

# Collapsed hexagonal $\omega$ phase in a compressed TiZr alloy: Angle-dispersive synchrotron-radiation x-ray diffraction study

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An *in situ* high-temperature high-pressure angle-dispersive synchrotron radiation diffraction study has revealed the  $\omega$ -to- $\omega'$  isostructural transformation in the equiatomic TiZr alloy. Volume collapse across the phase transformation is about 14%. On further compression the collapsed  $\omega'$  structure transforms to a noncollapsed cubic  $\beta$  structure with the partial atomic volume increase about 13%. Observed effects are discussed in terms of the *s-d* electron transfer and nonadiabatic electron-phonon interactions.

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## I. INTRODUCTION

The last decade has seen considerable activity, on both the theoretical and experimental fronts, in the study of the pressure-induced phase transitions in group IVb elements Ti, Zr, and Hf. The fundamental interest in the group IVb metals and their alloys stems from the fact that they have a narrow *d* band in the midst of a broad *sp* band, and this has a major impact on their electronic and superconducting properties. The electronic transfer between the nearly free-electron *s* band and the tight-binding *d* band has been considered as the driving force behind many structural transitions.<sup>1-4</sup> With increasing pressure and a concomitant volume reduction, a lowering of the *d* band relative to the *s* band results in an increase of the number of *d* electrons. The increase in *d*-electron population by transfer of electrons from the *s* band should then lead to a decrease of the metallic radius. This assumption is supported by numerous theoretical calculations of the electronic structure of the IVb metals under pressure;<sup>1,3,4</sup> however, experimental arguments in favor of this hypothesis have never been obtained so far. Our paper presents the results of an *in situ* high-temperature and high-pressure synchrotron diffraction study of the equiatomic disordered TiZr alloy. We present experimental evidences not only for the electron driven atomic volume collapse but also for the unprecedented pressure induced partial phase volume increase, in TiZr alloy.

## II. EXPERIMENTAL METHODS

Synchrotron radiation powder-diffraction measurements were performed at the high-pressure (ID30) beam line at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) by the angle-dispersive technique using monochromatic radiation ( $\lambda=0.3738$  Å). The beam was focused down to a pin hole 12  $\mu\text{m}$  full width at half maximum (FWHM) in diameter. The two-dimensional Debye-Scherrer rings recorded with a Bruker CCD detector were converted to one-dimensional intensity vs  $2\theta$  pattern, using ESRF's Fit2D software.<sup>5</sup> The sample-to-detector distance and the image

plate inclination angles were precisely calibrated using a silicon standard. Full-profile refinements of the powder x-ray diffraction data were carried out using the FULLPROF package.<sup>6</sup> High-pressure experiments were performed in a four-pin diamond-anvil cell.<sup>7</sup> Whole cell was heated providing completely homogeneous temperature distribution within pressure chamber. Diamonds with culets of 300  $\mu\text{m}$  were mounted on the seats with 30° opening angle. Gaskets were made out of a 250- $\mu\text{m}$ -thick Re sheet that was preindented to 20 to 25  $\mu\text{m}$  thickness. The sample was packed into the hole of 100–120  $\mu\text{m}$  in diameter. We used Au wire (99.99%, 5 mm in diameter), placed near the center of the pressure chamber, as the internal pressure standard.<sup>8</sup>

Alloy samples were prepared from Ti and Zr iodide rods melted in vacuum by electric arc. The purity of molten Ti and Zr was 99.98 and 99.96 %, respectively; the interstitial impurities were taken into account. The alloy composition controlled with x-ray diffraction technique was found to be Ti<sub>49.6</sub>Zr<sub>50.4</sub>. Special attention was paid to the homogeneity of the samples and the absence of any kind of precipitation or phase separation. The quenched samples from the electrically heated DAC were recovered and analyzed using SEM (LEO 1500), electron microprobe (CAMECA SX 50), and PHILIPS CM20 FEG analytical transmission electron microscope at BGI. We have found that high-pressure and temperature treatment did not result in any chemical reaction, and the chemical composition and homogeneity of recovered material was identical with starting one.

