Band structure of cubic ZrO$_2$ containing oxygen vacancies and calcium ions

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G A Ol'khovic, I I Naumov and O I Velikokhatnyi

Institute of Strength Physics and Materials Science, Russian Academy of Science, 2/I Academicheskii pr., Tomsk 634048, Russia

Abstract. The theoretical analysis of the electronic structure of ZrO_2 containing oxygen vacancies and calcium ions is carried out. The electronic band-structure calculations for zirconium dioxide in the cubic fluorite structure containing oxygen vacancies and calcium ions are made according to the LMTO method. The values of the total and partial densities of states are calculated. The results are used for the analysis of charge transfer between the components. Mainly an ionic character of bonding for all systems investigated is found.

1. Introduction

Ceramic materials based on zirconium dioxide (ZrO_2) hold a central position among the non-metallic construction materials. The high-temperature cubic (c) phase of ZrO_2 (space group, O_h^5) has the fluorite-type structure with three atoms per cell. The c-phase becomes unstable below 2600 K and transforms into the tetragonal (t) phase (space group, D_{4h}^{15}) with double the number of the atoms per cell (changing from three for the c-phase to six for the t-phase). Finally, below 1300 K the t-phase transforms to the monoclinic (m) phase (space group, C_{2h}^5) with another doubling of the number of atoms per cell (from six in the t-phase to 12 in the m-phase). These materials have been called 'ceramic steel' mainly because of their unique mechanical properties connected with phase transitions of the martensite type.

The high operation characteristics of zirconium ceramics are explained by a whole series of structural phase transitions which take place in these materials (especially of the martensite type (c–t) and (t–m)). The nature of these transitions is still unclear. This is the reason why a theoretical analysis of the electronic structure of ZrO_2 was carried out.

The behaviour of the variation in the electronic characteristics of ZrO_2 was investigated in [1] by the method of the linear combination of muffin-tin orbitals (LMTO) with regard to the c–t–m phase transitions.

Compared with other methods, the LMTO method has the following evident advantages:

(1) the small number of basic functions (usually nine orbitals per atom) and, hence, the possibility of carrying out calculations for large elementary cells including tens of atoms;

(2) a universal calculation scheme suitable for all types of crystal independently of the chemical elements;

(3) the possibility of generalizing this method for the case of non-ideal crystals with defects and impurities, amorphous systems, molecules, etc.

In the LMTO technique the atomic sphere approximation (ASA) is used; the Wigner–Seitz cells are replaced by overlapping spheres of the same volume. The charge distribution and the crystal potential are averaged over angles inside these spheres. The electronic structure of only ZrO_2 has been studied in [2, 3]. At the same time, the optical characteristics of all three phases of ZrO_2 have been calculated in [4]. Good agreement of the calculated optical characteristics with experimental data demonstrates that the results obtained are plausible and lends support to the validity of the calculation LMTO method. In fact the most frequently used ZrO_2 is not pure but 'stabilized'. In the latter the high-temperature c-phase is stabilized up to the room temperature, allowing the formation of CaO, Y_2O_3 [5] and various other oxide configurations. The influence of the additions is reflected in the increase in the c–t transition temperature to that required for the application, and the transition itself becomes close to type II. A similar effect is achieved by deviation of the composition from stoichiometry, i.e. ZrO_{2-x}. Mechanisms to explain the stabilizing influence of the ions Me^{2+} and Me^{3+} and of the oxygen vacancies are not available at present and have to be considered from a fundamental microscopic level. That is why a theoretical analysis of the electronic structure of ZrO_2 with the indicated ions and vacancies is necessary. The problems of this have been considered in the framework of the inculcated cluster method [6] and the scattering wave method combining the cluster and the band calculations [7]. According to [6] the substitution of Zr^{4+} ions by Me^{2+} and Me^{3+} results in a decrease in the dielectric gap and the formation of impurity levels inside the gap near the top of valence band (Me^{2+}) as well as in the middle (Me^{3+}). It was observed in [7] that the formation of oxygen vacancies in ideal ZrO_2 is accompanied by the capture of one or two electrons, turning them into an F^- or F^+ centre. When periodically arranged, the F centres form a band having an S-like behaviour. However, in the case of the periodic dipoles V–Ca and V–Y (V–vacancy) the vacancy states prove to be unfilled, which corresponds to the case of a vacancy without electrons.

