TOPICAL REVIEW

Charge distribution near bulk oxygen vacancies in cerium oxides

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Abstract

Understanding the electronic charge distribution around oxygen vacancies in transition metal and rare earth oxides is a scientific challenge of considerable technological importance. We show how significant information about the charge distribution around vacancies in cerium oxide can be gained from a study of high resolution crystal structures of higher order oxides which exhibit ordering of oxygen vacancies. Specifically, we consider the implications of a bond valence sum analysis of Ce7O12 and Ce11O20. To illuminate our analysis we show alternative representations of the crystal structures in terms of orderly arrays of coordination defects and in terms of fluorite-type modules. We found that in Ce7O12, the excess charge resulting from removal of an oxygen atom delocalizes among all three triclinic Ce sites closest to the O vacancy. In Ce11O20, the charge localizes on the next nearest neighbour Ce atoms. Our main result is that the charge prefers to distribute itself so that it is farthest away from the O vacancies. This contradicts the standard picture of charge localization which assumes that each of the two excess electrons localizes on one of the cerium ions nearest to the vacancy. This standard picture is assumed in most calculations based on density functional theory (DFT). Based on the known crystal structure of Pr6O11, we also predict that the charge in Ce6O11 will be found in the second coordination shell of the O vacancy. We also extend the analysis to the Magnéli phases of titanium and vanadium oxides (MnO2n−1, where M = Ti, V) and consider the problem of metal–insulator transitions (MIT) in these oxides. We found that the bond valence analysis may provide a useful predictive tool in structures where the MIT is accompanied by significant changes in the metal–oxygen bond lengths. Although this review focuses mainly on bulk cerium oxides with some extension to the Magnéli phases of titanium and vanadium, our approach to characterizing electronic properties of oxygen vacancies and the physical insights gained should also be relevant to surface defects and to other rare earth and transition metal oxides.

(Some figures in this article are in colour only in the electronic version)
1. Introduction

Non-stoichiometric phases of a number of transition metal and rare earth oxides have become widely studied in the past decade because of their potential in technological applications. Important examples are derived from the ‘parent’ materials TiO$_2$, VO$_2$, ZrO$_2$, HfO$_2$, CeO$_2$, by doping with metal ions or reduction by removal of oxygen atoms. A key scientific question in all these materials is the structure and electronic properties of oxygen vacancies. Ceria (cerium oxide) is a technologically important material with applications in high temperature electrochemical processes associated with this reversible chemical reaction. There have been, broadly speaking, three different approaches for investigating this problem. Crystallographers have attempted to establish general principles for O vacancy ordering in the reduced ceria phases. In 1974, Martin proposed the coordination defect model [20]. He suggested that when CeO$_2$ is reduced to the various defective phases, CeO$_{2-x}$, according to equation (1), O vacancies are formed in the lattice structure.

\[
\text{CeO}_2 \rightleftharpoons \text{CeO}_{2-x} + \frac{x}{2}\text{O}_2(g), \quad 0 \leq x \leq 0.5. \tag{1}
\]

The crystal structure adopted by any such defective phase, CeO$_{2-x}$, is understood to be the one that provides the most favourable energetics for the arrangement of all the O vacancies within the structure. In a widely accepted view of the microscopic description of O vacancy formation and ordering in CeO$_{2-x}$ phases, the two electrons associated with a missing O atom when an O vacancy forms fully localize on two of the four equivalent Ce$^{4+}$ ions which form a tetrahedron around the vacancy site, as shown in equation (2) [16, 17, 6, 18]:

\[
4\text{Ce}^{3+} + \text{O}_0 = 2\text{Ce}^{4+} + 2\text{Ce}^{4+} + V_0 + \frac{1}{2}\text{O}_2(g) \tag{2}
\]

where we have used the Kroger–Vink notation [19] so that the symbols have the following meanings: Ce$_x$O$_{2-x}$—a Ce$^{4+}$ ion on a Ce lattice site, O$_0$—O$^{2-}$ ion on an O lattice site, Ce$^{3+}$—a Ce$^{3+}$ ion on a Ce lattice site and V$_0$—neutral O vacancy site. This mechanism, which we will henceforth refer to as the standard picture, is illustrated in the schematic in figure 1. The localization of an electron on a Ce$^{4+}$ ion converts it to the slightly larger Ce$^{3+}$ ion with one electron in the 4f orbital. In the reverse process where a defective phase, CeO$_{2-x}$, is oxidized, two 4f electrons from the two neighbouring Ce$^{3+}$ ion sites move onto the site where an O atom is incorporated and then delocalize into the O 2p valence band. Thus, the reversible processes of oxidation and reduction in equation (1) have been considered to involve the extremal states of the Ce 4f electrons in which they are fully delocalized and fully localized respectively [17].

![Figure 1. Schematic of the standard picture of charge redistribution following the formation of an oxygen vacancy in CeO$_2$. The tetrahedron of Ce atoms (black circles) with an O atom at its centre (grey (orange in colour version) circle) is shown along with the charges on these atoms in the simple ionic picture description of CeO$_2$. The process of reduction shown by the arrow leads to a neutral O vacancy at the centre of the tetrahedron (empty circle) while two of the Ce ions have been reduced to the 3+ oxidation state.](image)
an O vacancy is created in the lattice of a rare earth oxide, the local environment of the vacancy undergoes relaxations in such a way that the four nearest neighbour Ce and six nearest neighbour O atoms form a stable structural entity which is referred to as a coordination defect. The crystal structures of the higher rare earth oxides are then determined and restricted by the topology of this coordination defect. In 1996, Kang and Eyring developed a different framework for describing vacancy ordering based on structural elements which are derived from the conventional unit cell of CeO$_2$ in a simple way [21]. As will be described in more detail later, there are thirteen of these structural elements, called modules, and they are the fundamental building blocks for all the crystal structures of the higher oxides in the Kang–Eyring fluorite-type module theory. As a result, it is possible to define what has been called a modular unit cell in which, instead of the usual atomic basis, the different modules form the basis. The value of this approach is the simplicity and elegance with which it provides insight into the superstructures observed in the reduced higher oxides in relation to the parent fluorite structure from which they are derived.

Neither crystallographic approach sought to explicitly account for the charge redistribution that occurs when an O vacancy is formed. However, as we will show, they provide useful vantage points from which to examine the problem. In contrast, the remaining two approaches in the strategy sought to specifically establish the nature and occupation of the Ce 4f level in the Ce oxides and consequently, the charge redistribution that occurs when an oxygen vacancy is created. The earliest literature in this direction emerged from spectroscopists [22], with their results being interpreted using either cluster models [23] or the single impurity Anderson model [24–26]. This work investigated the occupation of the Ce 4f level in the two extremal phases, CeO$_2$ and Ce$_2$O$_3$ and it was concluded that CeO$_2$ is mixed valence whereas Ce$_2$O$_3$ is a pure 4f$^1$ configuration. The result that CeO$_2$ is mixed valence is inconsistent with the ionic description underlying the standard picture. However, the models used to interpret the spectroscopic results are not parameter-free and the conclusions drawn from them have been contested [27].

Recently electronic structure calculations based of density functional theory (DFT) have been performed. In general, DFT results for CeO$_2$ assume empty Ce 4f states, which is the simple ionic picture of bonding in this oxide, e.g., [28]. To describe vacancy formation in CeO$_2$, the simplest case to consider is a $2 \times 2 \times 2$ supercell of CeO$_2$ from which a single O atom is removed. This supercell has the composition Ce$_{12}$O$_{15}$ (CeO$_{1.75}$). As this composition does not correspond to any known phases of reduced ceria, it is customary to require the structural parameters of the relaxed structure to match those of CeO$_2$ based on Vegard’s rule [29], i.e., there is a linear relationship between the lattice constant and the extent of reduction. As will be discussed in more detail in section 4.3, most of the DFT work supported the standard picture. However, the approximate functionals of DFT such as LDA, GGA, and LDA $+ U$ do not appear to describe well the electronic properties of the reduced phases [30–32]. Furthermore, recent calculations using hybrid functionals [33] and DFT $+ U$ [32–34] do not appear to support the standard picture.

As far as we know, a study of the charge distribution near bulk O vacancies in crystallographic phases of reduced cerium oxide apart from Ce$_2$O$_3$ (and the customary supercell of DFT calculations, i.e., Ce$_{1.97}$O$_{3}$) has not been done. Our study of the charge distribution in the well-characterized intermediate phases represents a complementary approach to answering the fundamental question of where the two electrons left behind when an O vacancy forms go. Furthermore, since no in situ studies have been done to identify the precise phases involved in ceria-based catalysis, it is also possible that the intermediate phases may play an important role in the engineering applications of these materials.

