Structures of the reduced niobium oxides $Nb_{12}O_{29}$ and $Nb_{22}O_{54}$

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Abstract

The crystal structure of $Nb_{22}O_{54}$ is reported for the first time, and the structure of orthorhombic $Nb_{12}O_{29}$ is reexamined, resolving previous ambiguities. Single crystal X-ray and electron diffraction were employed. These compounds were found to crystallize in the space groups $P2/m$ ($a = 15.7491(2)$ Å, $b = 3.8236(3)$ Å, $c = 17.8521(2)$ Å, $\beta = 102.029(3)°$) and $Cmcm$ ($a = 3.8320(2)$ Å, $b = 20.7400(9)$ Å, $c = 28.8901(13)$ Å), respectively and share a common structural unit, a 4×3 block of corner sharing NbO_6 octahedra. Despite different constraints imposed by symmetry these blocks are very similar in both compounds. Within a block, it is found that the niobium atoms are not located in the centers of the oxygen octahedra, but rather are displaced inward toward the center of the block forming an apparent antiferroelectric state. Bond valence sums and bond lengths do not show the presence of charge ordering, suggesting that all $4d$ electrons are delocalized in these compounds at the temperature studied, $T = 200$ K.
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1. Introduction

Niobium and oxygen form a series of complex shear structures between the compositions Nb_2O_5 and $Nb_{12}O_{29}$ [1–11]. With the exception of Nb_2O_5, all contain some fraction of reduced Nb^{4+} ($4d^1$) atoms. Their magnetic and electrical properties have been extensively studied. The electrical conductivity increases as Nb^{4+} content increases, transforming from insulating behavior in Nb_2O_5 to metallic behavior in $Nb_{12}O_{29}$ [12–15]. At the same time, the oxides become paramagnetic (Nb_2O_5 is diamagnetic) and monoclinic $Nb_{12}O_{29}$ even displays an antiferromagnetic transition at $T_N = 12$ K [12,13,16–19]. This makes the shear structures one of the only known series of compounds where Nb^{4+} displays magnetic behavior. The origin of this magnetism, especially the key structural components that give rise to it and the location of the magnetic electron(s), is of interest due to the fact that $4d$ systems usually form delocalized electronic states rather than localized magnetic ones.

The general structures of the niobium oxides are well known [1–4,6,20], having been studied with a variety of techniques, including electron, powder neutron, and X-ray diffraction [21–28]. The basic structural unit consists of corner sharing NbO_6 octahedra arranged into blocks, as idealized for the 3×3 and 4×3 cases in Fig. 1(a). These blocks are then stacked vertically in columns with octahedra from adjacent blocks sharing corners. The columns are then interleaved to form the overall atomic arrangement. Fig. 1(b) shows the idealized structure of $Nb_{22}O_{54}$, which is built from 3×3 and 4×3 blocks. Additional Nb atoms lie in tetrahedral sites formed at the intersections of adjacent blocks. Fig. 1(c) shows o-$Nb_{12}O_{29}$, which is similar but built solely from 4×3 blocks. The unit cell for each structure is also drawn. Previous work has shown that the Nb atoms are displaced from the ideal positions in the center of the NbO_6 octahedra [2,4]. However, precise single crystal determinations of the displacements have remained elusive due to the difficulty in growing crystals relatively free of stacking faults, point