## III. RESULTS AND DISCUSSIONS

### A. Phase transitions at ambient temperature

At room temperature the group-IV metals titanium and zirconium transform under pressure from the hexagonal close-packed (hcp)  $\alpha$ -phase [space group (SG)  $P6_3/mmc$ ,  $Z=2$ ] to the hexagonal  $\omega$  phase (SG  $P6/mmm$ ,  $Z=3$ ) at 7.4 GPa (Ref. 9) and at 2.2 GPa,<sup>10</sup> respectively. At 71 GPa Zr transforms from the  $\omega$  phase to its  $\beta$  phase with the body-centered cubic (bcc) structure (SG  $Im\bar{3}m$ ,  $Z=1$ ).<sup>10</sup> In contrast

with expectations, in Ti the  $\omega$  phase transforms, at  $P = 116$  GPa, to the base-centered orthorhombic  $\gamma$ -phase (SG  $Cmcm$ ,  $Z=2$ ).<sup>11</sup> However, recent experimental study has shown the existence in Ti of  $\beta$  structure at pressures above 40 GPa but the corresponding transformation is path dependent.<sup>12</sup> The transformation from  $\alpha$  to  $\beta$  phase, at ambient pressure, occurs at  $T=1155$  K in Ti and at  $T=1135$  K in Zr. Alloying the two metals shifts all transformation temperatures towards the experimentally easier accessible region. The components of the Ti-Zr system are completely soluble in all phases at ambient pressure, and corresponding alloys show a great similarity in high-pressure and high-temperature behavior.

At ambient temperature, in good agreement with previous publication,<sup>13</sup> we observed in equiatomic disordered TiZr two structural phase transitions with pressure increasing [Fig. 1(a)]. The first is the transition from the hcp  $\alpha$  phase to the hexagonal  $\omega$  phase ( $\Delta V/V=-0.65\%$ ). On further compression, the  $\omega$  phase transforms to the cubic  $\beta$  phase ( $\Delta V/V=-0.44\%$ ). The equiatomic TiZr samples remain in the bcc  $\beta$  structure up to at least 65 GPa, the upper pressure limit of our experiments. The transformations are sluggish but reversible. The amount of a new growing phase  $x_i$  increases exponentially [Fig. 1(b)] in the transition pressure range: for example,  $x_\beta=1.08 \exp\{(P-P_c)/0.14P_c\}$ , at the  $\omega$ -to- $\beta$  transformation ( $P_c=57.5$  GPa).

### B. Phase transitions at high temperature

At elevated temperatures, however, an increase in pressure reveals the important change in the phase sequence. At  $T>400$  K, a new phase, labeled  $\omega'$ , is detected in the pressure range intermediate between  $\omega$  and  $\beta$  phases. Figure 2 shows selected diffraction patterns of TiZr in the stability range of the new phase. One can observe the onset of new peaks and a progressive increase of their intensity while the intensity of the  $\omega$  reflections decreases continuously with an increase in pressure. The stability domain of the intermediate phase  $\omega'$  during isothermal pressure scans was found to overlap, first, with the stability domain of the  $\omega$  phase and then with the stability domain of the  $\beta$  phase [Fig. 2(b)]. The pattern No. 3, last in series, corresponds to a mixture of the new phase  $\omega'$  (32 vol. %) and the phase  $\beta$  (68 vol. %). Such behavior indicates the first-order character of both the phase transformations. The diffraction patterns from the new phase can be indexed with the same hexagonal  $\omega$ -structure but with a significant reduction in its volume. Figure 3 shows the experimental diffraction pattern from the TiZr alloy and the best full-profile fit with two hexagonal structures  $\omega$  and  $\omega'$ , with the corresponding unit cell lattice parameters  $a_\omega = 4.7352$ ,  $c_\omega = 2.9309$  Å;  $a_{\omega'} = 4.5198$ ,  $c_{\omega'} = 2.7787$  Å ( $\Delta V/V = -13.6\%$ ). The two-phase mixture gives good reliability indices ( $R_B^\omega = 7.78\%$ ,  $R_F^\omega = 8.54\%$ ;  $R_B^{\omega'} = 6.48\%$ ,  $R_F^{\omega'} = 8.25\%$ ;  $\chi = 0.705$ ). We conclude therefore as to an occurrence in TiZr of an *isostructural* phase transition  $\omega$  to  $\omega'$ . This is the first observation of such a transition type in IVb metals and their alloys, and only the second example of an isostructural transformation in a metal, the other being Ce (see Ref. 14).