In this study, we examine the standard picture for the oxidation and reduction in ceria described above, considering primarily two intermediate phases namely Ce$_{11}$O$_{20}$ and Ce$_7$O$_{12}$. A brief discussion of Ce$_{0.75}$O$_{1.75}$ is also included. We discuss this in light of our recent results on Ce site valencies obtained by an analysis of observed crystal structures using the bond valence method [35]. The two cases, Ce$_{11}$O$_{20}$ and Ce$_7$O$_{12}$, were chosen to illustrate the evolution of the charge distribution around O vacancies that occurs with reduction. Furthermore, apart from the extremal structures, namely CeO$_2$ and Ce$_2$O$_3$, these two examples along with Ce$_2$O$_3$ were the only crystal structures of the Ce oxides for which we were able to obtain highly accurate crystallographic data to enable the type of analysis we do here.

As is discussed later, both Ce$_{11}$O$_{20}$ and Ce$_7$O$_{12}$ have fluorite-related crystal structures. According to Kang and Eyring, Ce$_7$O$_{12}$ is the limiting intermediate oxide for which any further reduction leads to loss of the fluorite structure of CeO$_2$ [36]. However, the fluorite-related Ce$_2$O$_3$ phase was recently observed in the phase diagram of the Ce–O system [37]. In addition to the conventional unit cells, we will generally use the Kang and Eyring structural principle of modular units to discuss O vacancy ordering in reduced ceria phases [36, 21, 38, 39]. There will be occasional references to Martin’s coordination defect model [20, 16, 40] where this model may provide a better conceptual framework.

This paper is organized as follows: in section 2 we present the crystal structures of Ce$_{11}$O$_{20}$ and Ce$_{7}$O$_{12}$ both in the conventional way as well as in the representation of the Kang–Eyring fluorite-type module theory. We show how the Kang–Eyring fluorite-type module theory helps to understand the structure of O vacancies in Ce$_{11}$O$_{20}$ and Ce$_7$O$_{12}$ in relation to the parent fluorite structure. In section 3, we consider the implications of our bond valence calculations for the charge distribution in the local environment of the O vacancies. Section 4 discusses how our results conflict with the standard picture of charge localization in reduced ceria phases. We then make a prediction of the charge distribution to be expected in the Ce$_{0.75}$O$_{1.75}$ crystal based on the bond valence model in section 5. The possibility of direct f–f coupling between neighbouring Ce sites in crystals of the Ce oxides. We assess the validity of this idea from the Harrison method of universal parameters in section 6. Section 7 examines the usefulness of bond valence analyses in understanding metal–insulator
transitions using titanium and vanadium Magnéli phases as examples. Conclusions are presented in section 8.

2. Alternative representations of the crystal structures of Ce11O20 and Ce7O12

2.1. Coordination defect model

Martin proposed describing an O vacancy in a Ce oxide crystal as a structural entity made up of 4 Ce ions and 6 O ions around the vacancy site, as illustrated in figure 2 [20, 16]. The four Ce ions form the first coordination shell (a tetrahedron) of the vacancy site while the six O atoms form the second coordination shell (an octahedron). Compared to the perfect structure of CeO2, all four Ce ions are displaced 0.2 Å away from the vacant O site, while the O atoms are shifted 0.3 Å towards the vacancy. This structural unit has been called the coordination defect and it maintains its structural integrity in a crystal of the oxide (see figure 2). It is constructed from two types of subunits called octants, one of composition Ce4O called the δ phase and the other incorporating an O vacancy, the λ phase, of composition Ce4. The exploded view in figure 2 (b) shows these octants and how they are arranged to form the coordination defect. This model, in its original formulation, does not explicitly account for the changes in the valences of the Ce ions and the four Ce ions which are nearest neighbours to the O vacancy in the coordination defect are implicitly identical.

2.2. Modules

Soon after the elaboration of Martin’s coordination defect model [16], Kang and Eyring developed a simpler model for constructing the crystal structures of the higher rare earth oxides, i.e., oxides from Ce7O12 to CeO2 based on a different set of structural elements [21]. These so-called modules, include the CeO2 unit cell, with the rest derived from it by creating one or two O vacancies in certain prescribed ways, resulting in a total of thirteen modules. These modules are the fundamental building blocks for all the higher oxides under a prescription of rules defined by the authors [36]. In figure 3, we show the ten modules relevant to Ce11O20 and Ce7O12 in addition to the unit cell of CeO2. Kang and Eyring’s method accounted for all the higher oxides known at the time and was successful in predicting the existence of new structures [36]. The Kang and Eyring method enables a relatively simple way of visualizing vacancy sites which are otherwise difficult to decipher when the structure is cast in the conventional setting of its space group. This provides considerable facility in the analysis of the local environment of the O vacancy site. As a result, we will make frequent reference to this framework in the rest of this paper.

2.3. Ce11O20

The conventional unit cell of Ce11O20 is shown in figure 4. Note that for all ball and stick figures in this paper, the sticks between the Ce sites and the O vacancy site do not represent chemical bonds. Instead, the sticks are only included to show the geometric relationships between the atoms. The unit cell of Ce11O20 consists of one formula unit per unit cell with inversion as its point group symmetry. It has six Ce and ten O distinct sites along with their inversion images with the Ce(1) site as the centre of inversion. However, for a
description of the vacancy structure and charge distribution in this crystal, it is convenient to view all the lattice points in the O sublattice as roughly equivalent and to divide the Ce sublattice into two regions. The first region consists of the Ce(1) and Ce(2) sites which, in the Ce sublattice, occupy the second coordination shells of the O vacancies. The remainder of the Ce atoms are the first coordination shells of the O vacancies. The crystal structure of Ce_{11}O_{20} can be readily related to the fluorite structure of CeO_{2} from which it is derived by reduction. This relationship becomes clearer with the Kang–Eyring module representation. Kang and Eyring [36] have shown that the modular unit cell of Ce_{11}O_{20} has the modular composition 3F, 4D, 4U where the module types are as given in figure 3. They also provided the modular sequences for the [100] and [010] directions in this crystal as FFU^{3}D_{2}FU^{4}D_{1}D_{1} and FU^{3}D_{3}FU^{2}D_{3}FU^{2}D_{4} respectively. Using this information along with their module juxtaposition rules, we derived the modular sequence for the [001] direction to be D_{1}D_{2}FFU^{3}U^{1}U^{1}D_{3}. This then enabled us to construct the 3D modular unit cell of Ce_{11}O_{20} shown in figure 5. We note that this unit cell is not unique. There is only one type of O vacancy in the crystal of Ce_{11}O_{20} and if we only consider the Ce sublattice, each O vacancy has the four Ce(3)–Ce(6) sites forming its first coordination shell. These four Ce sites form a distorted tetrahedron. The O vacancy Ce(i) distances are shown in table 1 where i = 3–6. The second coordination shell consists of twelve Ce sites namely, two Ce(1), four Ce(2), two Ce(3), two Ce(4) and one of each of the Ce(5) and Ce(6) sites as shown in table 1. Of these twelve Ce sites in the O vacancy’s second coordination shell, only half a Ce(1) site and one Ce(2) site can be assigned to the particular O vacancy site. Thus, in total, an O vacancy in Ce_{11}O_{20} is proportionately associated with five and half Ce sites. It is convenient to work with an integral number of Ce sites when studying the charge distribution in the local environment of an O vacancy. In order to do this, we propose to partition the lattice so that we consider a vacancy cluster consisting of two neighbouring O vacancies which can then

Table 1. The first- and second coordination shells of the O vacancy in the Ce sublattice of Ce_{11}O_{20} and some selected distances between the sites. These Ce–Ce distances show that the average intra-tetrahedral separation between Ce sites (4.2 Å) is larger than the inter-tetrahedral separation (3.9 Å).

