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Lattice-dynamical study of the cubic-tetragonal-monoclinic transformations of zirconia

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Vibrational and elastic properties of cubic and tetragonal phases of zirconia are discussed within the framework of quantitative lattice-dynamical treatments. The results reveal mechanical instabilities of both phases originating from the stresses inherent for these structures, and show that c-t and t-m transformations of ZrO_2 are driven by successive condensations of the zone-boundary modes whose softening is induced by the interatomic tensions. [S0163-1829(96)03746-0]

Zirconia, with the melting point of 2700 °C, is an extremely refractory material having various industrial applications. It is remarkable that its structural stability with respect to change in temperature depends critically upon the presence of trace amounts of ''impurities'' like MgO, CaO, and Y_2O_3 which produce disorder in oxygen positions. Pure zirconia has a simple fluorite structure (O_h^5) in the highest-temperature phase, and, with decreasing temperature, undergoes two phase transitions (PT's).

First, it distorts to the tetragonal (D_{4h}^{15}) structure at about 2300 °C, and then to the monoclinic one (C_{2h}^5) at about 1000 °C.[1] An atomic arrangement of m-ZrO_2 drastically differs from that of c-ZrO_2: the coordination sphere of Zr, forming a ZrO_8 cubic unit in c-ZrO_2, becomes an irregular ZrO_7 polyhedron in m-ZrO_2; each oxygen is shifted from a center of an ideal OZr_4 tetrahedron, so that half of oxygens becomes threefold coordinated.

This is accompanied by considerable changes of physical properties of zirconia, in particular, of its vibrational spectra and elasticity. The understanding of the detailed nature of the above phase transitions and related phenomena is of practical importance and of fundamental scientific interest (in particular, it is challenging that among the members of the fluorite family including CeO_2, UO_2, and ThO_2 nothing other than ZrO_2 and its analog HfO_2 manifest such a behavior).

From the symmetry analysis,[2–4] it is suggested that the c-t-m transformation of ZrO_2 results from two successive condensations of the Brillouin zone (BZ) boundary phonons. The c-t PT corresponds to the condensation of *one* X_2^- triply degenerate phonon.[2,3] Its eigenvector consists of oxygen displacements only.[3] This phonon would become a *single* zone-center A_{1g} vibration of the t lattice. The other two X_2^- phonons would take up a position at the M point of the t-BZ, and, theoretically, their vanishing can induce the t-m PT.[4]

In our previous publication,[5] interatomic static tensions were considered as an universal dynamical factor which influences the mechanical stability of crystals. In particular, it was shown that the tensions, arising in the ideal c zirconia with decreasing temperature, could be responsible for the c-t PT. More recent qualitative[6] and quantitative[7] considerations are in line with this suggestion.

Using the results of a quasiharmonic lattice-dynamical model treatment presented below, we shall discuss the following questions: (i) Is the phonon condensation responsible for both c-t and t-m PT's of ZrO_2? (ii) Which soft modes drive the PT's? (iii) What is the microscopic mechanism of the lattice destabilization?

The rigid-ion approximation was used to describe the electrostatic interactions between atoms, and the Born–von Karman model was accepted for the short-range potential V.[8] Thus our approach resembled those used in Refs. 7 and 9. However, in contrast to works,[7,9] we have omitted the Zr-Zr attraction potential (no *objective* reason was found in favor of its inclusion). Thus, only the nearest-neighbor Zr-O and O-O repulsive interactions contributed to a non-Coulombic part of the dynamic matrix.

First, let us consider the c lattice with cubic (face-centered) unit-cell dimension $a=b=c=5.23$ Å. This corresponds to the geometry of pure ZrO_2 just before the c-t PT.[1] In such a case, the shortest Zr-O and O-O lengths are $R=2.265$ Å and $L=2.615$ Å, respectively. Our model of this lattice had the five parameters, $A_1=d^2V/dR^2$, $B_1=(1/R)dV/dR$, $A_2=d^2V/dL^2$, $B_2=(1/L)dV/dL$, and the effective charge of oxygen Z. The latter could be directly (and uniquely) derived from the TO-LO splitting of the T_{1u} phonon. Three estimates of this splitting have been found in literature, two of them being determined by using the IR reflection, 320–705 cm^{-1} (Ref. 9) and 375–695 cm^{-1},[10] and one by Raman spectroscopy, 317–640 cm^{-1} (see Table 1 in Ref. 7). After analyzing these data, we have taken the value of 320–660 cm^{-1} as the most dependable, from which $Z=-1.185e$ was derived. It was fixed in all our calculations. The $\omega(T_{2g})$ phonon frequency was taken to be equal to 600 cm^{-1},[11] and elastic constants $C_{11}=417$, $C_{12}=82$, $C_{44}=47$ GPa were assumed for *pure* c-ZrO_2.[12]

