THEORETICAL STUDY OF BONDING AND ELECTRICAL PROPERTIES OF $Ca_{0.95}Nb_3O_6$

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In recent years two analogous Nb compounds, $NaNb_3O_5F$ and $Ca_{0.75}Nb_3O_6$, featuring very short Nb-Nb distances, have been synthesized and their crystal structures determined (Hibble, Cheetham and Cox, 1987; Köhler and Simon, 1986). In the latter structure, the positions of the calcium ions are partially occupied, and the stoichiometric compound $CaNb_3O_6$ was not obtained. Despite the non-integer formal oxidation state of +3.3 for the Nb atoms, which might give rise to metallic character, no electrical measurements have been reported for the above compounds. For these reasons we attempted the synthesis of the stoichiometric compound $CaNb_3O_6$, its crystal structure determination, and the study of its electrical resistivity and electronic structure.

CRYSTAL STRUCTURE OF $Ca_{0.95}Nb_3O_6$

A mixture of CaO and Nb_2O_6 was reduced with acetylene soot by heating in vacuum at 1200 - 1250° C for 10 hours. The single-phase nature of the final product of sintering was confirmed by X-ray analysis using Cu-K_α radiation. The compound is orthorhombic, space group Immm, with unit cell parameters $a = 7.1156\,(9)$, $b = 10.2863\,(18)$, $c = 6.5756\,(9)$ Å, and $Z = 4$. Neutron diffraction measurements were carried out with $\lambda = 1.5118$ Å and the Rietveld analysis (Hewat, 1975) of the diffraction patterns produced the final convergence parameters $R_1 = 5.8\%$, $R_{WP} = 6.0\%$, $R_{exp} = 5.5\%$, by assuming a partial occupation of the Ca (4i) sites, corresponding to the formula $Ca_{0.95}Nb_3O_6$. The resulting atomic positions are given in Table I, and full details of the structure determination will be published elsewhere.

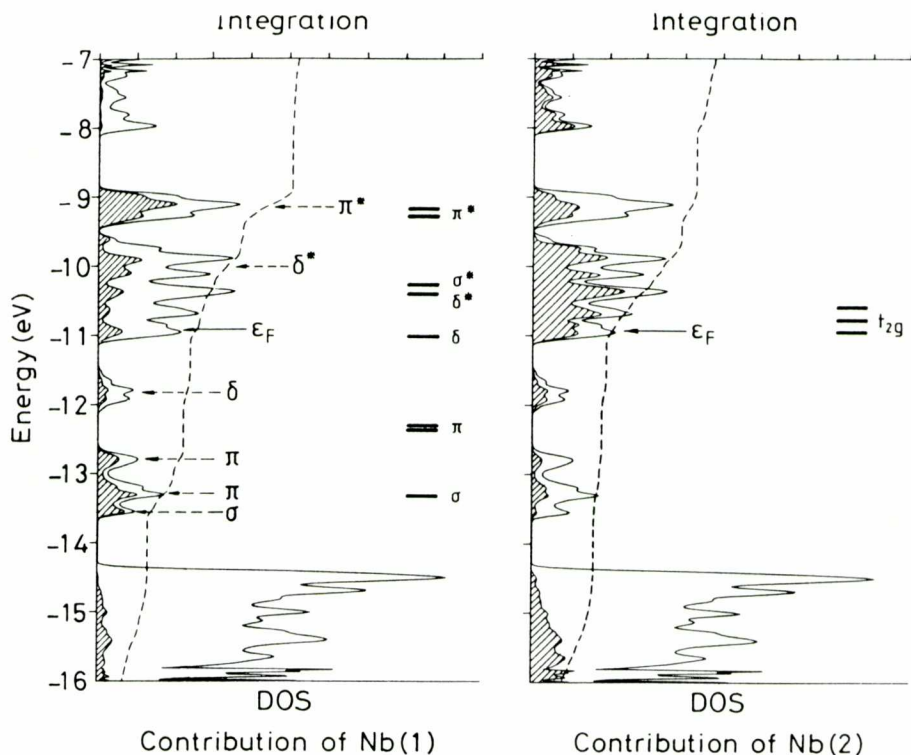Fig. 2. Density of states (DOS) for the anionic $(Nb_3O_6)^{2-}$ sublattice of $Ca_{0.95}Nb_3O_6$. The shaded areas indicate the contribution of the Nb1 and Nb2 atoms to the total DOS, and the integrals of such contributions are represented by the dashed lines. The bars at the right-hand side of each diagram present the energy of the d-block orbitals obtained from molecular orbital calculations on discrete clusters Nb_2O_8 (Nb1) and NbO_6 (Nb2).

state is +1, leaving nine positive charges (one electron) for two Nb2 atoms, i.e., a formal oxidation state of Nb2(4.5+).