| Ce site (from O vacancy) | Direct Ce–Ce distance (Å) |
|--------------------------|----------------------------|
| First coordination       |                            |
| Ce(6)                    | 2.5106 Ce(6)–Ce(3)         | 4.169 |
| Ce(3)                    | 2.5674 Ce(6)–Ce(4)         | 4.194 |
| Ce(4)                    | 2.5817 Ce(6)–Ce(5)         | 4.207 |
| Ce(5)                    | 2.6185 Ce(3)–Ce(4)         | 4.219 |
| Ce(6)                    | 2.6431 Ce(3)–Ce(5)         | 4.144 |
| Ce(4)                    | 2.6390 Ce(4)–Ce(5)         | 4.234 |

| Second coordination      |                            |
|--------------------------|----------------------------|
| Ce(5)                    | 4.3184 Ce(1)–Ce(5)         | 3.810 |
| Ce(6)                    | 4.4438 Ce(1)–Ce(6)         | 5.561 |
| Ce(2)                    | 4.4952 Ce(1)–Ce(2)         | 7.175 |
| Ce(3)                    | 4.5265 Ce(2)–Ce(3)         | 3.873 |
| Ce(2)                    | 4.5340 Ce(2)–Ce(4)         | 3.861 |
| Ce(1)                    | 4.5579 Ce(2)–Ce(5)         | 6.860 |
| Ce(1)                    | 4.5705 Ce(2)–Ce(6)         | 5.573 |
| Ce(2)                    | 4.6007                      |      |

Figure 4. The unit cell of Ce_{11}O_{20} whose space group is P 1. There are six distinct Ce sites in this crystal. However, to facilitate the discussion of vacancy structures and charge distribution, the Ce sublattice has been partitioned into two types of lattice points, as shown in the legend. The first set of lattice points consists of the Ce(1) and Ce(2) sites which, if we only consider the Ce sublattice, occupy the second coordination shells of the O vacancies. The second set consists of the remainder of the Ce sites and these form the first coordination shell of the O vacancies in the Ce sublattice of the crystal. There are ten distinct O sites in the crystal, but for our purposes, it is convenient to treat all the O sites in the O sublattice as roughly equivalent, as indicated in the legend.

Figure 5. The fluorite-type modular unit cell of Ce_{11}O_{20} derived using the Kang and Eyring rules [36]. In (a), the modular unit cell is constructed from transparent modules to show the location of the O vacancy site, as indicated by the shaded tetrahedra with the module types as identified in (c) and shown in detail in figure 3. A simplified block representation of the modular unit cell given in (a) is shown in (b). The exploded view with all the module types identified is given in (c). The modular composition is: top layer—U^{1}, F, U^{4}; middle layer—D_{1}, D_{2}, F, F, U^{5}; bottom layer—D_{2}, D_{3}, U^{2}. These figures make clear the distribution of the O vacancies within the crystal in relation to the original fluorite structure. There are large contiguous regions, modules F, where there are no O vacancies.
be associated with eleven Ce sites. Since the choice of the Ce(1) site is the most difficult to establish, we pick a Ce(1) site and construct the vacancy cluster around it. A Ce(1) site has four closest O vacancies all in the third coordination shell. Two of the O vacancies are located 4.558 Å away from the Ce(1) lattice point with the other two at 4.571 Å. Since the Ce(1) site is a centre of inversion, each of these pairs of O vacancies are related by inversion symmetry. We choose the pair with the shortest distance from the Ce(1) site to define the vacancy cluster consisting of two O vacancies. The cluster obtained by this procedure is illustrated in figure 6. This cluster should not be confused with the divacancy of Ce$_7$O$_{12}$ to be discussed later. The divacancy of Ce$_7$O$_{12}$ is a unique structural entity of the crystal arising from long range ordering of the vacancies whereas the cluster we define here is simply an analytic convenience. It cannot be strictly considered to be specified in a unique way since the pair of O vacancies we chose is only 0.01 Å closer to the Ce(1) compared to the other. On the O vacancy sublattice, each O vacancy has four nearest neighbours 6.134 Å away for the first pair and 6.138 Å for the second. There is no difficulty in identifying the Ce(2) site associated with each O vacancy since there is only one closest (4.495 Å) Ce(2) site. The distances are calculated from the crystallographic data of Kummerle and Heger [42]. Zhang et al [43] suggested another useful way of viewing the crystal structure of Tb$_{11}$O$_{20}$ which is also directly applicable to Ce$_{11}$O$_{20}$ because these compounds are isostuctural. Their perspective is based on the observation that the O vacancies are more or less uniformly distributed within the crystal structure with no evidence of vacancy pairing. The vacant O sites are distributed in a way such that the separation between the defects is maximized and thus, the repulsive interactions are reduced. The Ce ions in the first coordination shell relax outward in a more or less isotropic way (Ce–V$_{O}$ ranges 2.51–2.62 Å, see table 1). As the vacant Ce tetrahedra expand, the regions between them experience substantial compression, as indicated by the difference in the distances between the intra-tetrahedral ions (4.2 Å) and those of the inter-tetrahedral ions (3.9 Å). These distances are given in table 1. In this table, the intra-tetrahedral ion distances are given as the direct Ce–Ce distances in the first coordination shell while the inter-tetrahedral ion distances refer to these distances in the second coordination shell: Ce(1)–Ce(5), Ce(1)–Ce(3); Ce(2)–Ce(3) and Ce(2)–Ce(4). The inter-tetrahedral Ce ions have a coordination number of eight as in the parent fluorite structure. In discussing the charge distribution in the local environment of the vacancy, we will notice that the charge is distributed in a manner which is distinctly different between the intra-tetrahedral and inter-tetrahedral Ce ions.

2.4. Ce$_7$O$_{12}$

Figure 7 shows the unit cell of Ce$_7$O$_{12}$ in the conventional rhombohedral setting. In the Kang–Eyring framework, the modular composition of this crystal is D$_2$, D$_3$, D$_4$, W$^5_1$, U$^1$, U$^2$ and U$^4$ [36]. The modular unit cell constructed from this basis is depicted in figure 8. It is readily apparent from figure 8 where the O vacancy sites are located. There are two types...
Ce atoms (six) must be the Ce(2) sites of Ce7O12. There are seven Ce atoms in the formula unit, the rest of the Ce sites, Ce(1) and Ce(2), in the crystal lattice of Ce7O12, which are of S6 and i symmetry respectively [44, 42]. These distinct sites are indicated in the conventional unit cell of figure 7. Although Kang and Eyring did not explicitly identify the distinct sites in their modular unit cell according to their symmetries, it is apparent that by translating their unit cell in three dimensions, two distinct Ce sites are obtained; the S6 site with two nearest neighbour O vacancies around it and the i site with only one O vacancy. The S6 site has been called the divacancy site [36] and it forms a shared corner between two coordination tetrahedra of the O vacancies, as illustrated in figure 11. We list here some interatomic distances that we will use in our analysis of the divacancy cluster: Ce(2)–Ce(2) = 4.09 Å, Ce(1)–Ce(2) = 4.11 Å, Ce(1)–O(2) = 2.19 Å and for Ce(2)–O(1), there are two relevant bond lengths, namely 2.23 and 2.32 Å. The Ce–Ce distances are direct distances between these sites, not distances along the Ce–O bonds connecting them. It appears that the Ce sublattice has not changed much relative to CeO2.

It is helpful to visualize vacancy ordering in Ce7O12 by viewing the divacancy as a structural unit of the O vacancies in this crystal. This clarifies why the ratio of S6 to i sites is 1:6; all the Ce sites which are nearest neighbours to the two O vacancies forming a divacancy are of S6 symmetry. As there are seven Ce atoms in the formula unit, the rest of the Ce atoms (six) must be the Ce(2) sites of i symmetry. The formation of the divacancy structures as CeO2 is reduced to Ce7O12 is associated with some relaxation of the crystal lattice, although the Ce sublattice remains somewhat invariant [36]. We now examine this relaxation process, which is illustrated in figure 9 and based on Kummerle and Heger’s neutron diffraction data [42]. The bond lengths in CeO2 are 2.434 Å and 2.706 Å for the Ce–O and O–O bonds respectively. When a divacancy is formed, the bonds within the divacancy relax and diffraction data show that in Ce7O12, the ‘bonds’ lengths are [42]: 2.505 Å for O(1)–V̅O, 2.364 Å for O(2)–V̅O, 2.418 Å for Ce(1)–V̅O and 2.543 Å for Ce(2)–V̅O. This structural data indicates that compared to CeO2, the bonds within the divacancy have changed as follows: the O(1)–V̅O and O(2)–V̅O ‘bonds’ contract by 0.20 Å and 0.34 Å respectively while the Ce(2)–V̅O ‘bond’ gets longer by 0.109 Å. The Ce(1)–V̅O ‘bond’ is practically unchanged, showing only a small contraction of about 0.02 Å. Thus, we see that, just as was the case for Ce11O20, the O atoms are attracted to the vacancy site while the Ce(2) atoms are repelled away so that the O atoms now become the nearest neighbours of the vacancy site. This appears to be a general feature of vacancies in rare earth higher oxides [16, 36]. We note that the six O atoms around the vacancy relax by different amounts with the O(2) atoms being more strongly attracted to the vacancy site. We also note that according to the coordination defect model, the crystal structure of Ce7O12 has the highest packing density of the coordination defect.