A_2 and B_2 parameters have been initially estimated via a Lennard-Jones empirical potential which had been usefully applied to various oxides.[13] This yielded the values of 0.64 and of -0.05 mdyn/Å, respectively. We have estimated $A_1=1.1$ mdyn/Å from the Zr-O bond-force-constant–bond-length dependence.[14] For a given B_2 magnitude, the B_1 value was found via the equilibrium condition implying that the

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TABLE I. Structural characteristics (Å), model parameters (mdyn/Å, electron charge), and elastic constants (GPa) of pure cubic zirconia (c-ZrO$_z$), stabilized tetragonal zirconia (STZ), and pure tetragonal zirconia (PTZ). The experimental values of elastic constants (in parentheses) are taken from Ref. 12 for c-ZrO$_z$, and from Ref. 16 for PTZ (extrapolated from monoclinic data to the m-t PT point). The cubic a, b, and c directions are kept for all the structures.

c-ZrO$_2$		STZ			PTZ	
		Structure and parameters				
$a=b=c=5.23$	$c=5.21$	$c/a=1.008$	$\Delta=0.025$	$c=5.27$	$c/a=1.025$	$\Delta=0.065$
	$R^{\mathrm{I}}=2.17$	$A_1^{\mathrm{I}}=1.68$	$B_1^{\mathrm{I}}=-0.165$	$R^{\mathrm{I}}=2.063$	$A_1^{\mathrm{I}}=2.00$	$B_1^{\mathrm{I}}=-0.235$
$R=2.265$; $A_1=1.32$; $B_1=-0.116$						
	$R^{\mathrm{II}}=2.32$	$A_1^{\mathrm{II}}=1.15$	$B_1^{\mathrm{II}}=-0.065$	$R^{\mathrm{II}}=2.462$	$A_1^{\mathrm{II}}=0.56$	$B_1^{\mathrm{II}}=0.0$
	$L^{\mathrm{I}}=2.59$			$L^{\mathrm{I}}=2.63$		
$L=2.615$; $A_2=0.55$; $B_2=-0.06$		$A_2=0.55$;	$B_2=-0.06$		$A_2=0.55$;	$B_2=-0.06$
	$L^{\mathrm{II}}=2.60$			$L^{\mathrm{II}}=2.66$		
$z=-1.185$		$z=-1.185$			$z=-1.185$	
		Elastic constants				
$C_{11}=455$ (417); $C_{12}=64$ (82)	$C_{11}=454$	$C_{33}=453$		$C_{11}=395$ (340)	$C_{33}=326$ (325)	
$C_{44}=63$ (47)	$C_{12}=56$	$C_{13}=84$		$C_{12}=26$ (33)	$C_{13}=105$ (160)	
	$C_{44}=72$	$C_{66}=75$		$C_{44}=42$ (66)	$C_{66}=56$ (95)	

static short-range repulsive forces (bond tensions) dV/dR jointly with dV/dL have to balance the Coulomb volume compression forces.

Then the above A_1, A_2, B_1, and B_2 parameters were varied to fit the model results to the measured values of $\omega(T_{2g})$, $\omega_{\mathrm{TO}}(T_{1u})$, C_{11}, C_{12}, and C_{44}. The results thus obtained are given at the left of Table I and in Fig. 1(a) which shows phonon curves along the Γ-X direction. The main point of these results is that the ω (X_2^-) value is close to zero. This is exactly what would be anticipated for the c-t PT but has never been observed experimentally, although neutron measurements indicated some evidence for such an effect.[7] Then, within the model, the unit-cell parameter a has been increased to 5.27 Å. The resulting stabilization of the lattice $[\omega(X_2^-)=70\ \mathrm{cm}^{-1}]$ was found to be associated with the reduction of the static interatomic forces.