The nature of the vacancy 1S zone is connected with the formation of impurity (vacancy) states and their ordered arrangement in the crystal. The partial filling of this zone is the result of vacancy capture of electrons and the formation of F-centre-type states. In our case there are 1.423 electrons in the ASA sphere for the vacancy; hence the F centres formed are intermediate between F^- and F^+ centres.

The above-mentioned papers give only highly limited information about the electronic structure of 'doped' ZrO_2. The present paper analyses the variation in electronic structure of c-ZrO_2 under the substitution of O atoms by V and of Zr atoms by Ca by the LMTO method [8].

2. Model structures used in the calculation

The self-consistent calculation of the total and partial densities of states, and the charge transfer in Zr_2O_4, Zr_2O_3V, $ZrCaO_4$ and $ZrCaO_3V$, has been carried out to analyse the electronic structure.

The problem was simplified deliberately; instead of the real proportionality of ZrO_2 and CaO mole portions (usually from 8 to 16%) we considered a periodic arrangement of substitutions and in doing so we exaggerated the effect of substituting Zr^{4+} ions for Ca^{2+} ions (as was done in [9, 10]). This made possible a consistent study of the influences first of Ca^{2+} ions only, next of oxygen vacancies V only and finally of both together on the electronic structure of ZrO_2.

The small (doubled) primitive cell corresponding to the chemical formula of Zr_2O_4 and characterized by the translations $(\frac{1}{2}, \frac{1}{2}, 0)$, $(-\frac{1}{2}, \frac{1}{2}, 0)$ and $(0,0,1)$ has been chosen

deliberately. The primitive cells of the Zr$_2$O$_3$V, ZrCaO$_4$ and ZrCaO$_3$V crystals have been constructed from the initial cell in the simplest way: the first cell by the substitution of one of the four O atoms by V, the second cell by the substitution of one of the two Zr atoms by Ca and, finally, the third cell by the substitution of O by V and of Zr by Ca. The atomic positions are given in table 1.

Table 1. Atomic coordinates of samples investigated (in units of primitive cell rib).

Coordinates	Atom			
	Zr$_2$O$_4$	Zr$_2$O$_3$V	ZrCaO$_4$	ZrCaO$_3$V
$0, 0, 0$	Zr	Zr	Zr	Zr
$0, \frac{1}{2}, \frac{1}{2}$	Zr	Zr	Ca	Ca
$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	O	O	O	O
$\frac{1}{4}, \frac{1}{4}, \frac{3}{4}$	O	O	O	O
$-\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	O	O	O	O
$-\frac{1}{4}, \frac{1}{4}, \frac{3}{4}$	O	V	O	V

The crystals Zr$_2$O$_3$V, ZrCaO$_4$ and ZrCaO$_3$V are, of course, hypothetical with respect to both the composition and the structure. By definition they have the same lattice period equal to that for pure ZrO$_2$ ($a = 5.272$ Å [11]) and, moreover, show an ordered arrangement of Ca atoms and vacancies (in reality these may be distributed within their sublattice statistically).

The basis sets used in the calculations contain nine orbitals per Zr atom (1–5s, 3–5p and 5–4d), four orbitals per O atom (1–2s and 3–2p), nine orbitals per Ca atom (1–4s, 3–4p, 5–3d) and four orbitals per vacancy (1–1s and 3–2p). The latter arises because in the friable structures the interstitial sites have pseudo-atomic properties and need for their description (in the ASA approximation) the introduction of corresponding orbitals [12]. The ratio of ASA radius of oxygen atoms to the corresponding zirconium radius was chosen as equal to 1.2. The ASA radius of vacancies was taken to be equal to the oxygen radius and the calcium radius as equal to the zirconium radius. The exchange–correlation effects were taken into account by the Kohn–Sham [13] scheme. The process of self-consistency was assumed to be completed if the maximal difference of the eigenvalues for two subsequent iterations did not exceed 0.003 Ryd (corresponding to stability of the internal pressure to within 0.1 GPa and a charge transfer of 0.001).

3. Results and discussion

In this section we shall compare consistently the electronic structures of Zr$_2$O$_4$, Zr$_2$O$_3$V, ZrCaO$_4$ and ZrCaO$_3$V. Here the first and the last system are insulators and the others are metallic systems.