Figure 10. Charges of the different Ce ions in the vacancy cluster of Ce11O20, obtained from the bond valence model. The vacancy cluster consists of two vacancies connected by the Ce(1) site which is also a centre of inversion for the cluster. The four excess electrons that arise due to the removal of the two oxygen atoms do not localize on the cerium atoms nearest the vacancies. This is contrary to the standard picture.

3. Excess electrons delocalize away from the oxygen vacancy

Having discussed the O vacancy ordering in Ce11O20 and Ce7O12, as well as proposing some vacancy clusters suitable for the analysis of charge distribution in these crystals in the section 2, we now present the results of the bond valence calculations, I, in these clusters.

3.1. Ce11O20

Figure 10 shows the bond valence sums on the various Ce sites in the vacancy cluster of Ce11O20 which was introduced...
earlier, see figure 6. Clearly the charge from the vacancy does not localize on the Ce sites closest to the vacancy but rather, delocalizes onto the Ce(1) and Ce(2) sites. This contradicts the standard picture. The results of figure 10 can be compared with those of Tb$_{11}$O$_{20}$ with which it is isostructural. Based on a simple consideration of the crystal radii of the cations [45], Zhang et al [43] suggested the following valencies for the cations: Tb(1) and Tb(2)→+3, Tb(3) and Tb(4)→+3.75, Tb(5) and Tb(6)→+4. Here the numbering of the sites is the same as for Ce$_{11}$O$_{20}$ given in figure 6. Their assignment of the site valences qualitatively agrees well with our bond valence results for Ce$_{11}$O$_{20}$. The Tb$^{3+}$ and Tb$^{4+}$ ions are $f^8$ and $f^7$ configurations respectively and can be compared to the corresponding $f^3$ and $f^0$ configurations respectively for the Ce ions. They suggested the possibility of fast electron transfer between the neighbouring Tb(2) sites so that, instead of two Tb(2)$^{3+}$ and one Tb(2)$^{4+}$ instantaneous states, an average is obtained from the neutron diffraction data. It was suggested by the authors that the thermal ellipsoids of the atoms in Ce$_7$O$_{12}$, which are much higher than in CeO$_2$, could be evidence of the dynamic disorder arising from the fast electron transfer.

3.2. Ce$_7$O$_{12}$

The charge distribution in the divacancy of Ce$_7$O$_{12}$ is shown in figure 11. This figure clearly shows that, apart from the Ce(1) site which is of a different local site symmetry compared to the Ce(2) sites, the charge delocalizes over all three of the Ce atoms closest to the vacancy. Again, this contradicts the standard picture, which has the electrons completely localized on two of the neighbouring Ce atoms.

In I, we pointed out that a naive consideration of the stoichiometric valence of a compound may not be adequate to describe the charge distribution in Ce oxides. The above discussion on Ce$_7$O$_{12}$ and Ce$_{11}$O$_{20}$ demonstrates this point clearly. The simple stoichiometric valence approach strictly assigns integral valences to ions in a compound and, thus, assumes that the charge is fully localized on these sites. On the other hand, when one calculates an average stoichiometric valence, the assumption that the charge fully delocalizes over the relevant ions is made. However, for a given compound, the reality may be quite different from either of these scenarios of perfect localization/delocalization of the charge [46]. As illustrated by the examples of Ce$_7$O$_{12}$ and Ce$_{11}$O$_{20}$, it is possible within the same compound, to have sites where the charge is fully localized, others where it only partially localizes and yet others where it fully delocalizes. Recently Liebau et al proposed to distinguish between the stoichiometric valence of a compound and its structural valence, the latter being the valence obtained from the bond valence model [47]. The introduction of structural valence into the terminology is significant as this gives us a language for a concept which is more realistic in discussions of charge distribution in crystal structures.

4. Failure of the standard picture of charge localization near a vacancy

We now discuss the above results comparing them to the standard picture and propose an alternative view of how the charge redistributes itself following O vacancy formation in ceria as deduced from the bond valence model. As already mentioned, the conventional description of the electronic processes involved during O vacancy formation requires that the excess charge at the vacant O site be shared between two of the four Ce ions which form the first coordination shell of the vacancy. This means that the tetrahedron formed by the four Ce ions around the O vacancy consists of two Ce$^{3+}$ and two Ce$^{4+}$ ions. This description is based on the ionic model for these oxides, although Kang and Eyring do indicate that there may be some covalent character in these oxides [36].

4.1. Ce$_{11}$O$_{20}$

If we assume that the four electrons which are left when the two O vacancies are formed are localized within the cluster, then we can describe how the charge redistributes itself. In fact, from the bond valence results, which also showed mixed valence in CeO$_2$, the valence of Ce in CeO$_2$ is 3.73 and the corresponding valence of O is −1.87. A description of vacancy formation in CeO$_2$ to form Ce$_{11}$O$_{20}$ can then be illustrated in the bond valence model as shown in figure 12. Thus, according to the mixed valence description of the CeO$_2$ crystal from the bond valence model (see figure 12(a)), when an O vacancy is created in CeO$_2$, a charge of −1.87 is left behind as opposed to a charge of −2.0 in the ionic picture. This then means that, if we consider the vacancy cluster of figure 10 and equivalently, figure 12(b), the creation of the two O vacancies leaves a total charge of −3.74 in the cluster. From figure 10, we can see that compared to their original valences in CeO$_2$, the valences of Ce(5) and Ce(6) are virtually unchanged. Thus, considering the change in the valences of the remainder of the Ce sites, the total charge accumulation on the Ce sites in the cluster is −2.87. There is therefore a discrepancy of ∼1 between the total extra charge in the Ce$_{11}$O$_{20}$ crystal inferred from the bonding in CeO$_2$ (i.e. −3.74) and that directly calculated for this crystal.
by the bond valence calculations (−2.87). This discrepancy is entirely consistent with the accuracy of the bond valence model reported in I, although we note that the accounting of charge we have done here from CeO\(_2\) to Ce\(_7\)O\(_{12}\) is very simplistic. It ignores the many-body effects which may follow the injection of extra charge at the Ce sites when the O vacancies are created. Such an extra charge may change the degree of mixing between the Ce 4f- and the O 2p states in a way that may not be related in a simple way to their state in CeO\(_2\). It may happen that, for instance, due to a change in the hybridization of Ce 4f- and the O 2p states, the extra charge may not be confined to the Ce 4f as we assumed in calculating the discrepancy in the total charge, but rather, some of the charge may go into the O valence band. It is expected that the results in figure 10 would capture these many-body effects. An important point from the results of figure 10 is that −1.99 (∼70%) of the total charge of −2.87 goes to the three Ce atoms in the second coordination shell with the remainder being shared among the eight Ce atoms in the first coordination shell.

Figure 12. A schematic to illustrate the formation of Ce\(_7\)O\(_{12}\) from CeO\(_2\) through vacancy formation in the O sublattice. In (a), a part of the CeO\(_2\) lattice, which, after removing the two O atoms (light grey (orange) circles), gives a cluster corresponding to the one given in figure 6. Also note that compared to figure 6, here we have made the further simplification of replacing all the Ce–O–Ce bonds with direct Ce–Ce bonds except for the two O atoms which are subsequently removed to create vacancies. For these two atoms, no bonding detail is given in the schematic, except that we place each of them at the centre of a regular Ce tetrahedron, reflecting their coordination environment in CeO\(_2\). The numbers shown at the atomic sites are the valences of the respective atoms as determined by the bond valence method [35], and figure 10. In (b), the cluster of (a) after reduction to create the two O vacancies (empty circles). The colours in this figure denote the following: black circles—Ce sites which are not nearest neighbours to any O vacancies, grey circles—Ce atoms which are the nearest neighbours of at least one O vacancy, light grey (orange) circles—O atoms and empty circles—O vacancies.

If one just considers the cation sublattice, it is evident that the charge accumulates in regions of high strain (inter-tetrahedral Ce ions) where the Ce–Ce distances are slightly shorter compared to the intra-tetrahedral case. This led some authors to consider the possibility that there may be some direct f–f hopping in these dense regions [43]. As we will discuss in section 6 for the case of Ce\(_7\)O\(_{12}\), direct f–f hopping appears unlikely in these oxides.