The different localization of the bands around the Fermi level and the resulting charge distribution between both types of Nb atoms can be associated with the d orbitals of the Nb_2O_8 square prisms and NbO_6 octahedra. For Nb_2O_8 such levels are the σ, π, and δ bonding MO's and their antibonding counterparts δ*, σ* and π*, with the $d_{x^2-y^2}$ orbitals (Nb-O antibonding) at much higher energies. For the octahedral NbO_6 cluster, the relevant orbitals are the formally non-bonding t_{2g} and Nb-O antibonding e_g sets. A clear correspondence between the level ordering in the clusters and the band ordering in the solid has been found. A remarkable feature of the Nb-Nb bonding, as seen in the COOP curves, is that the largest part of the Nb1-Nb1 bonding levels, appear below the Fermi level (i.e., are oc-

cupied) and the antibonding ones are empty. The result is an approximate electronic configuration $\sigma^2\pi^4\delta^2$ for the Nb1-Nb1 pairs with a calculated Nb1-Nb1 overlap population of 0.734. On the other hand, the calculated Nb2-Nb2 overlap population is –0.004, consistent with the long Nb2-Nb2 distance of 3.348 Å.

The unusually short Nb-Nb distance found for the Nb1 atoms in $Ca_{0.95}Nb_3O_6$ and its isostructural analogues (Hibble, Cheetham and Cox, 1987) (Köhler and Simon, 1986) $Ca_{0.75}Nb_3O_6$ and $NaNb_3O_5F$ appear to be compatible with its formal description as a quadruple bond (Table III). Although the Nb1-Nb1 distances in the $Nb_3X_6^{n-}$ lattices are the shortest ones known so far, the lack of structural data for well established, unsupported Nb-Nb quadruple bonds makes the use of the bond length criterion inconclusive for deciding on the existence of a quadruple bond in $Ca_{0.95}Nb_3O_6$ and its isostructural analogues. We performed model calculations on dinuclear compunds $Nb_2O_8^{x-}$ with unambiguous bond order, as to obtain a calibration for calculated Nb-Nb overlap populations. The resulting calibration curve is presented in Figure 3, where the bond order coincides with the number of d electrons per Nb atom. There it can be seen that the Nb1-Nb1 overlap population obtained from band calculations on $Nb_3O_6^{2-}$ (0.73) is sensibly smaller than expected for a quadruple or even a triple bond.
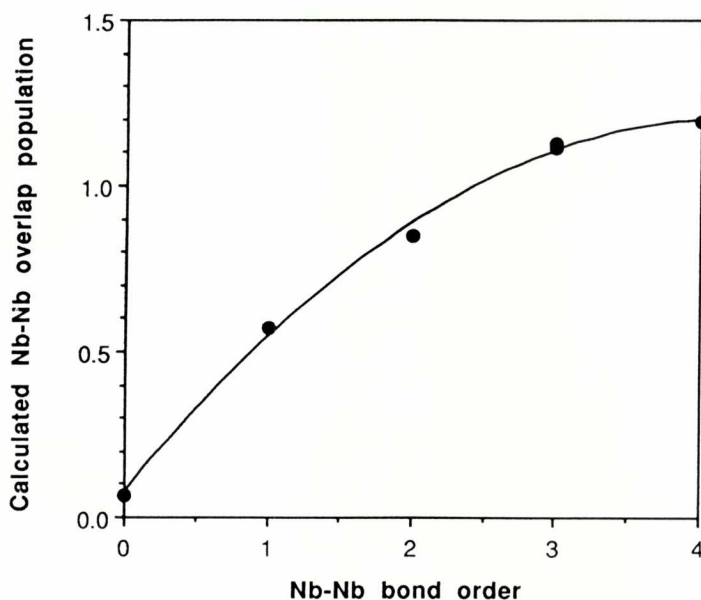

Fig. 3. Nb-Nb overlap population as a function of the formal bond order, calculated for $[Nb_2O_8]^{x-}$ clusters.

The fact that the Nb1-Nb1 overlap population is smaller than expected can be attributed to electron donation from the Nb1-Nb1 pairs to the Nb2 atoms. This interaction results in some Nb1-Nb2 bonding, with a calculated overlap population of 0.168 (Nb1-Nb2 *contacts* at 3.073 Å). In summary, one can describe the metal-metal bonding in this compound as Nb1-Nb1 quadruply bonded pairs, bridged by four Nb2 atoms, with some electron donation from the Nb1-Nb1 pairs to the Nb2 atoms effectively decreasing the Nb1-Nb1 bond order.

ELECTRICAL RESISTIVITY

Electrical resistivity measurements were performed by a four-probe technique on a compressed polycrystalline sample of dimensions 10 x 1 x 1 mm, in the temperature range $4.2 < T < 300$ K. The electrical behavior increases with temperature at low temperatures but is practically temperature-independent at room temperature, in good agreement with the theoretical prediction of a semimetallic character.

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ABSTRACT

The title compound has been synthesized and its crystal structure refined by using powder diffraction data. The structure is orthorhombic, space group *Immm*, with cell constants $a = 7.1156$ (9), $b = 10.2863$ (18), $c = 6.5756$ (9) Å, and Z = 4. Two types of Nb atoms are present in the structure: Nb1 atoms in Nb_2O_8 clusters with a Nb-Nb distance of 2.552 Å, the shortest reported so far, and Nb2 atoms forming layers of connected NbO_6 octahedra. The electronic structure obtained from Extended-Hückel tight-binding band calculations suggests the coexistence of Nb(1+) ions in the Nb_2O_8 clusters with formally quadruple Nb-Nb bonds, together with Nb(4.5+) ions in the layers of octahedra. Deviations from this simplified model are analyzed. The electrical behavior, measured in the temperature range $4.2 < T < 300$ K, is interpreted as semimetallic on the basis of the calculated band electronic structure.

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