The detailed analysis of partial contributions to the total electronic density of states of these systems should allow us to understand the mechanism of conservation of the dielectric state of ZrO$_2$ doped by CaO+V. The analysis of charge transfer between the components of Zr$_2$O$_4$, Zr$_2$O$_3$V, ZrCaO$_4$ and ZrCaO$_3$V is necessary to illustrate the transformation of ZrO$_2$ to the metallic system (ZrCaO$_4$ and Zr$_2$O$_3$V) or the conservation of the dielectric state of ZrCaO$_3$V due to substitution of Zr^{4+} ions by Ca^{2+} (ZrCaO$_4$) or of oxygen ions by vacancies (Zr$_2$O$_3$V). We shall see that ZrO$_2$ remains an insulator only in the case when there are compensative vacancies V side by side with Ca ions. To understand the stabilization

of c-ZrO_2 it is necessary to study also the influence of Me^{3+} ions and V vacancies on the electronic structure of ZrO_2. This investigation was carried out in [18] where, in spite of our computer difficulties, we considered the chemical formula of mole comounds with a real concentration of $(ZrO_2)_6Y_2O_3V$, which corresponds to the real mole portions of ZrO_2 and Y_2O_3. First let us consider the electronic structure of the c-phase (figure 1). It is characterized by six separated energy bands. The first and the second bands are formed by the 2s and 2p states of oxygen on the whole, the third and fourth bands by the 4d states of zirconium and, finally, the fifth and sixth bands by the 5s and 5p states. The first two bands (2s and 2p) correspond to the filled states, and the rest to vacant or excited states. In general the system considered represents a typical insulator with an energy gap between the 2p band and the 4d subband equal to 0.22 Ryd (3.0 eV) approximately. The small contribution of the 5s and 4d functions to the density of filled states testifies to the ionic character of bonding and the charge transfer from zirconium atoms to oxygen atoms (see below). It should be pointed out that, if the basis is enlarged and the 4f orbits of Zr and the 3d orbits of O are included, then the band structure undergoes small changes only above the conduction band. Instead of three separate bands the total s–p–d f hybridized band appears. Note also that the calculated electronic structure of pure c-ZrO_2 is in a good agreement with previous calculations [3, 14, 15].

The main change in the electronic structure for the transition from Zr_2O_4 to Zr_2O_3V is the appearance of the band formed on the whole, by vacancy states (figure 2(a)). This is the 1s band which is located directly under the 4d subband of zirconium.

The physical origin of formation of this zone consists of the capture of an 'electron cloud' by the vacancies. It corresponds to the formation of the state when the electron density is localized on the vacancies to a marked degree (in the present case they have a similar s behaviours). Note that this also causes the formation of local states of F^+ and F^- centres usually located in the forbidden band of the ideal crystal.

For the transition considered, the number of electrons (per doubled cell) decreases from 32 to 26. Since the oxygen 2s and 2p bands can contain only 24 electrons, the 1s band of the vacancy is also filled. The Fermi level is located in the sharp minimum of $N(E)$ at the energy separating the 1s states of V from the 2p states of V and the 4d states of Zr. This minimum corresponds to the final $N(E)$ 3 electrons Ryd^{-1} cell so that, in contrast with Zr_2O_4, Zr_2O_3V becomes a metal. All the above is qualitatively in agreement with [16].

It is interesting that the variation in electronic structure for the transition from Zr_2O_4 to Zr_2O_3V is analogous to that for the doping of semiconductors by donor impurities or n-type impurities. Indeed, in both cases the superfluous electrons appear with regard to the number necessary for ionic bonding and covalent bonding, respectively. In the case of semiconductors the superfluous electrons are known to form a new energy (impurity) level in the forbidden gap directly under the bottom of conduction band. As a result, the Fermi level is displaced to the bottom of the conduction band [16] and on heavy doping to a situation where the states of the conduction band are filled even at 0 K, i.e. the Fermi level is found inside this band (such a semiconductor is called 'degenerate').

In the case of Zr_2O_3V the impurity s states of the vacancy are also formed in the forbidden band (between 2p and 4p bands, but essentially close to the latter). Thus Zr_2O_3V may be considered as a degenerate semiconductor (to be exact, as a dielectric). With increasing concentration of vacancies the system is easily seen to return strictly to the state of a semiconductor. Indeed in both cases the width of the 1s band of vacancies becomes narrow and the Fermi level is found in the forbidden energy gap.

