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Articles

Pair Potentials and the Ordered Defect Structure of NbO

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By using computed interatomic pair potentials, we show how the ordered defect patterns found in crystalline NbO can be attributed to local repulsive forces. The results show a driving force for vacancy formation and for ordering to form square planar Nb sites, in agreement with ideas concerning the importance of metal–metal interactions.

Introduction

One of the fascinating aspects of solid-state chemistry is that even simple solids can exhibit complex behavior. Many early transition metal binaries follow this rule by forming rather wide homogeneity ranges near 1:1 stoichiometry, distributing vacancies over the sites of the parent rock salt structure. These vacancies can appear on the metal sublattice (e.g., $Sc_{1-x}S$), the anion sublattice (e.g., TiC_{1-x}), or both sublattices. Notable examples of this last type of vacancy formation are found in the oxides TiO, VO, and NbO. Monoclinic TiO is properly formulated as $Ti_{0.83}O_{0.83}$,[1] and NbO, as $Nb_{0.75}O_{0.75}$.[2] NbO is particularly intriguing, as the coordination of both Nb and O is square planar, an unusual coordination geometry for oxygen and for a d^3 metal. Figure 1 shows a portion of the NbO structure, emphasizing this square planar coordination. This figure also clearly shows how NbO is related to its parent rock salt structure, with one Nb atom removed from the corner and one O atom removed from the center of the cubic cell. The electronic structure of NbO has been studied at various levels of theory.[3–7] Notably, our earlier work has focused on defect ordering and the electronic factors stabilizing the unusual coordination geometries found in NbO.

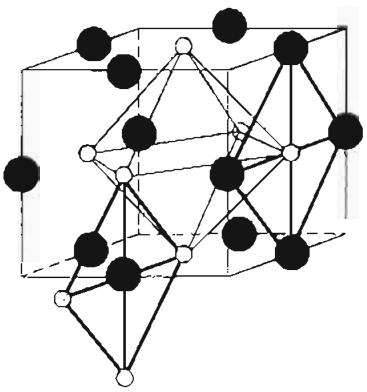

Figure 1. Schematic drawing of the NbO structure emphasizing square planar coordination around Nb and O. Large circles represent O; small circles represent Nb.

We earlier found that with the formation of square planar Nb, the antibonding $4d_{z^2}$ orbital of Nb mixes with the Nb 5s orbital, substantially enhancing metal–metal bonding at low d counts with respect to a hypothetical defect-free rocksalt lattice. This process is shown schematically in Figure 2. The COOP curves of ref 7 provide evidence supporting this conclusion, comparing the hypothetical rock salt structure to the observed NbO structure. Briefly, they show that formation of the ordered defect structure augments Nb–Nb bonding and stabilizes the square planar oxygen atom by Nb–O π bonding. Furthermore, the d^3 electron count appropriate for Nb optimizes the Nb–O overlap population in the observed structure. Addition of extra electrons beyond three populates antibonding Nb–O π^* levels, apparently offsetting any parallel gain in Nb–Nb bonding. Moreover, electron counts below three fail to capitalize on the opportunity for increased metal–metal bonding afforded by the NbO structure.

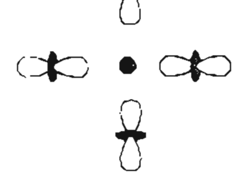

Figure 2. (a) Effect of oxygen vacancies on the Nb d orbital manifold. (b) Local orbital topology about an oxygen site showing enhanced z^2 orbital overlap.

