11], which made it possible to see the details of the transition process. When heated to $\sim 1100^\circ$C no changes were observed. At higher temperatures, movement of the interference fringes was observed. Above 1200°C the transition became visible due to the rapid formation of a twin substructure, accompanied by cracking. Due to cracking and jumping of the crystals, they had to be clamped between sapphire or MgO plates. The authors also noted that in the case of observing two single-crystals located next to each other, their cracking temperatures were not the same, differing by 35°C.

From the above it follows that transition $m'' \leftrightarrow t$ in single-crystals ZrO_2 occurs simultaneously with cracking, which is accompanied by DTA peaks. It is clear that cracking will correspond to jumps in the dilatometric curve and in the temperature dependence of electrical conductivity.

In a defect-free single-crystal the DTA peak would characterize the heat of the phase transition. In a real single-crystal, the DTA peak is the sum of thermal effects caused by both the phase transition and the process associated with cracking and the sample surface increasing.

However, for the real single-crystal, the question remains: whether all stresses in the sample disappear after cracking? Apparently not. Therefore, the moment of cracking is not the completion of the phase transition $m'' \leftrightarrow t$. The clear two-stage nature and extension of the reverse jump, measured on single-crystal ZrO_2 by the electrical conductivity method in the paper [37], clearly confirms this.

3.2. Transition $m'' \leftrightarrow t$ in ceramic samples ZrO_2

The ceramic sample can be considered as an ensemble of micron-sized single-crystals interconnected by boundaries. Therefore, the behavior of ceramic samples ZrO_2 should be similar to the statistically averaged behavior of the ensemble of single-crystals. But this is not entirely true. The decreasing of single-crystals by several orders of magnitude and the binding of their boundaries in ceramic sample leads to change in the properties of such ensemble with respect to the phase transition $m'' \leftrightarrow t$.

The processes occurring during the transition in ceramic sample ZrO_2 are clearly determined by the strength of the grains binding along the boundaries, i.e., they depend on the sample density. Extreme cases are observed in porous and dense samples. In a sufficiently porous sample (our case), weak boundaries cannot slow down the change in grain habit during transition, and the grains do not twin due to stress and are not destroyed. The sample cracking occurs along weak grain boundaries, which is well illustrated by a micrograph of the sample after sintering (Figure 1).

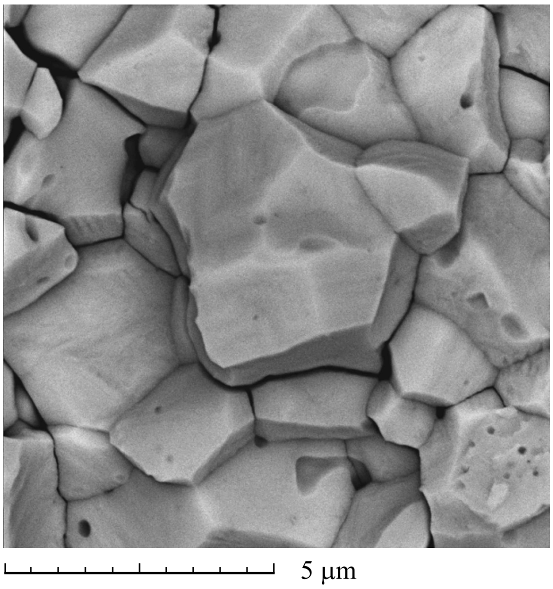

Figure 1. SEM images of broken ceramic sample ZrO_2 sintered at 1500°C (3 h).

In a dense ceramic sample, such as in the paper [38], when the sample was sintered in vacuum at 2000°C for 20 h, the dense boundaries do not allow the grain to change the habit, and grains twin along planes and crack.

The physical pattern of the transition in the ceramic sample is generally clear. Both direct and reverse $m'' \leftrightarrow t$-transition in polycrystal should begin with the fine grains, which have the least difficulty in changing habit (with or without cracking). The transition should end in the largest grains, which have the greatest difficulties in changing habit and require the greatest overheating (or overcooling) to implement the transition. This explains the stretching of the $m \leftrightarrow t$-transition in the polycrystal by 150−200°C.

Stresses accumulating in the polycrystalline sample during stretched transition upon reaching the ultimate strength lead to its sudden cracking. The moment of cracking will correspond to jump in the dilatometric curve or in the electrical conductivity curve, the temperature of which exceeds the beginning of the transition by more than 100°C. However, the phase transition does not complete, as it is shown by structural methods, although the excess of the temperature jump cannot be called significant [1–8]. From this pattern we can conclude that the moment of polycrystal cracking is certainly caused by the $m'' \leftrightarrow t$-transition process, but is not the transition itself, correlating with the ultimate strength of the sample.