The effect discussed evidently concerns directly the increase in conductivity near the melting point of ZrO_2. In fact, with increasing temperature, one should expect an increase
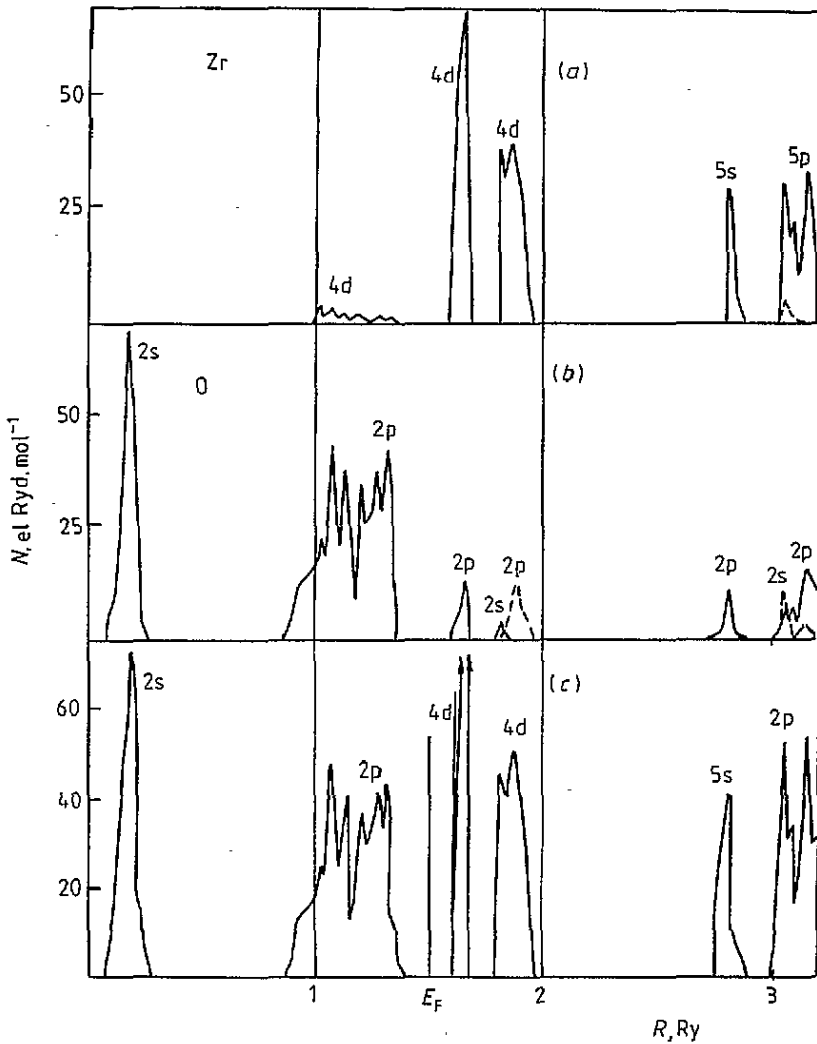
Figure 1. (c) Total and (a, b) partial ((a) Zr; (b) O) densities of states for ZrO_2.

in vacancy concentration and. hence, metallization of the system.