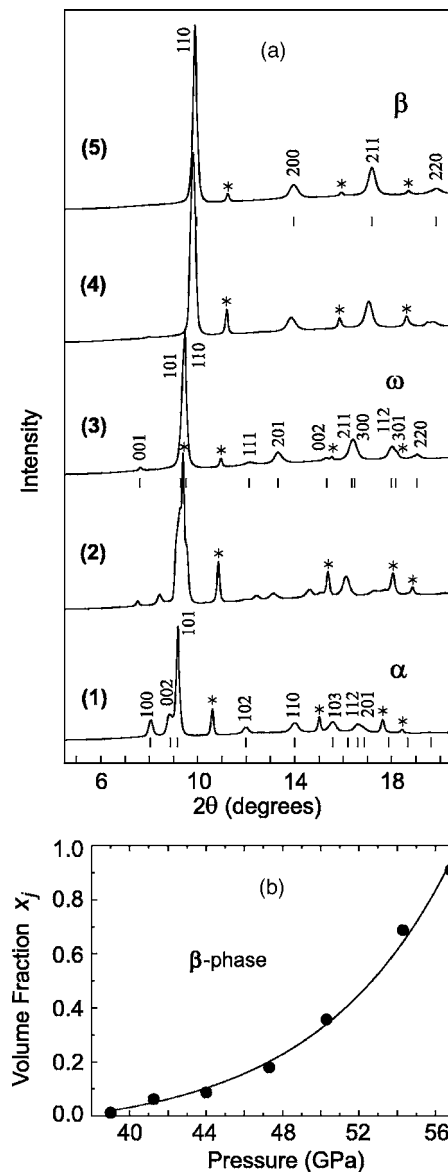


FIG. 1. (a) Angle-dispersive x-ray-diffraction patterns of the TiZr sample at room temperature and various pressures during compression: (1) 3 GPa, (2) 18.6 GPa, (3) 28.5 GPa, (4) 52.5 GPa, (5) 61 GPa. The tick marks indicate the calculated peak positions for the corresponding structures. Asterisks denote Au peaks. (b) Volume fraction variation for the  $\beta$ -phase in TiZr under compression at room temperature: dots represent experimental data, line is the best fit with an exponential function.

The crystal structures of TiZr alloy determined to 60 GPa and 900 K in the present experiments are summarized in the phase diagram of Fig. 4. Some features of its topology are worth noting. First, one notes coexistence of four phases  $\alpha$ ,  $\beta$ ,  $\omega$ , and  $\omega'$ , at the same point on the phase diagram of TiZr at about 10 GPa and 825 K. In general, the Gibbs rule forbids coexistence of more than three phases of a given compound at one  $(P, T)$  point. However, it still holds when all phases merging at the triple point are assumed to be independent, i.e., no parent phase and no order parameter are defined. In the present case, the thermodynamic potentials correspond to phases, which are not independent and consist in

