

Magic electron counts for networks of condensed octahedral niobium clusters in oxoniobates

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Many metal-rich compounds feature rather complex metal-metal bonded networks, often infinite, which can be viewed as a result of vertex-, edge-, or face-sharing between simple polyhedra of metal atoms. The octahedron is the most common motif in these networks. Such a description of these networks has led to the idea of cluster condensation, since compounds containing metal clusters with isolated octahedral cores also exist. Metal clusters and networks resulting from their condensation represent an important class of solid state compounds.

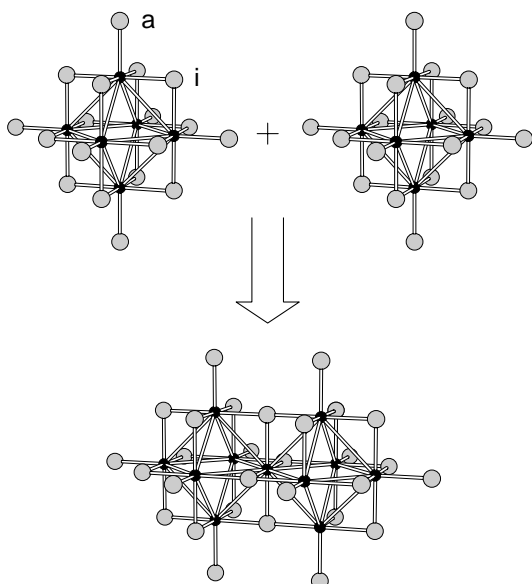


Figure 7: Formal condensation of two monomeric octahedral oxoniobate clusters through vertex-sharing, accompanied by loss of some oxygen ligands of the outer coordination sphere (O^a).

Chemical bonding in condensed cluster networks is of special interest because such networks represent a link between molecule-like metal clusters with isolated cores (monomeric clusters) and three-dimensional metals. In our study we attempt to exploit the structural similarity between monomeric clusters and condensed cluster networks in order to understand the electronic structure of the latter. The idea is to relate the well-known molecular orbitals

of monomeric metal clusters (with the octahedral M_6 core, for example) to molecular or crystal orbitals of condensed cluster networks. We hope that such an approach can provide additional insight into chemical bonding in condensed cluster networks, many of which have already been studied theoretically with various methods.

Reduced oxoniobates were chosen for the analysis because they feature monomeric octahedral niobium clusters, as well as zero-, one-, two- and three-dimensional condensed cluster networks (Figs. 7, 8).

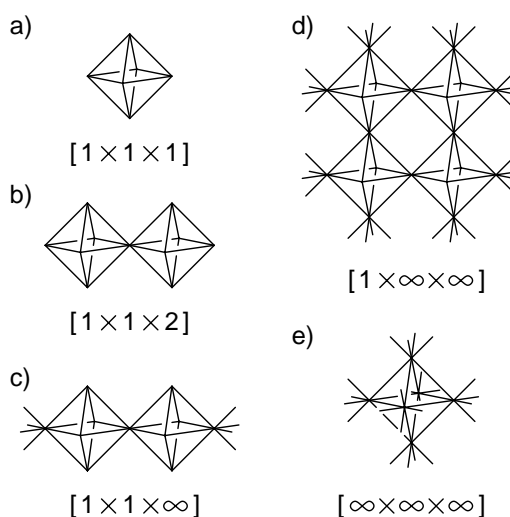


Figure 8: Some condensed cluster networks found in oxoniobates (only the Nb backbones are shown):

- a) monomeric cluster,
- b) dimer, as in Fig. 7,
- c) linear chain of clusters,
- d) square network of clusters and
- e) cubic network of NbO.

The $[p \times q \times r]$ notation refers to the number of niobium octahedra participating in cluster condensation along the three orthogonal directions.

Bonding in the monomeric Nb_6O_{18} cluster is optimized when the lowest seven Nb–Nb bonding orbitals are filled with 14 electrons. The simplest way to construct the molecular or crystal orbitals of the condensed cluster networks is to build them from the seven MOs of the monomeric cluster, much like the networks

themselves are built from octahedral blocks. One such construction is shown in Fig. 9, using the one-dimensional condensed cluster network (Fig. 8 c) as an example.

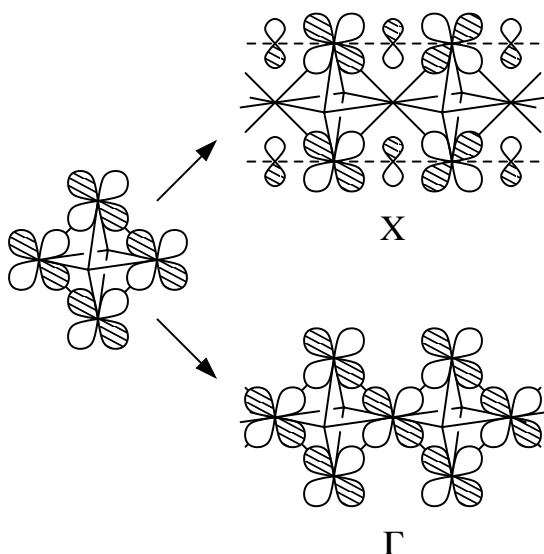


Figure 9: Crystal orbitals for a one-dimensional condensed cluster network (Fig. 8 c) at Γ and X can be related to the Nb–Nb bonding MOs of the monomeric Nb_6O_{18} cluster, as shown schematically for one of the t_{2g} MOs.

While both crystal orbitals depicted in Fig. 9 can be related to a t_{2g} Nb–Nb bonding MO of Nb_6O_{18} , only the crystal orbital at the Γ point retains metal-metal bonding. The phase-change requirement imposed on the crystal orbital at

the X point leads to a loss of Nb d orbital contributions at the shared vertices and substantial participation of oxygen p wavefunctions at the Nb–O–Nb bridges. The consequent elimination of Nb–Nb bonding, together with strong Nb–O π antibonding, makes occupation of this crystal orbital unfavorable.

This bonding analysis was carried out for all appropriate molecular or crystal orbitals of the condensed cluster networks depicted in Fig. 8. Based on this analysis, the number of crystal orbitals (bands) which were likely to be occupied at each of the special points of the corresponding Brillouin zones was estimated. Contributions of special points were then averaged according to the relative weights of the special points, resulting in the following approximate magic electron counts per Nb octahedron (i.e. electron counts optimal for chemical bonding in the considered networks): 14 electrons for the Nb_6O_{18} cluster, 12 for the dimer (Fig. 8 b), 11 for the 1D chain (Fig. 8 c), $10-10\frac{1}{2}$ for the 2D square network (Fig. 8 d) and $7\frac{3}{4}-8\frac{1}{2}$ electrons for the 3D cubic network (Fig. 8 e). These numbers closely match the experimentally observed electron counts. Furthermore, they agree with our electronic structure calculations at the extended Hückel level and they are consistent with another electron counting scheme previously derived in our group for these condensed cluster networks.