On the transition from Zr_2O_4 to $ZrCaO_4$ the bands which would be formed mainly by calcium atoms. do not appear in the range of filled states (figure 1). As a result, the structure of the density of states remains the previous structure in this range. As the total number of electrons decreases from 32 to 30 in the present situation and the 2s and 2p bands of oxygen may contain 32 electrons as before, the 2p band is filled only partially, and the system becomes metallic. This is similar to the high-temperature superconductivity ceramic La_2CuO_4, the metallic state of which is conditioned by the partial filling of the bands formed by the 2p states of oxygen on the whole [17]. Continuing the analogy with the superconductors, note that the electronic structure variation when going from Zr_2O_4 to $ZrCaO_4$ is similar to that when doping semiconductors by the p-type impurities. In fact, on such doping, the energy levels in valence band which remain unfilled are similar to what is observed at the transition from Zr_2O_4 to $ZrCaO_4$. The analysis of partial contributions to
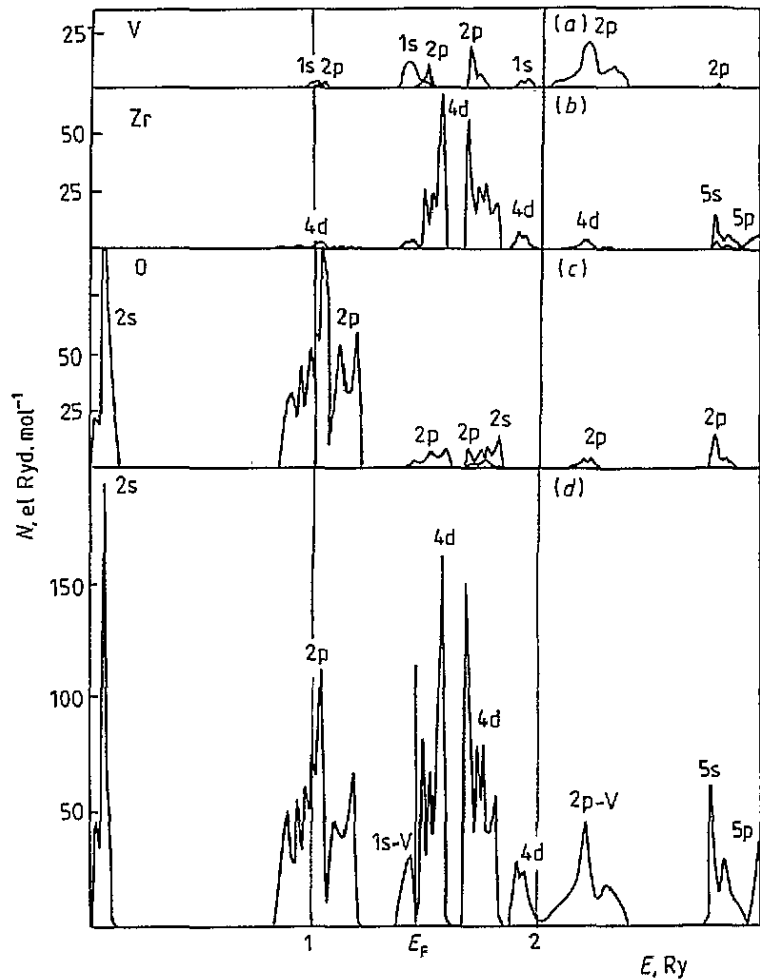
Figure 2. (d) Total and (a–c) partial ((a) V; (b) Zr; (c) O) densities of states for Zr_2O_3V.

the density $N(E)$ of states shows that in $ZrCaO_4$ the Ca atoms behave rather as atoms of the 3d metal and not of the 4d metal (figure 3(a)). Indeed, if in the separate Ca atom the 3d levels stay vacant but the 4s levels are filled immediately, then in $ZrCaO_4$, the 3d-states of Ca begin to be filled while the 4s states remain unfilled and vice versa. One may suggest that the 4d character of Ca atoms is 'forced' on them by the 4d character of zirconium atoms via hybridization of these wavefunctions in the crystal (figure 3(a) and 3(b)). Although the Ca atoms contribute to the density of filled states owing to the 3d function, this contribution is still small when compared with those from the oxygen or even zirconium atoms. This testifies to the small total charge of valence electrons in the ASA spheres of Ca, i.e. the high degree of their ionization.