While the earlier study clearly provides compelling evidence for the stability of the NbO structure at d^3, it would be a satisfying complement to understand the local interactions between Nb and O atoms that destabilize the rock salt structure in favor of the defect structure. In other words, are there inherent instabilities due to occupation of neighboring metal and oxygen sites that are alleviated by defect formation? We might also ask if the square planar geometry about Nb is critical to the interactions in these

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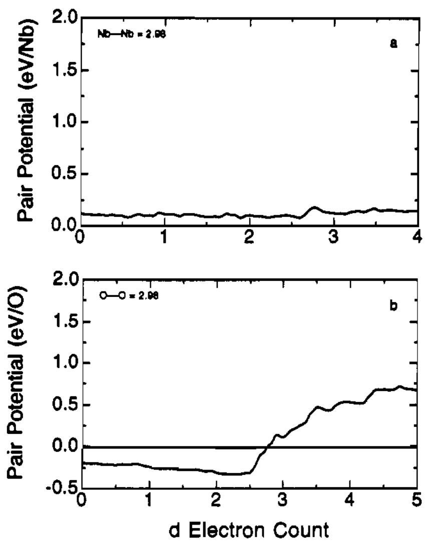

Figure 3. (a) Nb–Nb pair potential for NbO in a hypothetical rock salt structure. (b) O–O pair potential for NbO in a hypothetical rock salt structure.

systems. In this paper we use the idea of an interatomic pair potential to comment on these questions.

Pair Potentials in NbO

We begin by looking at the hypothetical rock salt structure of NbO and its Nb–Nb and O–O pair potentials. We refer the reader to the Appendix for details concerning the computation of these parameters. Briefly, if the pair potential is zero or close to zero, then the reference structure is a stable one. If the pair potential is positive and large, then one way the reference structure may relax to remove such stress is to eject one of the atoms concerned. We have used such an approach to study such diverse systems as organometallic complexes,[8] adsorbates on metal surfaces,[9] and high T_c cuprate superconductors.[12] Figure 3a shows the computed Nb-Nb pair potential as a function of d count. This potential (as well as all other calculated pair potentials) is normalized to account for the 12 symmetry equivalent interactions between nearest-neighbor atoms. Note that throughout the electron counts of interest this curve is essentially flat, featureless, and close to zero. In particular there is no peak characteristic of a repulsion. This result indicates that the Nb–Nb pair interactions are not responsible for the instability of the rock salt structure. In other words, loss of metal does not lead to a structure with greater stability.

The O–O pair potential contrasts starkly with the Nb–Nb potential and agrees completely with experiment. As Figure 3b shows, the O–O pair potential is flat and somewhat negative from d^0 through d$^{2.5}$, where it abruptly turns up. Using the rule that the "foot" of the pair potential peak signals the onset of instability,[8,9] we see that electron counts greater than d$^{2.5}$ can lead to oxygen loss. While the size of the potential is not large, particularly at d^3, we are not well calibrated on how the magnitude of pair potentials should be interpreted, and its reliability as calculated via extended Hückel methods is unclear. Rather, we focus on the electron count dependence of the peak onset, a dependence tracked reliably by semiempirical methods of the extended Hückel type.[10] Clearly, the peak onset is in agreement with the formation of oxygen defects in the NbO rock salt lattice at the d^3 electron count. Elsewhere[11] we show that calculations on TiO place the "foot" of the O–O pair potential peak below d^1, indicating the parameter sensitivity of the O–O pair potentials.

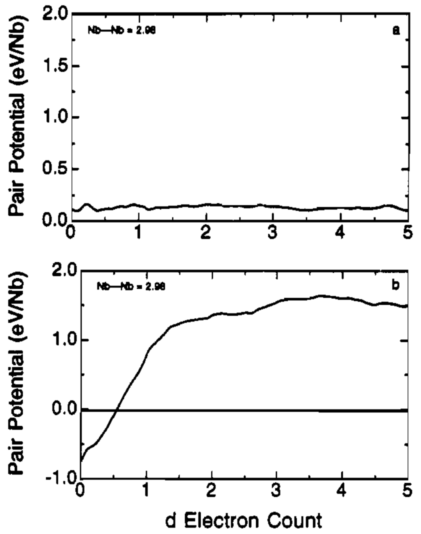

Figure 4. Nb–Nb pair potential for NbO in hypothetical rock salt structure with oxygen defects about (a) a "butterfly" Nb and (b) a square planar Nb.

