

Crystal Structure and Coexistence of Localized and Delocalized Electrons in Nb₁₂O₂₉

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The electronic structure of Nb₁₂O₂₉, the first member of the NbO_{2.5-x} (0 ≤ x ≤ 0.083) family of phases, has been studied. It is suggested that in order to understand the coexistence of antiferromagnetism and metallic conductivity in this phase a new crystal structure determination is needed. © 2000 Academic Press

The possible role of antiferromagnetism on the high T_c superconductivity of copper oxides has been a matter of considerable discussion. Examining a possible electron-hole relationship between d^9 Cu²⁺ and d^1 Ti³⁺, Nb⁴⁺, etc. in the possible observation of superconductivity in transition metal oxides, Cava *et al.* (1) found that Nb₁₂O₂₉ exhibits both metallic conductivity and antiferromagnetic order at 12 K. Nb₁₂O₂₉ (2) is just the first member ($x = 0.083$) of a family of phases with formula NbO_{2.5-x}, where x can have values between 0 and 0.083 (3). These authors also found that the oxides Nb₂₂O₅₄ ($x = 0.046$), Nb₄₇O₁₁₆ ($x = 0.032$), and Nb₂₅O₆₂ ($x = 0.020$) exhibit a Curie-Weiss behavior although they do not magnetically order down to 2 K. Studies of the transport properties of this family of phases by Rüscher *et al.* (4) suggest that these systems are one-dimensional conductors. Low-dimensional transition metal oxides and bronzes with low filling of the d -block bands exhibit a very exciting physical behavior and have been the object of many experimental and theoretical studies (5, 6). Thus, we believe that the NbO_{2.5-x} family of compounds deserves much more attention than it has received until now. In this communication we would like to point out the need for a new crystal structure determination of the first member of the series, Nb₁₂O₂₉, in order to start building an understanding of the correlation between the crystal and electronic structure of this interesting family of phases.

The basic structural unit of the ideal crystal structure of Nb₁₂O₂₉ is the (3 × 4) block of octahedra (Nb₁₂O₅₅) shown in Fig. 1a. When two successive (3 × 4) blocks share three octahedral edges as shown in Fig. 1b, an Nb₁₂O₅₁ chain along the a -direction results (Fig. 1b). Edge-sharing condensation of Nb₁₂O₅₁ chains in such a way (see Fig. 1c) that the height of two successive chains along the c -direction differs by 1/2 the octahedral height leads to Nb₁₂O₄₁ layers. The ideal 3D crystal structure of Nb₁₂O₂₉ results when these layers repeat infinitely by sharing vertices along the b -direction. Thus, Fig. 1c is just the projection of the crystal structure of Nb₁₂O₂₉ along the b -direction.

According to the stoichiometric formula, two electrons per formula unit can fill the bottom of the d -block bands of Nb₁₂O₂₉. Since only six of the 12 octahedra of the (3 × 4) block are symmetry inequivalent, it seems that there must be two identical d^1 Nb atoms. However, this is quite puzzling given the electric and magnetic properties of this compound that indicate the existence of both localized and delocalized electrons. In view of the potential interest of this family of compounds, we decided to carry out tight binding extended Hückel type calculations (7) for Nb₁₂O₂₉. (see Table 1 for the exponents and parameters used.) This type of calculation has given, so far, excellent results for many low-dimensional transition metal oxides (6). The crystal structure reported by Norin (2) was used in our calculations.

The bottom part of the d -block band structure calculated for Nb₁₂O₂₉ is shown in Fig. 2. Since the unit cell contains four formula units, all bands in Fig. 2 are really blocks of four bands. The existence of both localized and delocalized electrons could be easily explained if both dispersive and flat bands were partially filled. However, since there are only two electrons per formula unit (i.e., eight electrons per repeat unit of the solid) to fill the d -block bands, the lowest