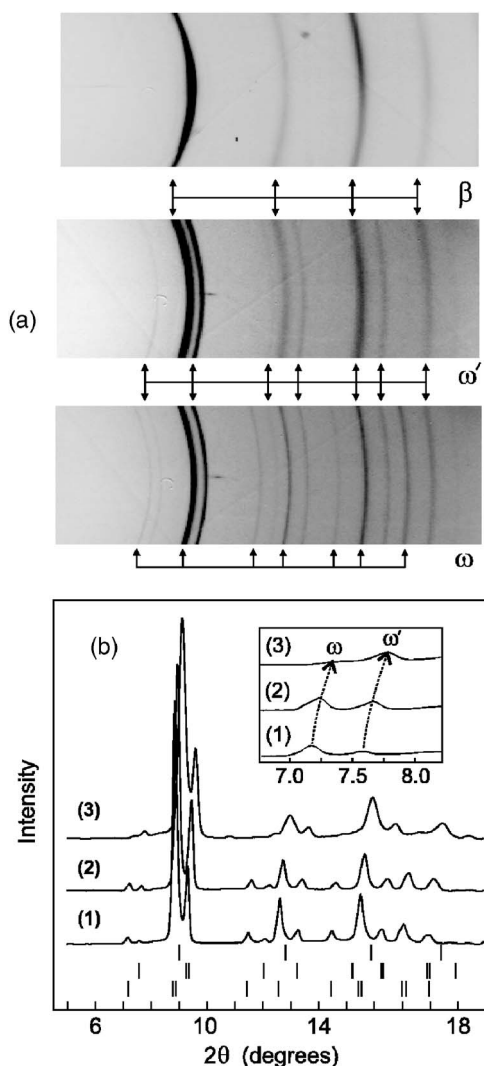


FIG. 2. Selected diffraction patterns of TiZr during a quasi-isothermal compression cycle at high temperature. (a) Debye-Scherrer diffraction rings of TiZr alloy as recorded on a CCD detector. The positions of diffraction rings assigned to  $\beta$ ,  $\omega'$ , and  $\omega$  structures marked by arrows. (b) Integrated patterns collected at (1) 8.8 GPa, 815 K; (2) 18 GPa, 815 K; (3) 24.8 GPa, 745 K. The tick marks in (b) indicate the calculated peak positions for (from bottom to top)  $\omega$ ,  $\omega'$ , and  $\beta$  structures. The inset shows the evolution of the (001) peaks from the  $\omega$  and  $\omega'$  structures in the angular range devoid of  $\beta$ -structure reflections.

extremes of the same nonequilibrium potential of the common parent  $\beta$  phase with multicomponent order parameters well defined.<sup>15,16</sup>

Second, significant for the alloy properties is the negative slope,  $\partial T_{\omega-\omega'}/\partial P < 0$ , observed for the  $\omega$ - $\omega'$  phase boundary. The collapsed  $\omega'$  structure exists therefore as a high-temperature one with respect to the noncollapsed  $\omega$  structure through the whole pressure range of its stability. Due to this topological feature heating up TiZr across the  $\omega$ - $\omega'$  boundary should result in the decrease in the atomic volume and the corresponding negative thermal expansion. The effect is similar to that observed recently in the Pr metal.<sup>17</sup>

However, an even more striking feature is the atomic volume evolution at the  $\omega'$ -to- $\beta$  transformation. The corre-

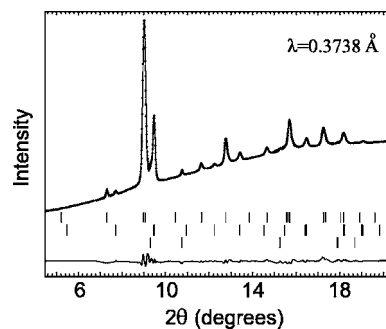


FIG. 3. Diffraction pattern and Rietveld fit of hexagonal structures of TiZr described in the text, at 16.9 GPa and 825 K. The solid symbols represent experimental data, the solid line running through the data refers to the calculated pattern. The corresponding difference curve is plotted below the diagram. The tick marks indicate the calculated peak positions for (from bottom to top)  $\omega$ ,  $\omega'$ , and  $\beta$  structures.

sponding partial atomic volume jump  $\Delta V/V$  at the compression of TiZr, is about 13% but has a positive sign, and the high-pressure structure, therefore, has a larger atomic volume than the low-pressure one. In contrast, the asymptotically estimated atomic volume decrease for a hypothetical direct  $\omega$ -to- $\beta$  transformation, for the same thermodynamic path, should be less than 2% [Fig. 5(a)]. It should be pointed out again that all observed in TiZr transformations are reversible.