4.2. Ce\(_7\)O\(_{12}\)

Based on the results of figure 11, we can now discuss the electronic features of the local environment of the O vacancy in Ce\(_7\)O\(_{12}\). The formation of the Ce\(_7\)O\(_{12}\) divacancy from the CeO\(_2\) crystal lattice according to the BVM is schematically illustrated in figures 13(a) and (b). It can be seen that two corner-sharing Ce tetrahedra of CeO\(_2\) lose an O atom each from the centre of the tetrahedron. Our bond valence calculations show that the valences of the Ce(1) and Ce(2) sites in Ce\(_7\)O\(_{12}\) are +3.67 and +3.21 respectively. The valence at the Ce(1) site is comparable to the value of +3.73 calculated for Ce in CeO\(_2\) using a bond valence method analysis of the crystal structure. If we use the Kang and Eyring modular unit cell with its 8 O vacancies, 4 Ce(1) and 24 Ce(2) sites and further assume that we start from mixed valence CeO\(_2\) where the valences are +3.73 and −1.87 for the Ce and O sites respectively, we can get some estimate of how the excess charge on the O vacancy sites is distributed in the modular unit cell. The valence of the Ce(1) sites does not change much from its value before the O vacancy is created. Thus, virtually all the charge left at the vacancy site by an O atom is evenly distributed within the first coordination shell of the vacancy site among the (three) Ce(2) sites. On this basis and only considering a simple analysis using the bond valence results for CeO\(_2\), the valence at the Ce(2) sites is then readily calculated to be +3.11 (i.e., 3.73 − 1.87/3) which is comparable to the independently calculated value of +3.21 within the error bounds (±0.1) of the method. That the excess charge is not distributed evenly among all four of the Ce atoms in the first coordination shell contradicts the standard picture. If the charge was evenly distributed among all four Ce atoms, the valences would be +2.79 and +3.26 for the S\(_8\) and i sites respectively.

The above picture from the BVM can be contrasted with the standard picture description of the same process, as illustrated in figures 13(c) and (d). Here, there are two ways one could assign the valences of the Ce sites in the divacancy. One way is to assign valences of +4 to three of the i sites, two on the first tetrahedron and one on the second. The remainder of the Ce sites are then assigned the valence of +3, as illustrated in figure 13(d)(i). An alternative arrangement of the charges is illustrated in figure 13(d)(ii). Here, the three +4 valences are assigned one each to one of the i sites from the first and second tetrahedra with the third being assigned to the S\(_8\) site.

4.3. Comparison with calculations based on density functional theory

Most DFT calculations (performed in the supercell of composition Ce\(_{32}\)O\(_{63}\)) characterizing the location and character
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Figure 13. Schematic illustrating the charge distribution following divacancy formation, based on a bond valence sum analysis of the crystal structures of CeO$_2$ and Ce$_7$O$_{12}$. (a) Part of the CeO$_2$ lattice showing two neighbouring O atoms (light grey (orange) circles), each inside a tetrahedron of Ce atoms (black circles). The numbers shown are the bond valence sums for each of the atoms. When the two neighbouring O atoms are removed due to the reduction of CeO$_2$, the divacancy of Ce$_7$O$_{12}$ is formed as shown in (b). The bond valence sums on the Ce sites of triclinic symmetry (grey circles) have decreased from +3.73 in CeO$_2$ to +3.21 reflecting the presence of the additional charge left behind when the two O atoms are removed. The bond valence sum on the $S_6$ Ce site is virtually unchanged.

Figure 14. The unit cell of Ce$_6$O$_{11}$ which consists of four formula units. The Bravais lattice is monoclinic and of space group $P2_1/c$.

of the excess charge near bulk O vacancies concluded that the charge localizes on two of the nearest neighbour Ce ions [28, 17, 30, 48, 18, 49, 50, 12]. This is what we have called the standard picture. It appears that this picture was first brought into question by Castleton et al [32] in a paper where the question of charge localization was extensively explored. They concluded that it was not possible to fully localize the Ce 4f electrons on these Ce sites in the DFT $+U$ framework while at the same time preserving a correct description for all the other electrons. We are not aware of any subsequent DFT $+U$ reports directly addressing this question in the conventional supercell. The more recent work used a periodic electrostatic embedded cluster method (PEECM) [51]. This work found that the charge preferred to localize well away from the O vacancy, being on Ce sites of the third coordination shell. As this shell coincided with the boundary of the quantum mechanical part of the cluster used in the calculation, the authors raised the possibility that the result may be an artefact of the method.

We also note that Burow et al [51] obtained three different Ce–Ce distances of 4.07, 4.12 and 4.20 Å in the first coordination shell. These distances are shorter than those reported in table 1 for the vacancy cluster of Ce$_{11}$O$_{20}$. However, since the structures in question are different, one should be cautious about such comparisons.

Our results are also in agreement with some recent reports on the location and localization of the excess electrons for surface and subsurface O vacancies [33, 34]. These authors argued that the localization of charge on next nearest neighbour Ce sites was mainly controlled by the lattice relaxation due to electrostatics, as reflected in the lowering of the Madelung potential. However, it should be remarked that a bulk O vacancy is in a different coordination environment relative to either a surface or subsurface O vacancy. It is therefore possible that the comparison between our results for bulk O vacancies and those reported for surface/subsurface O vacancies may not be simple. Indeed, some authors have reported differences in the location of the charge between surface/subsurface and bulk O vacancies [51]. Nevertheless, it is interesting to note that, until these more recent results, the standard picture was considered applicable to surface and subsurface O vacancies as well [18, 49, 52].

5. Predicted charge distribution in Ce$_6$O$_{11}$

We make a few remarks about a possible charge distribution around the O vacancies in this crystal whose unit cell is shown in figure 14. Complete crystal structure data is not available but we make predictions of the charge distribution to be expected in this crystal from a generalization of the bond valence results
of Ce$_7$O$_{12}$ and Ce$_{11}$O$_{20}$. The proposed vacancy cluster for studying the charge distribution in the local environment of the oxygen vacancy in this crystal is shown in figure 15. We did not find a full crystallographic characterization of this crystal and therefore it is not possible to perform accurate bond valence calculations for it. The results reported in I for this crystal were based on the positional parameters of Pr$_2$O$_{11}$. If one were to accept these results (table 1 of I), then since Ce(1), Ce(2), Ce(3) and Ce(4) coordinate the O vacancy with Ce(5) and Ce(6) in the second coordination shell for the Ce sublattice, we see that the charge distribution does not quite follow the pattern one would expect from the results obtained for Ce$_{11}$O$_{20}$ and Ce$_7$O$_{12}$. The overall charge in the vacancy cluster is larger by about $-1.2$ compared to what one would expect starting from mixed valence CeO$_2$. This discrepancy is twice what we found in the case of Ce$_{11}$O$_{20}$ if the discrepancies are normalized to the total number of Ce sites in each vacancy cluster. As a result, the three Ce sites Ce(1), Ce(2) and Ce(3) which one would expect to have valences close to $+3.7$ have much lower valences. We do not believe that this is the correct charge distribution in the local environment of the O vacancy for this crystal. Instead, we prefer to extrapolate the argument which emerges from the bond valence results of Ce$_{11}$O$_{20}$ and Ce$_7$O$_{12}$. Doing so leads to the prediction that the correct charge distribution for this crystal should be as illustrated in figure 15, where all the charge goes to the two Ce sites in the second coordination shell i.e. Ce(5) and Ce(6). Of the known crystal structures of the reduced higher oxides of ceria, Ce$_{11}$O$_{11}$ is the closest to the customary supercell used in DFT, in that it is the least reduced. The prediction we have made here would suggest that, except in an artificial way, it should not be possible to localize the electrons from the O vacancy site in the first coordination shell for the customary supercell used in DFT for studying this problem. An experiment giving the full crystallographic data for this phase would help resolve this question.

6. Delocalization via f–p hybridization

The possibility of the direct hopping of electrons between f-orbitals on neighbouring Ce sites has been suggested to explain the charge distribution in reduced ceria phases [43]. We briefly explore this suggestion considering the example of Ce$_7$O$_{12}$. There are two immediate questions one may like to answer about the charge distribution obtained for this phase from the bond valence calculations. First, how does an f-electron delocalize among the Ce(2) sites? Is this through direct f–f hopping or through the more indirect two-step process of f–p hopping which involves an O site bonded to both Ce sites? Second, why does this delocalization of the charge not extend to include the Ce(1) which is also in the same first coordination shell of the O vacancy? We are not in a position to give a detailed answer to these questions in the present paper, but only some preliminary indications based on Harrison’s method of universal parameters [53]. We do not believe that the delocalization of the f level charge between the Ce(2) sites is a result of direct f–f coupling between these sites.