On the basis of the cluster calculations, Ellis and Lam [6] concluded that the substitution of the zirconium atom by Ca leads, on the one hand, to the decrease in the forbidden gap and, on the other hand, to the formation of Ca states above the valence band at the same time. Neither of these conclusions was confirmed in our calculations; the dielectric gap remained almost the same as in Zr_2O_4 and no states of Ca were observed in the gap above
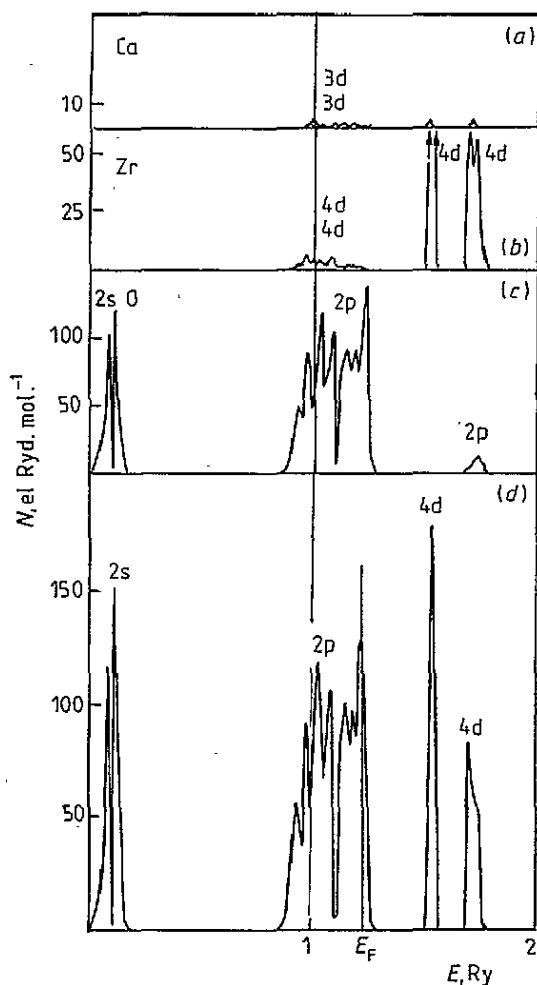
Figure 3. (*d*) Total and (*a*–*c*) partial ((*a*) Ca; (*b*) Zr; (*c*) O) densities of states for ZrCaO$_4$.

the valence band.

For the transition from ZrCaO$_4$ to ZrCaO$_3$V the electronic structure changes as for the transition from Zr$_2$O$_4$ to Zr$_2$O$_3$V (compare figures 3 and 4 with figures 1 and 2); the vacant 1s band appears. The total number of electrons in this case decreases from 30 to 24, but the 2s and 2p bands of O may now contain just such a number of electrons. Then one may also say that the concentrations of effective impurities of n and p type balance each other and there is no deficiency (or abundance) of electrons compared with the quantity necessary for the ionic bonding. Hence it follows that, to realize the non-conducting state it is necessary that, side by side with the metallic ions, 'compensative' vacancies exist (as occurs in real systems).

Let us discuss the charge distribution between the components and turn our attention to table 2. The valence charges inside the ASA spheres of different components Z, and the values ΔZ characterizing the charge transfer between these spheres are represented in this table (the vacancy is believed to be a component and, obviously, for this vacancy $Z_V = -\Delta Z$). It follows from table 2 that the charge flows from the Zr and Ca spheres, but it
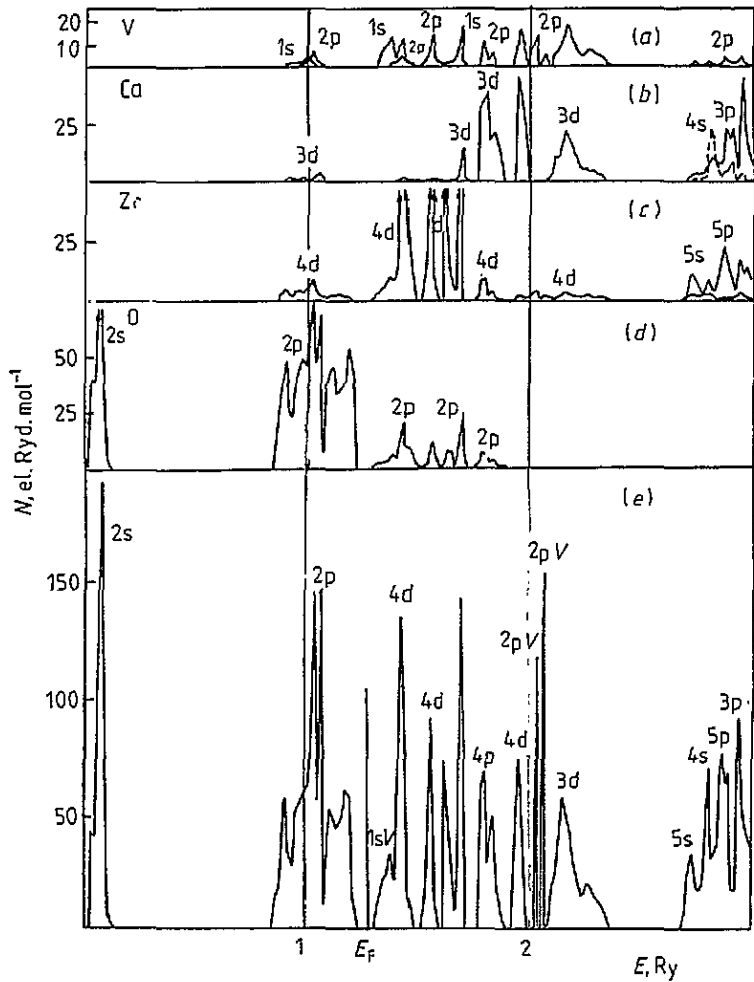
Figure 4. (e) Total and (a–d) partial ((a) V; (b) Ca, (c) Zr; (d) O) densites of states for ZrCaO$_3$V.