Our experimental information is not sufficient for unambiguous conclusion whether  $\omega'$  is a stable or metastable phase. On one hand, in the narrow pressure range ( $\sim 5$  GPa), we have observed only coexistence regions  $\omega/\omega'$  and  $\omega'/\beta$  but never a single  $\omega'$  phase, the fact generally indicating the metastable status of a structure. On the other

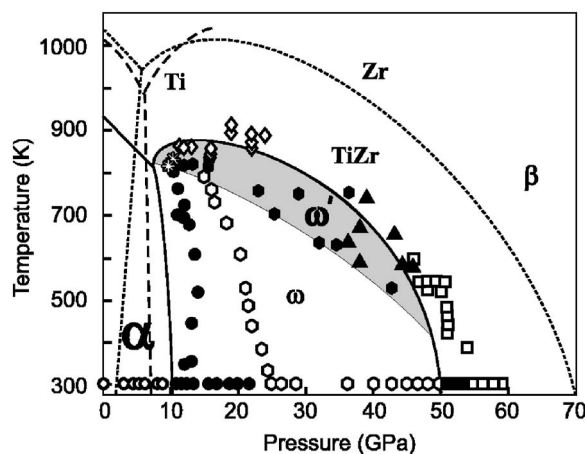


FIG. 4. Partial phase diagram of the equiatomic TiZr alloy. Open circles are the  $\alpha$ -phase, solid circles the two-phase  $\alpha/\omega$  mixture, open hexagons the  $\omega$ -phase, open squares the  $\beta$ -phase, solid squares the  $\omega/\beta$  mixture, solid hexagons are the  $\omega/\omega'$  mixture, solid triangles the  $\beta/\omega'$  mixture, open diamonds are the triple-phase  $\beta/\omega/\omega'$ , and asterisk  $\alpha/\omega/\omega'$  mixtures. The phase boundaries are estimated from present results. Phase transition lines for pure Ti and Zr are displayed for reference. Shaded is the stability domain of the  $\omega'$  phase.

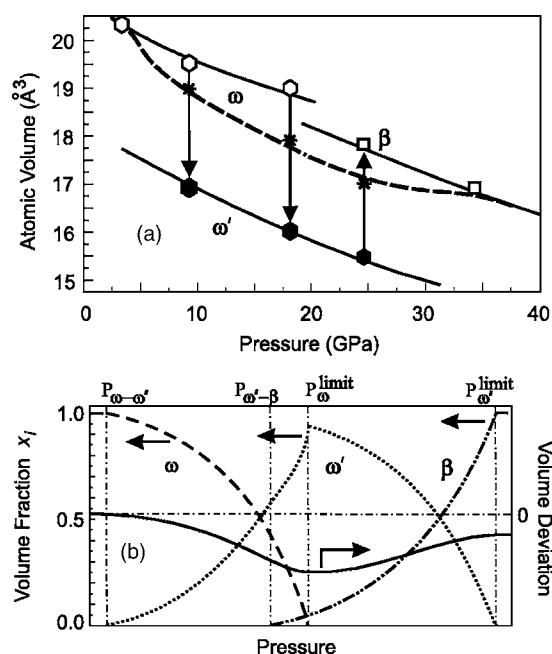


FIG. 5. (a) Atomic volume variation in TiZr for the same thermodynamic path as for Fig. 2. Open and full symbols correspond to the individual phase atomic volume, while asterisks show the average “sample atomic volume”  $v_s$ . Solid lines display equations of state for individual phases, dashed line is the “sample equation of state.” (b) Theoretical curves, in the model of exponential phase growth, for the volume fraction variation and the sample volume deviation from an equilibrium equation of state.