We now consider the two relevant cases, i.e., direct f–f hopping between neighbouring Ce sites and the indirect f–p hopping which involves an O site between the Ce sites in question. In each of these cases, we consider two situations: electron hopping between two Ce(2) sites which delocalizes the charge between these sites and the electron hopping between a Ce(2) and a Ce(1) site which could also delocalize the charge between these sites.

For the case of direct f–f coupling, the relevant distances are: Ce(1)–Ce(2) — $4.11$ Å. These distances are quite comparable and they give the same direct f–f hopping matrix element, $t_{ff}$, estimated [53, 54] to be about 0.01 eV. This matrix element is the most favourable of all the four nonvanishing f–f matrix elements and represents a $\sigma$–$\sigma$ interaction between the two orbitals. This result would suggest that, if direct f–f coupling were the dominant mechanism of charge delocalization, then charge would delocalize over all four Ce atoms which are nearest neighbours to the O vacancy.

In the case of f–p hopping, we again, consider two cases: hopping along the Ce(1)–O(2)–Ce(2) bonds which we designate ‘O(2) hopping’ and the ‘O(1) hopping’ which occurs along Ce(2)–O(1)–Ce(2). For O(2) hopping, the respective matrix elements, $t_{fp}$, for electron hopping between Ce(1) and O(2) as well as O(2) and Ce(2) are [53, 55] $0.67$ and $0.46$ eV. These matrix elements refer to a $\sigma$–$\sigma$ interaction between the two orbitals which are the more favourable of the two nonvanishing matrix elements. Since, for f–p hopping to couple f states between two Ce sites, a two-step process involving the hopping of an f-electron from one Ce(2) site to an O 2p level followed by the hopping of an electron from the O 2p to the 4f level of the other Ce(2) site is required, the overall matrix element for O(2) hopping, $t_{eff}$, becomes 0.15 eV.
of this oxide, but as we discuss later, it is not well established whether or not these two transitions coincide. The MIT is accompanied by a change in the electrical conductivity of up to five orders of magnitude [65–67] as well as a sharp change in optical properties [68]. The (M1) phase is transparent to infrared radiation while the (M2) phase is opaque [69]. The novel electrical response across the MIT has been exploited in critical thermistors and threshold switches [70]. The optical switching for infrared light has found applications in switching devices [69, 71] and smart thermochromic windows [72, 73]. Applications of V oxides have recently been reviewed by Wu et al [74].

The fundamental understanding of the MIT in both the Ti and V Magnéli phases is a complex many-body problem in condensed matter physics and an active area of research. We do not intend to review this area here (see, e.g., [75, 76]). Briefly, explanations based on strong electronic correlations [77–80], electron–phonon coupling [81–84] and a combination of both effects [85–89] have been given.

In seeking to understand the crystal structures of the Magnéli phases, one might hope to follow a similar approach to that taken above for the Ce oxides: that is, one could view them as resulting from the creation of O vacancies in the dioxide structures, namely, TiO2 and VO2. However, in contrast to the Ce oxides, where the Ce cation sublattice remains largely invariant with reduction, there is significant relaxation of the cation sublattices of the Magnéli phases while the anion sublattices undergo only minimal change. As a result, it has been proposed that for a unified treatment of these crystal structures, a picture based on viewing these structures as built around a rigid anion framework is more informative [76]. In this framework, it is no longer possible to discuss the O vacancies as point defects, as was done for the Ce oxides. Instead, the defects are accommodated as ordered long range structures called crystallographic shear (CS) planes which separate slabs of composition MO2. Each slab has the rutile structure and is infinite in two dimensions with a thickness of n O octahedra in the third. We will not discuss any further the details of these structures, as these have been extensively covered elsewhere (see e.g., [76]).

Since the analysis of the O defects in the crystal structures of the Magnéli phases in terms of the CS planes does not lend itself to an examination of the charge distribution near O vacancies, we do not consider this problem here. We restrict our discussion to the question of whether or not the bond valence model could be used to predict the MIT as a function of temperature (within a given phase) and composition (across a homologous series). We note that BVM results have already been reported for some of the phases we discuss in this section but in all such cases the method of Zachariasen was used [90]. The method of Zachariasen is no longer widely used so we calculated all the results reported in tables 2 and 3 self-consistently using the method of Brown in a procedure described by Shoko et al [35]. We also point out that there is some discussion in the literature of the MIT of the Magnéli phases in terms of the BVM but what we present here is a more comprehensive assessment of this approach.

7. Titanium and vanadium oxides

Ti oxides find uses in photocatalysis [57], gas sensing [58], optical coatings [59], electrochemistry [60] and tribology [61]. The most important uses of V oxides are in industrial catalysis and electrochemistry [60] and tribology [61].

Here, we treat the oxides of Ti and V together in order to highlight some important similarities between some of the oxides of these metals. In oxides, Ti and V exist in formal oxidation states ranging from +2 to +4 and +2 to +5 respectively. This enables these metals to form several different oxides with a rich variety of structural motifs. The more important of these structures are classified into two distinct homologous series of the type M2nO2n+1 and M3nO2n+2, where n is an integer and M = Ti or V. The first series constitutes a class of oxides known as the Magnéli phases which have also been identified in oxides of other metals, e.g., Mo, Nb and W.

Our discussion here is limited only to the Magnéli phases, where we explore the potential for the BVM to distinguish between the insulating and metallic phases of these oxides. Research in Magnéli phases of Ti and V is driven both by their technological potential as well as the desire to understand the fundamental science of the metal–insulator transition (MIT) which occurs in these materials.

Technologically, Magnéli phases have been investigated for their potential as host structures for superconductivity [63] and for their novel electrical and optical switching properties. In VO2, for example, a first-order structural phase transition (SPT) occurs at 337 K which separates the low temperature (LT) monoclinic phase (M1) from the high temperature (HT) tetragonal rutile phase (M3) [64]. The (M1) phase is insulating while the (M3) phase is metallic and, therefore, the SPT of VO2 is closely associated with the MIT of this oxide, but as we discuss later, it is not well established whether or not these two transitions coincide. The MIT is accompanied by a change in the electrical conductivity of up to five orders of magnitude [65–67] as well as a sharp change in optical properties [68]. The (M1) phase is transparent to infrared radiation while the (M3) phase is opaque [69]. The novel electrical response across the MIT has been exploited in critical thermistors and threshold switches [70]. The optical switching for infrared light has found applications in switching devices [69, 71] and smart thermochromic windows [72, 73]. Applications of V oxides have recently been reviewed by Wu et al [74].

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In seeking to understand the crystal structures of the Magnéli phases, one might hope to follow a similar approach to that taken above for the Ce oxides: that is, one could view them as resulting from the creation of O vacancies in the dioxide structures, namely, TiO2 and VO2. However, in contrast to the Ce oxides, where the Ce cation sublattice remains largely invariant with reduction, there is significant relaxation of the cation sublattices of the Magnéli phases while the anion sublattices undergo only minimal change. As a result, it has been proposed that for a unified treatment of these crystal structures, a picture based on viewing these structures as built around a rigid anion framework is more informative [76]. In this framework, it is no longer possible to discuss the O vacancies as point defects, as was done for the Ce oxides. Instead, the defects are accommodated as ordered long range structures called crystallographic shear (CS) planes which separate slabs of composition MO2. Each slab has the rutile structure and is infinite in two dimensions with a thickness of n O octahedra in the third. We will not discuss any further the details of these structures, as these have been extensively covered elsewhere (see e.g., [76]).

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We see that the overall matrix element, \( t_{\text{eff}} \), is the same in the two cases. Again, this would suggest that the charge should completely delocalize over all the Ce sites in the divacancy, which contradicts the results of the bond valence method. Thus, we conclude that the Harrison parameters cannot fully explain the charge delocalization in the Ce7O12 divacancy. However, they appear to exclude the possibility of direct f–f hopping, since \( t_{\text{eff}} \) is an order of magnitude larger than \( t_f \). These approximate results give some indication of why the charge delocalization may not extend to include the Ce(1) site. An alternative way of looking at the indirect f–f coupling is to view it as a hybridization of the 4f states at the two Ce(2) sites and the O 2p states at the O atom connecting them through Ce–O bonds. This indirect coupling is analogous to the superexchange mechanism first discussed by McConnell [56].

The fundamental understanding of the MIT in both the Ti and V Magnéli phases is a complex many-body problem in condensed matter physics and an active area of research. We do not intend to review this area here (see, e.g., [75, 76]). Briefly, explanations based on strong electronic correlations [77–80], electron–phonon coupling [81–84] and a combination of both effects [85–89] have been given.