During the direct $m'' \leftrightarrow t$-transition the volume of the tetragonal lattice decreases, which facilitates shear deformation inside the monoclinic matrix. Neutron diffraction

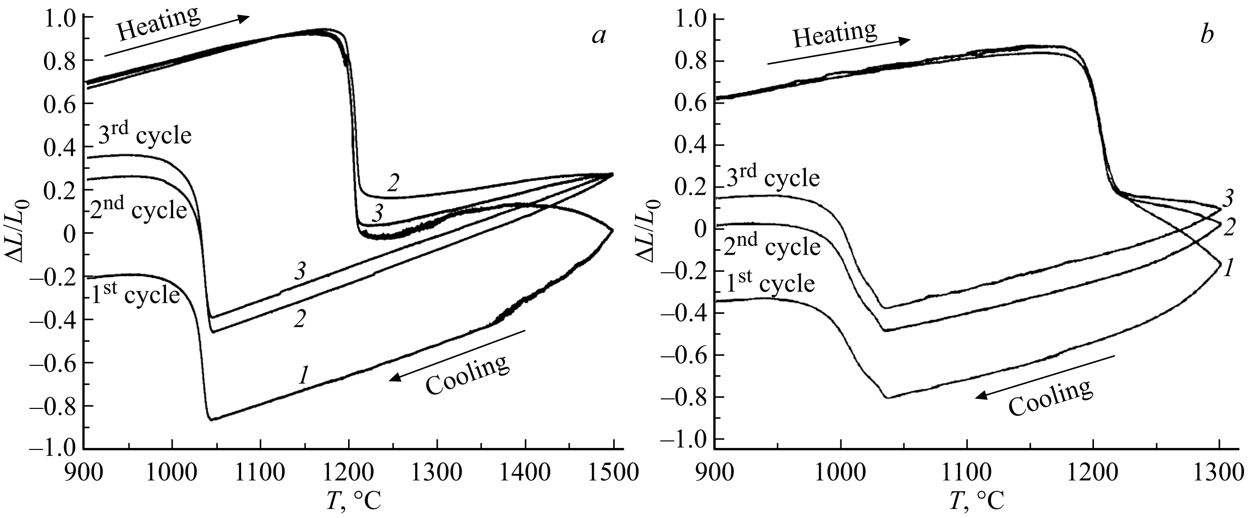

Figure 2. Sections of dilatometric curves taken up to *a*) 1500°C and *b*) 1300°C on ceramic samples ZrO_2 for three consecutive measurement cycles. The samples were sintered at 1500 and 1300°C, respectively.

study confirms that grains t-phase of the ZrO_2 when they appear at the beginning of the transition have minimal microstresses [39]. Consequently, the temperature at which the first tetragonal grains appear can be taken as temperature close to the thermodynamic equilibrium for the $m'' \leftrightarrow t$-transition in ZrO_2. The kink in the dilatometric curve in this region [38], corresponding to the beginning of the transition, allows us to assume that this temperature is not higher than 1050°C.

3.3. Dilatometric features of $m'' \leftrightarrow t$-transition in ZrO_2

The characteristic feature of the dilatometric curves for ZrO_2 in the region of the phase transition under study is the presence of clearly expressed jumps during heating and cooling: see, for example, [38]. Our dilatometric curves also have this form: during heating the jump is observed at 1208 ± 10°C and reverse jump — approximately by 150°C lower (Figure 2). During heating, the jump is accompanied by a decrease in the size of the sample, and during cooling by increasing.

The cooling curves in the dilatometric cycle heating–cooling always go below the heating curves (Figure 2), which is due to sintering (shrinkage) of the sample in the high-temperature section above the jump. Sintering is especially evident in the first cycle heating–cooling when survey up to 1500°C (Figure 2, *a*). Gradual sintering is clearly visible when survey up to 1300°C (Figure 2, *b*): after jump during heating the curves go down, not up, as should be during thermal expansion of the material, which indicates the sample shrinkage. In this case, the amount of shrinkage decreases with each subsequent cycle.

Before measurements the samples were sintered at 1500 and 1300°C, respectively, for 3 h, so significant shrinkage below sintering temperatures should not be observed. It follows that sintering is provoked by the energy of mechanical stresses that are created in the sample as a result of the transition. The „rerpair“ of cracks in ceramic samples of ZrO_2 already at 1200°C is indicated in the paper [40]. During the reverse jump, the sintered samples crack again.

During heating the beginning and end of the jumps observed on the curves, are rounded (Figure 2). One could assume that these roundings are due to the inhomogeneity of the temperature field, but during cooling the jumps begin very sharply, acute angles around 1040°C are visible, although the end of the reverse jumps is also rounded. Hence, the roundings are not associated with the inhomogeneity of the temperature field. They are clearly due to the fact that the phase transition begins before the jump and ends after it. This type is typical for the deformation curves of materials under load as they approach their ultimate strength.