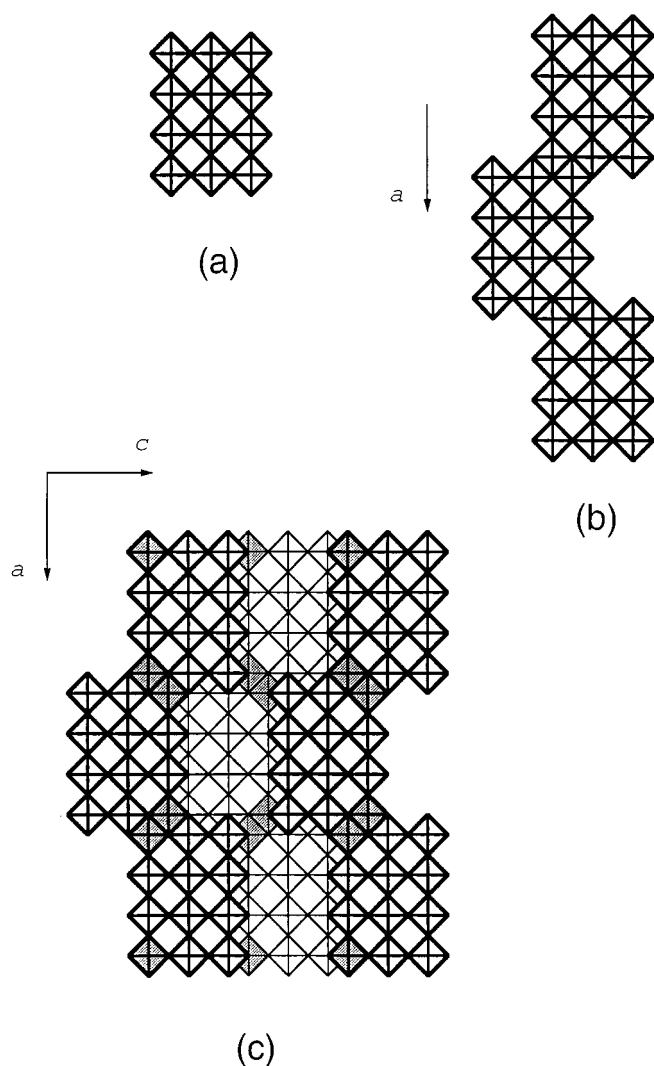


FIG. 1. Idealized crystal structure of orthorhombic Nb₁₂O₂₉: (a) Nb₁₂O₅₅ (3 × 4) block octahedra; (b) Nb₁₂O₅₁ chain along the *a*-direction; (c) Nb₁₂O₄₁ layer, where thin and thick lines are used to distinguish octahedra at levels differing by one-half of the octahedron height. The Nb₁O₆ octahedra are shaded. Figure 1c can be seen as the projection of the crystal structure of Nb₁₂O₂₉ along the *b*-direction.

group of four bands should be completely filled and the next group of four bands should be empty. Consequently, according to these calculations there should be a band gap at the Fermi level and Nb₁₂O₂₉ should be semiconducting. Should we conclude that the tight binding extended Hückel calculations fail in this particular case? Before doing this we should consider the following facts. First, the lowest group of four bands is dispersive, but only along the *b**-direction. If these bands were partially filled it would probably lead to metallic behavior. Second, the next group of four bands is practically nondispersive along all directions and, if par-

TABLE 1
Exponents and Parameters Used in the Calculations

Atom	Orbital	H_{ij} (eV) ^a	ζ_1	ζ_2	c_1^b	c_2^b
Nb	5s	-6.71	1.89			
	5p	-3.88	1.85			
	4d	-8.14	4.08	1.64	0.6401	0.5516
O	2s	-31.60	2.275			
	2p	-16.78	2.275			

^a A. Vela and J. L. Gázquez, *J. Phys. Chem.* **92**, 5688 (1988).