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to delocalized charge in the LT- and HT phases respectively. Thus, we immediately see that the electron which was localized on the Ti(1) site in the LT phase delocalizes between the Ti(1) and the Ti(2) sites, which both become the Ti(1) site in the HT phase. Therefore, the overall conclusion from the BVM is that the MIT in Ti$_3$O$_5$ is a result of the change from localized to delocalized charge.

7.1. The Ti Magnéli phases

In this section, we discuss the three Ti Magnéli phases, which include Ti$_2$O$_3$, Ti$_3$O$_5$ and Ti$_4$O$_7$. Ti$_2$O$_3$ undergoes a continuous MIT around 400–600 K without a change in the crystal symmetry [91]. Ti$_4$O$_7$, which is one of the most widely studied Magnéli phases of Ti, undergoes two consecutive first-order electrical conductivity transitions. A LT semiconductor–semiconductor (SS) transition occurs at ∼130 K which is followed by a HT semiconductor–metal transition at ∼150 K [92–95]. Ti$_3$O$_5$ exhibits a MIT at 460 K which is accompanied by a SPT from the monoclinic LT- to the orthorhombic HT phase [96]. The BVS results calculated for the various Ti sites in these oxides are given in table 2.

Table 2 shows that the respective Ti site valences in LT Ti$_3$O$_5$ are +3.0, +3.9 and +3.3, which should be compared to the corresponding formal valences of +3.0, +4.0 and +3.0 respectively. One then sees that the BVM results give a total Ti charge per formula unit (f.u.) of +10.2, whereas the formal result should be +10.0, giving an error of +0.2 charge/f.u. Nonetheless, with the exception of the Ti(3) site, the conclusion from the BVS is that the charges are localized. In the HT phase, only two distinct Ti sites exist and the BVS are +3.4 and +3.2 respectively. To understand how the charge redistributes itself in the HT- relative to the LT phase, one first notes that there are 4 f.u./unitcell in both the LT- and HT phases of Ti$_3$O$_5$. It is then evident that the Ti(1) and Ti(2) sites in the LT phase become the Ti(1) site in the HT phase. Thus, we immediately see that the electron which was localized on the Ti(1) site in the LT phase delocalizes between this and the Ti(2) site, which both become the Ti(1) site in the HT phase. Therefore, the overall conclusion from the BVM is that the MIT in Ti$_3$O$_5$ is a result of the change from localized to delocalized charge in the LT- and HT phases respectively.

The BVS for Ti$_4$O$_7$ show that the charge is localized in the low temperature (LT) phase whereas it is delocalized for both the intermediate temperature (IT) and high temperature (HT) phases. The results then suggest that the SS transition is explained by the change from localized to delocalized charge, whereas no explanation can be given for the MIT from these results. This scenario seems to be almost the opposite of what one would expect. For a simple system, it is to be expected that the change to metallic conductivity would be associated with the transition from localized to delocalized charge. Thus, from this simple argument, one would expect both the IT- and HT phases to be metallic. However, Ti$_4$O$_7$ is not a simple system and the two phase transitions cannot be explained by the BVM. Considerable research effort has been directed at elucidating this problem and the picture that seems to emerge is that the changes which occur on the Ti sublattice may be more relevant for discussing the phase transitions [99, 84, 100, 101]. In the LT phase, Ti$^{3+}$–Ti$^{3+}$ pairs form and these are covalently bonded. This results in a highly ordered structure of bipolarons on the Ti sublattice. The SS transition is then explained by the loss of the long range order of the bipolarons, giving a bipolaron liquid state in the HT phase. The transition from the IT semiconducting phase to the HT metallic phase is explained by charge delocalization. Since the BVM does not consider the bond length relationships within the Ti sublattice, it cannot capture the bipolaron formulation of the SS transition in Ti$_4$O$_7$. We remark here, however, that the picture we have just described for Ti$_4$O$_7$ was recently challenged [102]. In this report, it is argued that there is no bond formation between the Ti$^{3+}$–Ti$^{3+}$ pairs in the LT and IT phases but that the main physics relates to a combination of strong electron correlations and electron–phonon coupling.

7.2. The V Magnéli Phases

Among the various Magnéli phases, the end members, V$_2$O$_3$ ($n = 1$) and VO$_2$ ($n = \infty$) along with V$_4$O$_7$ have been extensively studied in an effort to elucidate the microscopic mechanisms of the MIT which occur in these crystals. The MIT temperatures for the various Magnéli phases are as follows [76]: V$_3$O$_5$—168 K, V$_4$O$_7$—430 K, V$_6$O$_7$—250 K, V$_3$O$_5$—135 K, V$_6$O$_{11}$—170 K, V$_3$O$_7$—metallic and VO$_2$—340 K.

Our BVS results for the different V sites in selected crystals of the Magnéli phases of V are listed in table 3. For a discussion of the MIT, these results are presented as in figure 16, where the difference in the charge distribution between the insulating and metallic phases is clearer. The examples of V$_3$O$_5$ and V$_6$O$_7$ best illustrate the MIT within a given Magnéli phase as a function of temperature. In both cases, the insulating phases are characterized by a distinct bimodal charge distribution corresponding to localized valences of +3 and +4 respectively. In contrast, the corresponding metallic phases exhibit a delocalization of the charge, as can be seen from the clustering of the BVS near the value of the average stoichiometric valence.

V$_3$O$_5$ undergoes a MIT at 430 K which is accompanied by the P2/c → I2/c SPT [103, 104]. However, unlike in the other Magnéli phases, where the change in the electrical conductivity is several orders of magnitude, in this oxide, the change is only an order of magnitude [105]. The MIT is believed to be driven by charge differentiation and spatial ordering, with the LT phase charge-ordered while the HT phase exhibits charge disorder [103, 104]. For the LT phase, the BVM predicts that the charge localizes on the V sites giving the
The results for V₂O₃ and VO₂, the results show that, within a given phase (see V₃O₅, V₄O₇), the electronic conductivity occurs. If metallic conductivity occurs. If the charge were found to be delocalized at the lower temperature, then one would confidently conclude that the BVM is a good predictor of the MIT in these oxides. Secondly, since the higher Magnéli phases after V₇O₁₃ undergo temperature-dependent MIT, e.g., V₈O₁₅ (70 K) and VO₂ (340 K), this phase is unusual within the homologous series. Thus, the electronic conductivity of the Magnéli phases has a composition dependence which is such that there is a unique intermediate composition at which metallic conductivity occurs.

This composition dependence of the electronic conductivity in the Magnéli phases is remarkably similar to the prediction we made elsewhere about the Ce oxide phases of the CeₙO₂₋ₙ homologous series [106]. In that report, it was predicted that Ce₇O₁₂ would exhibit metallic conductivity based on results of a bond valence analysis. If metallic conductivity is experimentally confirmed for Ce₇O₁₂, it is then quite curious that it occurs at the same value of n for the two completely different structures.

7.3. Comparison with calculations based on density functional theory

There are limited reports which discuss the question of what happens to the two electrons left in the crystal when a neutral O atom is removed from the crystal of the dioxide to form a given bulk Magnéli phase. Liborio and Harrison found that O point defects are only stable at very low concentrations [115]. Ganduglia-Pirovano et al [31] have reviewed DFT work on bulk O vacancies in reduced TiO₂ and VO₂ and the reader is referred to this review for details. It has to be noted that these calculations are not performed on supercells which do not correspond to any of the characterized crystal phases of the reduced dioxides. Thus one needs to be cautious about generalizing the supercell results to thermodynamic phases, e.g., those represented by the Magnéli phases. Nonetheless, we summarized the main results here.

For the reduced TiO₂, the picture from DFT-based calculations is unclear. Inconsistent conclusions have been reached by different groups. Results obtained include a localization of most of the excess charge on the O vacancy site [116], a localization on the nearest neighbour Ti sites [117], and a delocalization of the charge [118].

A study of bulk O vacancies in V₅O₈₋ₓ combining photoemission spectroscopy and DFT calculations concluded...