hand, reversibility of the corresponding transformations, and the thermodynamic arguments speak in favor of the stable  $\omega'$  phase. Indeed, the onset of a metastable underlying phase or intermediate state should provide a gain in energy, while the observed in TiZr change in the phase sequence evidently increases the required transformation energy as it replaces a single moderately first-order phase transition  $\omega$ - $\beta$  ( $|\Delta V/V| \approx 1\%$ ) by two strongly first order transformations  $\omega$ - $\omega'$  and  $\omega'$ - $\beta$  ( $|\Delta V/V| \approx 14\%$  for each). Nevertheless, stability status of the  $\omega'$  phase is an important but not crucial point in the novelty and high impact of the observed phenomena.

### C. Electron transfer

Two points then should be discussed: (i) factors causing the reverse  $d$ - $s$  electron transfer at the  $\omega'$ -to- $\beta$  structural phase transition and (ii) the correspondence of the observed pressure induced atomic volume increase to the fundamental principles of thermodynamics. For the  $\omega$ -to- $\omega'$  transformation the analogy with the electron driven isostructural phase transition in Ce is evident, even the magnitude of the volume decrease is comparable [in Ce, at ambient temperature  $\Delta V/V \approx -17\%$  (Ref. 14)]. Following theoretical models<sup>1,3,4</sup> atomic volume collapse in hexagonal TiZr alloy can be considered, therefore, as induced by the  $s$ - $d$  electron transfer. However, further compression of the material at high temperature discloses an unprecedented and fundamental difference in the electrons behavior in TiZr. The structural  $\omega'$ -to- $\beta$  phase transition not only stops the electron  $s$ - $d$  transfer,

responsible for the large atomic volume decrease, but it also triggers the reverse  $d$ - $s$  redistribution of electrons, the recovery of the initial  $s$ -band population and the corresponding atomic volume increase.

A clue to the  $d$ - $s$  electron transfer mechanism can be seen in the change of the site symmetry of metal atoms at the phase transformation. Anisotropic (uniaxial) atoms array with the site symmetry  $G_\omega^1 = 6/mmm$  and  $G_\omega^2 = \bar{6}m2$ , in the hexagonal structure, is changed to isotropic one  $G_\beta = m\bar{3}m$ , in the cubic structure. This could disfavor populating anisotropic  $d$  orbitals, just started in TiZr, and promote backward filling of isotropic  $s$  orbitals. The scenario is essentially based on the competition between corresponding electron and structural instabilities (surprisingly, in behalf of the latter), and this is a good challenge for first-principle calculations as successfully carried out previously in order to describe electronically driven effects in transition metals.

### D. The $\beta$ -to- $\omega$ transformation

The key role of the structural instability in the new phenomenon makes necessary to analyze in detail the corresponding transformation mechanism. The order parameter for the structural  $\beta$ -to- $\omega$  transformation is of a displacive type and relates to the deep cusplike anomaly on the longitudinal phonon branch  $\omega_L(\mathbf{q})$  with  $\mathbf{q}=[X,X,X]$ .<sup>18</sup> This critical phonon  $L(1,1,1)$  is responsible for destabilization of the parent  $\beta$ -structure and for displacement of atoms to the positions characteristic of the  $\omega$  structure (for details, see Refs. 15 and 16, and references therein). The other order parameter, responsible for electron  $d$ -band populating, is nonsymmetry breaking one. Due to its totally symmetric character the electron order parameter is coupled to any symmetry-breaking one in such a manner, quadratic in the latter and linear in the former,<sup>19</sup> that a change in a structural order parameter can trigger off its variation indeed. However, generally the adiabatic behavior of a crystal, stemmed from the considerable difference in the energy of electron and phonon bands, allows neglecting such an effect. Our observation indicates therefore that the adiabatic picture is hardly valid for the electron-phonon interaction in TiZr alloy. Then, in a nonadiabatic system, the triggering role of structural instability is not so surprising.