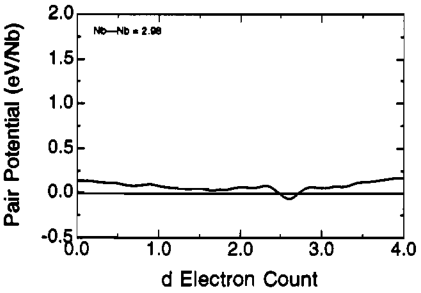

Figure 5. Nb–Nb pair potential in the observed NbO structure.

Let us see the effect on the Nb–Nb pair potential now that oxygen atoms are predicted to leave the rock salt structure. In the first of two model calculations, we consider a defect structure in which two *cis* oxygen atoms have been removed from a Nb atom used to probe the pair potential. Note that this *cis*-divacant structure is not the local Nb geometry actually observed in NbO. Figure 4a shows the Nb–Nb pair potential for this Nb atom. (We parenthetically note that this potential is also normalized to 12 interactions, despite the fact that the 12 neighbors are no longer symmetry equivalent.) Just as in the hypothetical rock salt NbO, it is featureless throughout the relevant d counts. This is quite an appropriate result. Key to the model described above is the stabilization of the Nb $4d_{z^2}$ orbital induced by the generation of the square planar geometry. The *cis*-divacant geometry in the present defect model is not expected to behave similarly, and the flat pair potential curve reflects this.

In the second defect model two oxygen atoms are removed *trans* to one another. This produces a square planar Nb, the observed coordination geometry in NbO. The Nb–Nb pair potential curve of Figure 4b is in sharp contrast to that for the *cis*-divacancy model. Here there is a strongly repulsive pair potential for all electron counts above d^1 (as $4d_{z^2}$ orbitals are filled), indicating that it is the *trans* oxygen vacancies which have led to this Nb–Nb repulsion and hence to Nb defect formation. Figure 5 shows the Nb–Nb pair potential in the actual NbO structure. It is always close to zero, so that no metal atom loss is indicated. These two results nicely complement the model constructed above from an analysis of the energy bands of NbO itself.[7]

In a nutshell, the electronic driving force for the "defect" NbO structure is then simple to understand using this pair potential approach. Oxygen vacancies are favored for d counts greater than zero since the local geometry at the metal leads to occupation of the $4d_{z^2}$ orbital, well-directed for metal–metal bonding. The

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Table I. Extended Hückel Tight-Binding Parameters

		H_{ii} (eV)	ζ_1	c_1	ζ_2	c_2
Nb	5s	−10.100	1.890	1.000		
	5p	−6.860	1.850	1.000		
	4d	−12.100	4.080	0.6401	1.640	0.5516
O	2s	−32.300	2.275			
	2p	−14.800	2.275			

d count corresponding to the "foot" of the pair potential peak will be system dependent, as described for NbO and TiO. It depends on the radial extent of the *n*d orbitals concerned and their interaction with oxygen and other metal atoms. The metal atoms show no tendency to leave the parent structure since the remaining metal atoms are still six-coordinate, and such enhanced metal–metal bonding does not occur. However, the metal–metal pair potential becomes repulsive once some oxygen atoms are missing since metal–metal bonding is now enhanced upon metal vacancy formation. The generation of such "defect" structures is thus a synergistic event; both oxygen atom and metal atom losses are vital. It suggests that the mechanism for metal atom loss in the early transition metal chalcogenides (e.g., $Sc_{1-x}S$) has a different origin, since here metal–metal bonding of the type shown in Figure 2 is presumably much less important.[11] In addition there is no non-metal atom loss.

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Appendix

Pair potentials were computed within the framework described in refs 8 and 9. A 2 × 2 × 2 cubic supercell of rock salt was used in the tight-binding calculations; thus, the stoichiometric supercell contains 32 metal atoms and 32 oxygen atoms. Nb or O vacancies were removed from the center of this supercell so as to minize their interaction with defects in neighboring supercells. Standard extended Hückel tight-binding parameters for Nb and O are collected in Table I.