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**Table 3. Bond valence sums of the different V sites in the crystals of selected Magnéli phases, VₙO₂₋ₙ, n = 3–7, ∞.**

| Site | V₂O₃ | V₂O₅ | V₃O₅ | V₄O₇ | V₅O₉ | V₆O₁₁ | V₇O₁₃ | VO₂ |
|------|------|------|------|------|------|-------|-------|-----|
|      | 148 K| 298 K| 298 K| 458 K| 120 K| 298 K | 298 K | 298 K|
| V1   | 2.8  | 2.9  | 3.8  | 3.3  | 4.0  | 3.5   | 4.1   | 3.6  |
| V2   | —    | —    | —    | —    | —    | —     | —     | —   |
| V3   | —    | —    | —    | —    | —    | —     | —     | —   |
| V4   | —    | —    | —    | —    | —    | —     | —     | —   |
| V5   | —    | —    | —    | —    | —    | —     | —     | —   |
| V6   | —    | —    | —    | —    | —    | —     | —     | —   |
| V7   | —    | —    | —    | —    | —    | —     | —     | —   |
| V8   | —    | —    | —    | —    | —    | —     | —     | —   |

Reference [107] [108] [103] [104] [109] [110] [111] [112] [113] [114]

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**Figure 16. Bond valence sums for the different V sites in the crystal structures of the Magnéli phases.** With the exception of V₂O₅ and VO₂, the results show that, within a given phase (see V₃O₅, V₄O₇ and V₅O₉), the charge delocalizes significantly in moving from the insulating to the metallic phase. For V₆O₁₁ and V₇O₁₃, only results for the metallic phases are given. The results show that most of the charge is delocalized, which is consistent with the observed metallic conductivity.

The results for the end members, V₂O₃ and VO₂, are the expected values respectively. As pointed out by Hong and Asbrink [104], the ideal valence of V₁ in the HT phase should be +3.5, or in our case, +3.4. Thus, the BVM suggests that the metallic conductivity observed in HT V₃O₅ results from the delocalization of the electron, which, in the LT phase, is localized at V₂.

The results for the end members, V₂O₃ and VO₂, are not very informative, as the insulating phases are virtually indistinguishable from their metallic counterparts. It also appears that the BVM does not describe well the charge distribution in these oxides, giving values of +2.8 and +4.3 where +3.0 and +4.0 are the expected values respectively.

The results for V₆O₁₁ and V₇O₁₃ are given only for the room temperature phases. V₆O₁₁ is known to undergo a MIT at 170 K, but we did not find crystallographic data for the insulating phase. Because V₇O₁₃ is metallic at all temperatures, it is interesting for at least two reasons. First, if crystal structure data were available for low temperatures, say <70 K, then obtaining BVS at the lower temperature would provide a good test for the BVM. If the charge were found to be delocalized at the lower temperature, then one would confidently conclude that the BVM is a good predictor of the MIT in these oxides. Secondly, since the higher Magnéli phases after V₇O₁₃ undergo temperature-dependent MIT, e.g., V₈O₁₅ (70 K) and VO₂ (340 K), this phase is unusual within the homologous series. Thus, the electronic conductivity of the Magnéli phases has a composition dependence which is such that there is a unique intermediate composition at which metallic conductivity occurs.

The results for V₂O₃ and VO₂, the results show that, within a given phase (see V₃O₅, V₄O₇ and V₅O₉), the charge delocalizes significantly in moving from the insulating to the metallic phase. For V₆O₁₁ and V₇O₁₃, only results for the metallic phases are given. The results show that most of the charge is...
that when a neutral O atom is removed from the perfect crystal, the two electrons that remain are shared between the vacancy site and the nearest V sites [119]. Of the total excess charge, 1.52 was found to remain on the vacancy site while 0.48 was shared among the nearest V sites.

7.4. Conclusion

The MIT and SS transitions in Magnéli phases of both Ti and V display some rich physics which may include strong electron correlations and strong electron–phonon coupling. Our BVM results suggest that for phases where strong electron correlations dominate the physics of the transition, the BVM could give a good prediction of the transition. On the other hand, for systems where the electron–phonon coupling on the cation sublattice controls the transition, the BVM gives no information about the physics. This is because the BVM does not take into account bond length relationships within the cation sublattice. Thus the BVM fails to describe phase transitions where bipolaron dynamics are important.

Finally, we remark that our results for the MIT of the oxides suggest that the MIT should coincide with the structural phase transition (SPT). However, the question of whether the MIT and the SPT coincide appears to still be an open problem and an active area of research. The case of VO$_2$ may be cited in this [120].

8. Conclusions and future directions

The main goal of this review was to answer the question: when an oxygen atom is removed from bulk cerium oxide where do the two excess electrons go? The approach taken was to consider high resolution crystal structures of Ce$_{11}$O$_{20}$ and Ce$_4$O$_{12}$ and see how they could be viewed as ordered arrays of oxygen vacancies in an underlying CeO$_2$ crystal. The charge distribution in the local environments of the O vacancies can then be deduced from the bond valence model. An important conclusion is that the results are incompatible with the widely accepted standard picture of charge localization on two cerium ions next to the vacancy. Instead, we found that the charge distributes itself predominantly in the second coordination shell of cerium ions. Furthermore, one excess electron can be delocalized over more than one cerium ion.

Our conclusions concerning the charge distribution near oxygen vacancies are significant for several reasons. First, they contradict many (but not all) atomistic simulations based on density functional theory. Second, the actual charge distribution around the defect has important implications for the other questions we posed at the beginning of this review. The charge distribution has a significant effect on the relative stability of surface and subsurface vacancies [33]. Also, if the charge around oxygen surface and subsurface vacancies is not simply localized on Ce ions next to the vacancy this could change our understanding of the catalytic activity of these surfaces, since it has been claimed or assumed that it is associated with Ce$^{3+}$ ions at the surface [121, 18]. The charge distribution around the vacancies has implications for electronic and ionic conduction, a subject we have discussed elsewhere [106].

Since our determination of the charge distribution around vacancies is indirect it will be important to see whether the same conclusions are obtained on experiments on these higher order oxides with complementary probes such as magnetic susceptibility [122], electron spin resonance (ESR), nuclear magnetic resonance, and photoemission spectroscopies. For example, ESR spectra [123] should quite be distinct for the standard picture of electrons localized onto Ce$^{3+}$ ions and our alternative picture of partial delocalization over the second coordination shell and unique charge (and spin) distributions associated with single vacancies and divacancies.

A variety of spectroscopic probes have shown that the formation of oxygen vacancies is also associated with new electronic states which are located in energy between the valence band of nominally ‘oxygen 2p’ states and the ‘localized 4f’ states. [124, 125] DFT-based calculations which do not sufficiently include the effect of electronic correlations fail to produce these states [31]. Generally the energy of defect states is correlated with the extent of electron localization around defects. Hence, we suggest that spectroscopic studies of ordered phases of higher order oxides could be a fruitful approach to characterizing the electronic properties of defects and complementary to the structural approach we have reviewed. We expect that the energies of the electronic states associated with each of the vacancies we have considered will be different and correlated with the extent of charge delocalization that we find. Such experimental results will provide significant constraints on theories.

Another objective of this review was to test the bond valence analysis on transition metal oxides. For this, we selected the Magnéli phases of Ti and V which are crystallographically well-characterized from their single crystals. Discussing the charge distribution near O vacancies in these oxides (as was done for the Ce oxides) was not possible because the O vacancies in these oxides do not occur as point defects. Rather, they are accommodated into the structure as crystallographic shear planes which do not lend themselves to such an analysis. We, however, addressed the important question of the change in the charge distribution across a MIT in these oxides. The main result from this was that, for crystal structures where the M–O bond lengths undergo significant changes in moving from the insulating to the metallic phase, the BVM provides a useful guide for understanding some of the microscopic physics involved.

This review only considered bulk cerium, titanium and vanadium oxides. However, we believe our approach to characterizing electronic properties of oxygen vacancies in terms of a bond valence sum analysis and the physical insights gained should also be fruitful in the study of surface defects and to other widely studied oxides such as those of hafnium and zirconium.

A common theme throughout this review is the question of whether or not the valence d and f electrons localize on metal sites or delocalize throughout the crystal. This may bring to mind the well-known question of whether a valence bond or molecular orbital (MO) picture is the more appropriate description for the electronic properties of molecules. For an interesting and entertaining conversation on this debate,
see [46]. How is this broader question, relevant? First, VB theory tends to localize electrons too much. Molecular orbital MO theory tends to delocalize electrons too much. Second, our empirical valence bond sum approach is a very local picture and somehow capturing the same physics and chemistry as VB theory. Third, LDA is close to MO theory (it is a band theory, i.e., a non-local picture) and tends to delocalize electrons too much. Many of the LDA, and LDA + U calculations on cerium oxides artificially force electrons to localize on cerium ions. Finally, it is interesting that such VB versus MO issues were discussed in Mott’s original paper on the metal–insulator transition [126].

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