flows to the O and V spheres. The outflux of charge Z from the Zr spheres changes slowly for the transition from one system to another, although it decreases in the order Zr$_2$O$_4$, Zr$_2$O$_3$V, ZrCaO$_4$ and ZrCaO$_3$V. The outflux from Ca spheres is approximately half that from Zr, but the valence of Ca is also half that of Zr; on the whole the order of ionization of Zr and Ca atoms is found to be very similar ($\Delta Z/Z \simeq 0.70$). The influx of charge to the V and O spheres is different essentially for Zr$_2$O$_3$V and ZrCaO$_3$V. In the first case the charge influx to the vacancy sphere is found to be larger than that to the oxygen sphere, but in the second case it is less than half that to the oxygen sphere. The explanation for this result is as follows: in Zr$_2$O$_3$V, the 1s states of V are filled but, in ZrCaO$_3$V, only the states hybridized with 2p states of oxygen are filled (figures 2(a) and 4(a)). This has already been noted in [7]. In general the comparatively large charge transfer between the components in all systems testifies to the mainly ionic character of bonding in these materials.

Table 2. Valency electron charges Z located in the ASA spheres of different components and values of charge transfer from one sphere to another, $\Delta Z = Z - Z_v$ (Z is the valence of the separated atom).

ASA sphere	Zr_2O_4		Zr_2O_3V		$ZrCaO_4$		$ZrCaO_3V$	
	ΔZ	Z_v	ΔZ	Z_v	ΔZ	Z_v	ΔZ	Z_v
Zr	2.770	1.230	2.679	1.321	2.670	1.330	2.647	1.353
Ca	—	—	—	—	1.420	0.580	1.467	0.533
O	1.385	7.385	−1.312	7.312	−1.020	7.020	−1.187	7.187
V	—	—	−1.423	1.423	—	—	−0.552	0.552

4. Conclusions

The change in electronic structure of c-Zr_2O_4 containing oxygen vacancies and calcium ions is analysed. According to the results of calculations, the oxygen vacancies in ZrO_2 form their own band of 1s type located near the bottom of the conduction band. At the same time, the Ca atoms do not form their own band and therefore their addition results in a simple displacement of the Fermi level downwards in energy and to 'metallization' of the systems $ZrCaO_4$ and Zr_2O_3V. To keep the insulating state the presence of 'compensative' vacancies side by side with the Ca ions is necessary ($ZrCaO_3V$). In the presence of vacancies alone, the dielectric state may be considered only for small concentrations because of the formation and filling of a vacancy band separated from the 4d band by a small energy gap. This gap vanishes for concentrations above some critical concentration, and the system becomes metallic (Zr_2O_3V). All samples investigated demonstrate the mainly ionic character of bonding. To understand the stabilization of the c-ZrO_2 it is necessary to study also the influence of Me^{3+} ions and V vacancies on the electronic structure of ZrO_2. This investigation was carried out in [18] where, in spite of our computer difficulties, we considered the chemical formula of mole compounds with the real concentration of $(ZrO_2)_6Y_2O_3V$, which corresponds to real mole portions of ZrO_2 and Y_2O_3. The results of the investigation [4, 18] and the present work allow us to propose the mechanism of stabilization of c-ZrO_2 described above. In addition to c–t transitions there are the t–m transitions in ZrO_2 which can be investigated also in the framework of the proposed approach.

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