### E. Thermodynamic aspect

In the thermodynamic aspect, our finding should be examined with respect to the principle of Le Chatelier. In the case of a metastable intermediate phase, which never has energy lower than  $\omega$  and  $\beta$  phases, no contradiction arises at all. Indeed, the Le Chatelier principle predicts a system in thermodynamic equilibrium to exhibit moderation of the perturbed factor as a result of a variation in one of the factors governing the equilibrium. The compensating change in volume, under the pressure increase, should have therefore the opposite direction, i.e., volume should decrease under compression. However, the above principle relates to a single-phase equilibrium system showing no strong interactions, i.e., a sole degree of freedom replies to a perturbation, and only the single-phase term  $PV$ , in the Gibbs energy,  $G=E$



$-TS+PV$ , relates to the variation of pressure and volume.

First, the order of events in TiZr indicates, on the contrary, the existence and the important role of a strong coupling of different microscopic degrees of freedom. Equally with the strong interaction of localized and delocalized electrons, characteristic of the systems, which exhibit effects of valence instability, we concluded on strong coupling of the displacive (phonon) order parameter and the electron order parameter.

Second, an additional negative contribution to the Gibbs potential (energy of interphase boundaries, for instance) can minimize the total energy and make globally stable a mixture of stable and metastable phases. Such a scenario should allow even reversibility of a transformation path through a metastable intermediate structure. The reversibility of the  $\omega$ - $\omega'$  and  $\omega'$ - $\beta$  transformations, considered above as a sign of the  $\omega'$ -phase stability, does not exclude, therefore, a metastable intermediate phase. This seems to be the case for TiZr alloys.

The important feature of the structural transformation from the cubic  $\beta$  structure to the hexagonal  $\omega(\omega')$  structure (a non-Landau phase, in terms of Refs. 15 and 16) is the discontinuous onset and the further nonvariable character of the corresponding displacive order parameter. As mentioned above, the latter can be identified with the discrete antiparallel displacements of the part of atoms along the  $[111]_{\beta}$  cubic direction: two third of the atoms in the  $(111)_{\beta}$  layer collapse into double layers, whereas the third unshifted remains a single layers.<sup>15,16,18</sup> Considerable discontinuity in the order parameter variation should yield the first-order regime for the  $\beta$ -to- $\omega(\omega')$  structural transformation with the corresponding sluggish kinetics and the onset of a two-phase intermediate state, observed in our experiments indeed. Such sluggish kinetics is an intrinsic property of the transformation, stems from the existence of high energetic barriers, and should develop independently of compression conditions. Consequently, in the transformation process, invariance of the order parameter magnitude under the pressure variation reduces the effect to the pressure-controlled nucleation and gradual phase growth instead of the bulk transformation.

As long as the growing high-pressure  $\beta$ -phase has been found to have a larger atomic volume, two volumetric effects

different in sign compete in the  $\omega'/\beta$  two-phase pressure range. (i) Lattice contribution: the compression contracts the  $\omega'$  and  $\beta$  crystal lattices. (ii) Electronic contribution: the simultaneous increase of volume fraction  $x_{\beta}$  of the noncollapsed  $\beta$  phase diminishes shrinking effect of the pressure increase. Figure 5(b) schematically shows the deviation of the two-phase sample volume  $v_a = v_{\omega'}(1-x_{\beta}) + v_{\beta}x_{\beta}$  from the equilibrium equations of state (EOS)  $v_{\omega'}(P)$  and  $v_{\beta}(P)$  for the pure phases (metastable and stable) in the model of exponential phase growth, which was found to be valid for the corresponding transformation [see Fig. 1(b)]. Applying such a nonequilibrium EOS  $v_a(P)$  in the intermediate, between  $\omega$  and  $\beta$ , pressure range one obtains thermodynamically faultless result: the “atomic” volume  $v_a$ , averaged through the sample, decreases (but with reduced rate) with the pressure increase [Fig. 5(a)]. This is in full agreement with the classical Le Chatelier principle in spite of strong interactions existing in the system and the fact that the high-pressure structure, in the “nonclassical” pressure range, has enlarged atomic volume. An indirect analogy to the observed phenomenon could be seen in the process of hydrogenation of a metal under high pressure: the increase of hydrogen pressure in the chamber results in blowing up a metal matrix while the overall chamber volume decreases.