The above results support the hypothesis[5] that the reserve of stability of c-zirconia is dominated by the stresses inherent for this lattice. Due to a small radius and a large charge of the cation, the atoms are very closely spaced in c-ZrO$_2$. This distinguishes this structure among a number of fluorite-like lattices (for comparison, interanionic length L equals to 2.735 Å in UO$_2$, and to 2.725 Å in CaF$_2$). So, high internal tensions arise as a result of balance between the Coulomb forces (which in sum tend to decrease the interatomic separation) and the short-range repulsive forces. With the crystal

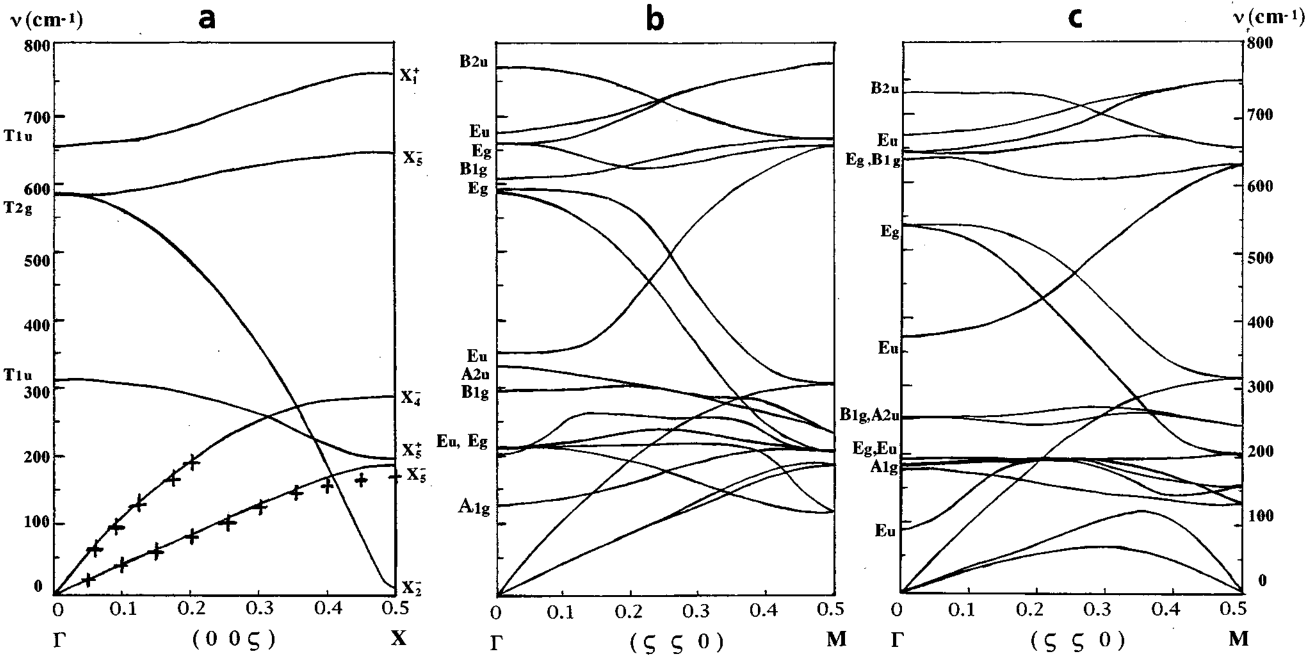

FIG. 1. Phonon dispersion curves: (a) of c-ZrO$_2$ (measured data shown by + are taken from Ref. 9); (b) of STZ; (c) of PTZ, (see Table I). X_2^-, X_4^-, X_5^-, X_1^+, and X_4^+ modes of the c phase become A_{1g}, B_{1g}, E_g, B_{2u}, and E_u modes, respectively, in the t phase (Refs. 3 and 5).

volume contraction on cooling, the tensions increase, thus diminishing the depth of potential wells of atoms, and eventually expel oxygens (whose wells are less deep) from high-symmetry $4d$ positions (see Ref. 5).