^b Contraction coefficients used in the double- ζ expansion.

tially filled, it would certainly lead to localized electrons. Third, both sets of bands are mainly built from *d*-orbitals of the Nb1 atoms (we use the same atomic labeling as in the original crystal structure determination (2)). The Nb₁O₆ octahedra have been shaded in Fig. 1c. Fourth, the dispersive bottom bands are mainly built from the Nb1 *xy* type orbitals (see Fig. 3a), as is usual in perovskite-related structures containing NbO₅ corner-sharing octahedral chains. However, contrary to what usually happens in such chains (6), the bands go down in energy when going from Γ to Y (i.e., when going from the center to the border of the

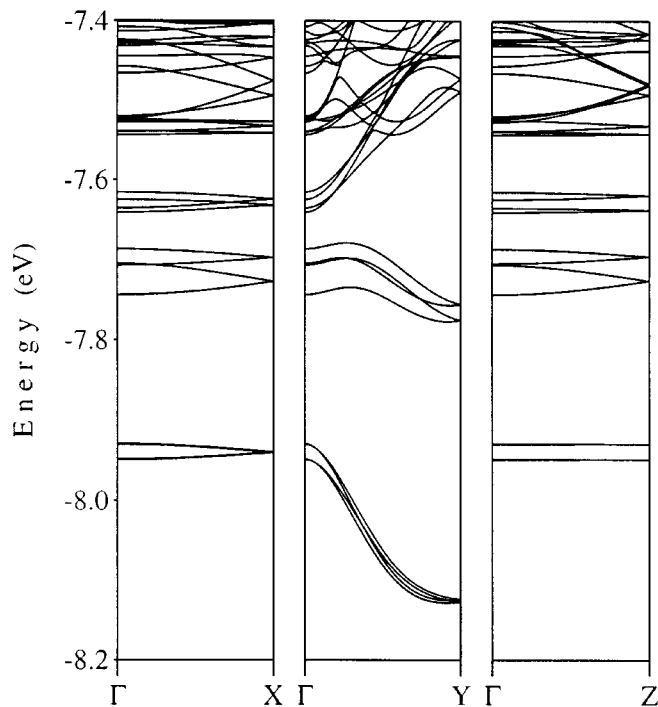


FIG. 2. Dispersion relations calculated for the lower part of the *d*-block bands of Nb₁₂O₂₉. $\Gamma = (0, 0, 0)$, $X = (a^*/2, 0, 0)$, $Y = (0, b^*/2, 0)$, and $Z = (0, 0, c^*/2)$.

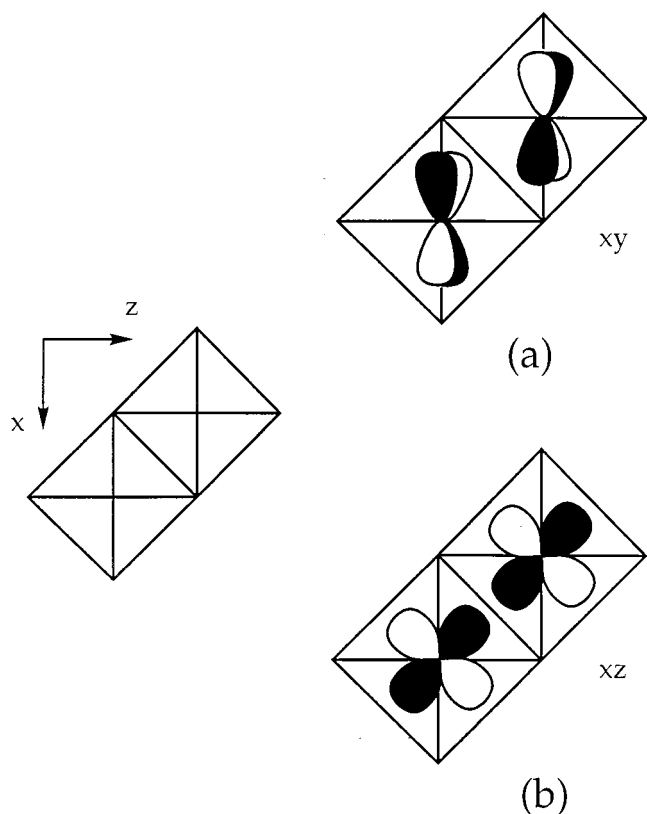


FIG. 3. Nb d -type orbitals which are the main components of the lowest (a) and second lowest (b) groups of bands in Fig. 2.