However, let's return to the acute angle for the reverse jump around 1040°C. Its presence indicates the asymmetry in the processes of direct and reverse transitions, which certainly exists and is determined by the very nature of the phases. During heating the occurring t-phase decreases in volume and is prone to twinning, while during cooling the occurring m''-phase increases in volume, experiencing strong compressive stresses and is not prone to twinning [5]. It is known that materials based on the stabilized t-phase have extraordinary strength [41]. If high strength is also maintained for the undoped tetragonal modification, then the separation of grains of the m''-phase from the tetragonal matrix during cooling will be very difficult. Apparently, the observed large hysteresis of the $m'' \leftrightarrow t$-transition and the acute angle at the jump during cooling should be attributed precisely to the manifestation of the special strength of the t-phase.

On the dilatometric curves taken during heating to 1500°C, the vertical sections of the direct and reverse jump are smooth and have no features (Figure 2, *a*). This indicates that in these sections the sample cracking occurs without stops or delays, as a single process. If the survey is carried out with heating up to 1300°C, then the type of the reverse jump changes: it becomes two-stage and significantly gentle (Figure 2, *b*). And this pattern is reproduced when the survey is repeated several times. A well-defined two-stage reverse jump was also observed by the electrical conductivity method on single-crystal ZrO_2 (99.85%) in the paper [37] after maximum heating temperature of about 1150°C. Note that double DTA peak during cooling was observed on powder ZrO_2 after survey up to 1300°C [15].

The two-stage nature of the reverse jump and its gentle nature mean that some stages of the direct phase transition $m'' \leftrightarrow t$ did not end at temperature 1300°C, and these unfinished stages slow down the reverse jump until a step appears (Figure 2, *b*). Heating to 1500°C is sufficient to complete these stages.

Three assumptions can be made about possible unfinished stages: 1) stresses remain in the sample after the $m'' \leftrightarrow t$-transition, 2) $m'' \leftrightarrow t$-transition did not complete, and monoclinic phase presents in the sample, 3) high stresses in the sample cause the appearance of high-pressure phases, if we take into account the data of [3,14,26–28].

The first assumption is obvious, since cracking is result of the stresses, that will certainly remain in the sample after the transition. However, stresses can explain the broadening of the reverse jump, but not its step pattern. The presence of step is the existence of some additional structure in the sample. For example, the remains of the monoclinic phase.

But the second assumption about the monoclinic phase presence above 1300°C should be discarded, since diffraction studies show that $m \to t$-transition is ends at temperatures no higher than 1230°C. For example, a thorough neutron diffraction study on powders ZrO_2 with particle size $10\,\mu$m [21] confirms that the lines of the monoclinic phase are observed not exceeding 1500 K (1227°C).

It is possible that it is the third reason responsible for the step appearance. This assumption is probably realized in the paper [39], the results of which, also obtained by the high-resolution neutron diffraction method, drastically differ from the general series. The authors surveyed the $m \to t$-transition in ZrO_2 up to 1800 K (1527°C) and report that they observed a monoclinic phase almost up to the maximum temperature, i. e. recorded it almost by 300 degrees higher than other researchers. Such large deviation suggests the presence of either specific properties in the sample or an error in the method.

Nevertheless, the temperature of 1800 K is too high to maintain the monoclinic structure of ZrO_2. The possible admixture of a few percent of HfO_2 cannot influence the phase transition temperature so much. It is most likely that the pattern of the phase transition is distorted by the presence of high-pressure orthorhombic phase, at its low content it is difficult to distinguish this phase from the monoclinic phase. Indeed, according to the authors data, the volume of the lattice cell of the tetragonal phase continuously increases to 1800 K (1527°C), while in the temperature dependence of the volume of the monoclinic cell the authors observe the kink at about 1500 K (1227°C), i. e., at the temperature below which the monoclinic phase is usually observed. With a further increase in temperature, the volume of the lattice cell of the monoclinic phase does not change. This behavior is consistent with the properties of the high-pressure phase of the cotunnite $PbCl_2$ type, the formation of which is accompanied by a decrease in volume, and it is stable up to 1800°C and 24 GPa [4].

4. Conclusion

The monoclinic-tetragonal $(m \leftrightarrow t)$ phase transition in ZrO_2 occurs as a sequence of transitions between polymorphs $m \leftrightarrow m' \leftrightarrow m'' \leftrightarrow t$, at that the stage $m'' \leftrightarrow t$ is accompanied by the appearance of significant stresses in the samples, which lead to cracking of both single-crystals and ceramic samples. Cracking does not complete the phase transition, but it corresponds to jumps in the dilatometric curves and in the electrical conductivity dependences.

The strength of the bond between grains along the boundaries of the ceramic sample determines the degree of their twinning during transition: the stronger the bond is, the stronger the twinning and cracking are.

The two-stage nature of the reverse jump in dilatometric measurements up to 1300°C is probably due to the presence of high-pressure phases after the direct phase transition.

To explain the significant hysteresis during the $m'' \leftrightarrow t$-transition, a model of difficulties in isolating the m''-structure from the strong tetragonal matrix is proposed.

The thermodynamic temperature of the direct $m'' \leftrightarrow t$-transition was estimated, it does not exceed 1050°C.

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Conflict of interest

The authors declare that they have no conflict of interest.

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