The ''path of escape'' is triply degenerate (three X_2^- phonons vanish simultaneously), but condensation along the cubic axis is the most preferable; according to our calculations, the electrostatic potential has the steepest decline in this direction. This agrees with the experimental data[6] which show that, in the stabilized (disordered) c-ZrO_2, the O atoms are mainly shifted in the (100) direction. Thus the stabilizing effect of disordering can be explained: in this case, $4d$ positions of oxygens are averaged, and the atoms, being in reality outside $4d$ sites, can shift, thus relaxing internal tensions. Due to this, the lattice can hold its (averaged) symmetry, and remain ''stable.''

Let us turn to t-ZrO_2. Due to the c-t PT, half of Zr-O bond lengths (R^{I}) become shorter than initial ones, and the other half becomes longer (R^{II}); oxygen-oxygen distances L remain practically unchanged (Table I). The two factors describe tetragonality of t-ZrO_2: shift Δ of oxygen atoms from their ideal fluorite positions, and the c/a ratio (equals to 1 for c-ZrO_2).

The two t structures were studied within our model treatment: (1) $c=5.21$ Å, $c/a=1.008$, $\Delta=0.025$; (2) $c=5.27$ Å, $c/a=1.025$, $\Delta=0.065$. Structure 1 corresponds to the *stabilized* t-zirconia (STZ) (Ref. 15) which does not undergo the t-m inversion on cooling; structure 2 is that of the pure t-zirconia (PTZ) just before the t-m PT.[1]

To keep as much as possible objectivity of the lattice-dynamical models of both structures, the values of short-range force parameters were correlated with the variations of bond lengths. Thus, all the O-O parameters were taken equal to those of c-ZrO_2 (Table I). Initial A_1^{I} and A_1^{II} values were estimated by using the above-mentioned bond-force-constant–bond-length dependence.[14] Since short-range parameters of our model relate, by definition, to the first and second derivatives of the pairwise potential V, initial B_1^{I} and B_1^{II} quantities were regarded as resulting from the B_1 value variation due to ΔR^{I} and ΔR^{II} changes of the Zr-O bond lengths:

$$B_1^{\mathrm{I}}=B_1+A_1\Delta R^{\mathrm{I}}/R^{\mathrm{I}} \quad \text{and} \quad B_1^{\mathrm{II}}=B_1+A_1\Delta R^{\mathrm{II}}/R^{\mathrm{II}}.$$

The values obtained were close to balance the forces on oxygens. Then the Zr-O bond parameters have been slightly varied (in keeping the O-O parameters and charge Z) to satisfy the equilibrium condition for each atom rigorously, and to reproduce the following effects relevant to c-t PT: (i) the splitting of long-wave vibrations, $T_{2g}\Rightarrow B_{1g}+E_g$, $T_{1u}\Rightarrow A_{2u}+E_u$; (ii) the activation of the four zone-boundary modes in Raman spectra, namely, *three modes in a low-frequency region,* $B_{1g}(X_4^-)$, $E_g(X_5^-)$ and $A_{1g}(X_2^-)$; and *one* $E_g(X_5^-)$ *mode in a high-frequency region* [see initial positions of those modes in Fig. 1(a)]; (iii) the variation of elastic constants [estimated by extrapolating measured data for m-ZrO (Ref. 16) to the t-m transition point].

Final sets of model parameters of STZ and PTZ thus obtained (Table I) have provided dispersion curves given in Figs. 1(b) and 1(c). These show that STZ has no instability at the M point, whereas PTZ is unstable: one doubly degenerate M phonon practically vanishes. Due to the $D_{4h}^{15}\Rightarrow C_{2h}^5$ change of symmetry, one component of this phonon becomes totally symmetric. So, its condensation can drive the t-m PT. The eigenvector of this phonon consists of z displacements of zirconiums and xy displacements of oxygens, and has no relationship to the two former X_2^- phonons at the M-point. Those are situated near 130 cm^{-1}. Thus the present results do not support the scenario of the t-m PT drafted in Ref. 5, and it is likely that they do not correspond to that implied in Ref. 4.