Brillouin zone along the chain direction). This immediately points to the existence of severe angular distortions in the Nb1O_6 octahedra. Indeed, as shown in Fig. 4, there is not only a large distribution of Nb–O bond lengths but also, more importantly, an extremely small O–Nb–O angle (126°) associated with the two apical oxygen atoms. We believe that this angle (but also the rest of the environment of the Nb1 atom) is not quite reasonably defined in the presently known structure (2). If this angle were closer to the ideal value of 180° , the dispersion of the lowest band would be as expected, i.e., would raise from Γ to Y .

In such a case the conditions for an acceptable explanation of the coexistence of localized and delocalized electrons in $\text{Nb}_{12}\text{O}_{29}$ will probably be realized. The lowest dispersive group of bands will go up in energy from Γ to Y and probably will cross the flat group of bands. Thus, both types of bands will be partially filled. Of course, the degree of filling of the two types of bands crucially depends on the geometrical environment of the Nb1 atom, and thus, it is a question that must await a new and more precise structural determination. However, we believe that the two groups of bands should be practically half-filled because as Cava *et al.* (1) pointed out the moment calculated from the χ vs T curve is only 42%, i.e., nearly half of the value

expected from the number of Nb^{4+} in the unit cell. We note that, as schematically shown in Fig. 3b, the flat bands are mainly built from an in-phase combination of the Nb1 xz orbitals (with a small contribution from the adjacent Nb3 atoms). Thus, if this group of bands is half-filled, this means that there is one localized electron every two Nb1 atoms, which explains the previous observation. This leaves half an electron per Nb1 atom to fill the dispersive bands. In view of the orbital character shown in Fig. 3b and despite the relatively long Nb1–Nb1 distance throughout the shared edge of the double octahedral unit (3.14 Å, but such a distance may be not quite precise), the localized electrons in $\text{Nb}_{12}\text{O}_{29}$ would be electrons in slightly bonding Nb1–Nb1 levels. The delocalized electrons would be associated with the Nb1 xy orbitals leading to dispersive bands through π -type interactions with the apical oxygen orbitals. Thus, our suggestion easily takes into account the puzzling observation noted above, that there are both localized and delocalized electrons but just one type of symmetry inequivalent d^1 Nb atom in $\text{Nb}_{12}\text{O}_{29}$.

Of course, although the explanation suggested here seems to simply account for the interesting physical behavior of $\text{Nb}_{12}\text{O}_{29}$, it is nothing but a suggestion which must await a new structural investigation. However, we think that there are serious reasons to believe that at least the local environment of the Nb1 atom is not enough well defined in the presently known crystal structure (2), and we urge a new crystal structure determination. Whatever the results of this new study are, they will be invaluable in order to test the present suggestion and in building a real understanding of the correlation between the crystal and electronic structure of this family of compounds, and thus of their interesting physical behavior.

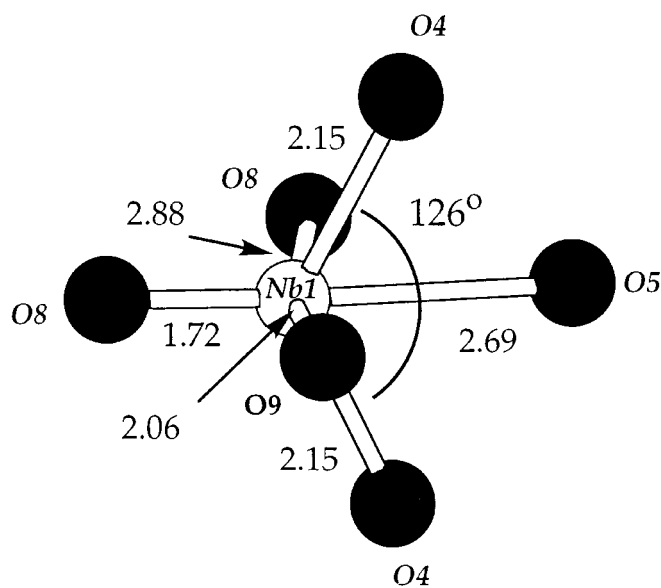


FIG. 4. Geometry of the Nb1O_6 octahedra in $\text{Nb}_{12}\text{O}_{29}$.

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