#### IV. CONCLUSION

In summary the electron-driven isostructural phase transition, revealed in the hexagonal  $\omega$  phase of TiZr, provides an argument for the existence and important role of the  $s$ - $d$  electron transfer in the structure stability in transition metals. Moreover, the observation of the reverse transfer, triggered by the phonon-driven phase transformation, indicates the equally important contribution of the electron-phonon coupling in the stabilization process but questions the adiabatic nature of the interaction.

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<sup>1</sup>J. C. Duthie and D. G. Pettifor, Phys. Rev. Lett. **38**, 564 (1977).

<sup>2</sup>S. K. Sikka, Y. K. Vohra, and R. Chidambaram, Prog. Mater. Sci. **27**, 245 (1982).

<sup>3</sup>H. L. Skriver, Phys. Rev. B **31**, 1909 (1985).

<sup>4</sup>M. Sigalas, D. A. Papaconstantopoulos, and N. C. Bacalis, Phys. Rev. B **45**, 5777 (1992).

<sup>5</sup>A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, and D. Hausermann, High Press. Res. **14**, 235 (1996).

<sup>6</sup>J. Rodriguez-Carvajal, Physica B **192**, 55 (1993).

<sup>7</sup>N. Dubrovinskaia and L. Dubrovinsky, Rev. Sci. Instrum. **74**, 3433 (2003).

<sup>8</sup>O. L. Anderson, D. G. Isaak, and S. Yamamoto, J. Appl. Phys. **65**, 1534 (1989).

<sup>9</sup>H. Xia, G. Parthasarathy, H. Luo, Y. K. Vohra, and A. L. Ruoff, Phys. Rev. B **42**, 6736 (1990).

<sup>10</sup>H. Xia, S. J. Duclos, A. L. Ruoff, and Y. K. Vohra, Phys. Rev. Lett. **64**, 204 (1990).

<sup>11</sup>Y. K. Vohra and P. T. Spencer, Phys. Rev. Lett. **86**, 3068 (2001).

<sup>12</sup>R. Ahuja, L. Dubrovinsky, N. Dubrovinskaia, J. M. Osorio Guillen, M. Mattesini, B. Johansson, and T. Le Bihan, Phys. Rev. B **69**, 184102 (2004).

<sup>13</sup>I. O. Bashkin, V. K. Fedotov, M. V. Nefedova, V. G. Tissen, E. G. Ponyatovsky, A. Schiwiek, and W. B. Holzapfel, Phys. Rev. B **68**, 054401 (2003).

<sup>14</sup>D. C. Koskenmaki and K. A. Gschneider, Jr., in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A.

- Gschneidner, Jr. and L. Eyring (North Holland, Amsterdam, 1986), Vol. 1, p. 337.
- <sup>15</sup>V. P. Dmitriev, S. B. Rochal, Yu. M. Gufan, and P. Tolédano, Phys. Rev. Lett. **60**, 1958 (1988).
- <sup>16</sup>P. Tolédano and V. Dmitriev, *Reconstructive Phase Transitions in Crystals and Quasicrystals* (World Scientific, Singapore, 1996).
- <sup>17</sup>A. Yu. Kuznetsov, V. P. Dmitriev, O. I. Bandilet, and H.-P. Weber, Phys. Rev. B **68**, 064109 (2003).
- <sup>18</sup>W. Petry, A. Heiming, J. Trampenau, M. Alba, C. Herzig, H. R. Schober, and G. Vogl, Phys. Rev. B **43**, 10933 (1991).
- <sup>19</sup>In terms of the group theory, it results from the rigorous rule that a square of any irreducible representation contains the totally symmetric one.