The quantitative analysis of the results shows that similar to the c-t PT these are the first derivatives of interatomic potentials, i.e., static internal tensions, which drive the t lattice unstable (via a tangential part of the dynamical matrix). The *tetragonal* distortion of the lattice provides anisotropy of the tensions: it increases the tensions which act on oxygen along z, and on zirconium within the xy plane. This weakens the *restoring forces* governing the vibratory motions of oxygens in the xy plane, and those of zirconiums along z, thus softening the above phonon.

Note that the A_{1g} normal coordinate of t-ZrO_2 is a single internal degree of freedom which dictates a microscopic pattern of the t distortion, thus playing the primary role in the changes of dynamical properties of ZrO_2 due to the c-t PT. So, a realistic description of the A_{1g} vibration is essential for the physically meaningful modeling of t zirconia. In this connection, the disagreement between the calculated A_{1g} vibration frequency of 180 cm^{-1} for PTZ [see Fig. 1(c)], and that of 600 cm^{-1} conventionally accepted in the existing literature (see, e.g., Ref. 17), is so fundamental that we feel it necessary to explain this point of our calculations with more detail.

First, let us consider elasticity of zirconia. Within Born's theory,[8] the elastic constant C_{ik} is expressed as follows (summation over repeated indexes is implied below):

$$C_{ik}=C_{ik}^0-F_{i\lambda}F_{k\lambda}/\omega_\lambda^2, \tag{1}$$

where C_{ik}^0 is a ''bare'' elastic constant, ω_λ is a frequency of normal coordinate Q_λ (which is necessarily Raman active), and $F_{i\lambda}$ is a coupling coefficient between Q_λ and external macroscopic strain U_i,

$$dU_i/dQ_\lambda=-F_{k\lambda}/C_{ik}^0. \tag{2}$$

Since c-ZrO_2 has no totally symmetric vibrations, C_{ik} ($i,k=1,2,3$) values are determined by the first term on the right-hand side of Eq. (1). This term remains practically unchanged in the t phase, and the changes of the above C_{ik} values due to the c-t transition are mainly associated with the advent of the A_{1g} soft mode (SM) in the t phase. This gives rise to the second contribution in Eq. (1), and thus accounts for the decrease of the volume elasticity. According to the calculations, $F_{i,\mathrm{SM}}$ is positive for $i=1,2$, and negative for $i=3$. This readily explains [see Eqs. (1) and (2)] why t-ZrO_2 has $C_{13}>C_{12}$, and $c>a$. However, if the A_{1g} mode had frequency near 600 cm^{-1}, this would practically annul the role of the second contribution in Eq. (1). In other words, from the viewpoint of the lattice dynamics, such a high frequency of the A_{1g} mode is not compatible with the behavior of the elastic properties of *pure* zirconia under the c-t transformation.

Second, let us concern with displacement patterns of the vibrations. A model-independent (symmetry) factor, namely, the distinction between eigenvectors of T_{2g} and $X_2^-(A_{1g})$ modes[5] would cause these modes to differ markedly in frequency. Actually, the O-O nearest-neighbor interactions, determining more than half T_{1g} eigenvalue, are ''switched off'' in the $X_2^-(A_{1g})$ mode. So it is physically unfeasible that the latter can approach the $\omega(T_{2g})$ position.

It can be added that some other points (which will be considered beyond this paper) make us to venture the opinion that, in practice, symmetry selection rules are significantly violated in t-ZrO$_2$, and the observed Raman spectra, conventionally regarded as originating from the six long-wave g vibrations, come to a great extent from the phonon-density distribution over the BZ.

In summary, the above results show that the static quasiharmonic lattice-dynamical treatment of zirconia is capable of revealing the nature of its structural instabilities, and mechanisms of the relevant PT's. According to the calculations, these originate from exceptionally high internal stresses inherent for symmetric ZrO$_2$ lattices built up from ZrO$_8$ polyhedra. Structure distortion (or disordering) produces internal degrees of freedom favorable for reducing those stresses, which stabilizes the lattice. In pure zirconia, this effect occurs via the c-t-m succession of PT's. Both transitions are associated with the mode softening driven by the interatomic static tensions which arise in the lattice on cooling. Eventually, due to dramatic structural changes all the atoms are brought into general positions, the lattice ceases to be ''overstressed'' and becomes stable.

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