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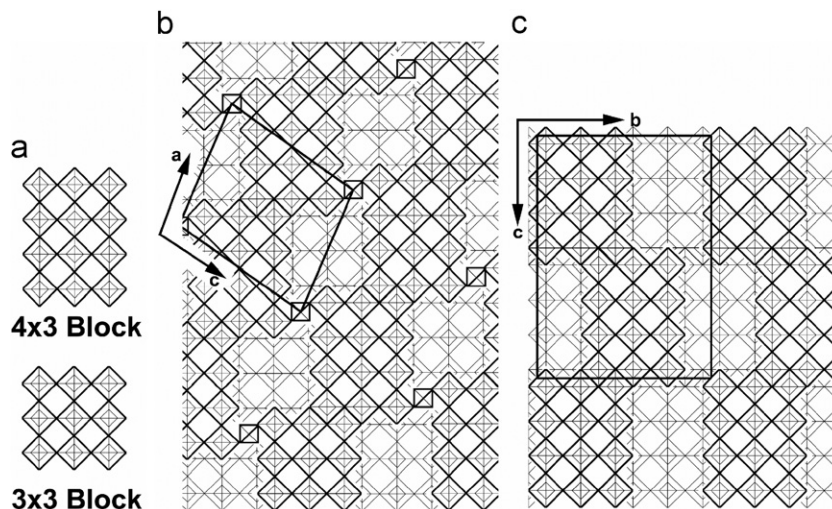 *E-mail address:* tmcqueen@princeton.edu (T. McQueen).

Fig. 1. (a) The idealized building blocks for $Nb_{22}O_{54}$ and o-$Nb_{12}O_{29}$, as viewed from the top. (b) The structure of $Nb_{22}O_{54}$ built from the basic units shown in (a), with extra Nb atoms in the tetrahedral holes between blocks. The unit cell is drawn. (c) The structure of o-$Nb_{12}O_{29}$, along with the expected unit cell. In both (b) and (c), the lighter blocks are displaced by $\frac{1}{2}$ the unit cell along the viewing direction.

Table 1
(a) Final crystal, data collection, and refinement statistics for $Nb_{22}O_{54}$ and o-$Nb_{12}O_{29}$. (b) Comparison of different Nb atom disorder model refinements of $Nb_{22}O_{54}$

(a) Final Refinements	$Nb_{22}O_{54}$	o-$Nb_{12}O_{29}$
Space group	$P12/m1$	$Cmcm$
a (Å)	15.7491 (2)	3.8320 (2)
b (Å)	3.8236 (3)	20.7400 (9)
c (Å)	17.8521 (2)	28.8901 (13)
β (°)	102.029 (3)	–
V (Å^3)	1051.42 (8)	2296.06 (19)
Z	1	4
μ (mm^{-1})	5.88	5.87
Crystal (mm^3)	$0.030 \times 0.034 \times 0.100$	$0.020 \times 0.030 \times 0.055$
T_{min}/T_{max}	0.7387/0.8592	0.7590/0.8852
Measured reflections	14057	11206
Independent reflections	3504	1944
Reflections ($F^2 > 2\sigma F^2$)	2712	1394
R ($F^2 > 2\sigma F^2$)	0.0595	0.0744
R (all)	0.0829	0.0941
wR^2 (F^2)	0.1269	0.1922
GooF	1.190	1.200
$\Delta\rho_{max}/\Delta\rho_{rms}$ (e/Å^3)	4.803/0.376	3.41/0.575
wR^2 weighting	$\dfrac{1}{\sigma^2(F_0^2) + (0.0265P)^2 + 4.44P}$	$\dfrac{1}{\sigma^2(F_0^2) + (0.000P)^2 + 397.87P}$
Parameters	241	127

(b) $Nb_{22}O_{54}$	Nb12 only	Nb12, Nb13	Nb12, Nb13, Nb14
R ($F^2 > 2\sigma F^2$)	0.0713	0.0612	0.0595
R (all)	0.0943	0.0844	0.0829
wR^2 (F^2)	0.1699	0.1346	0.1269
GooF	1.160	1.182	1.190
$\Delta\rho_{max}/\Delta\rho_{rms}$ (e/Å^3)	10.44/0.472	4.88/0.384	4.803/0.376
Parameters	234	238	241

defects and other imperfections. To the authors' knowledge, only the structures of orthorhombic (o-$Nb_{12}O_{29}$) and monoclinic $Nb_{12}O_{29}$ have been previously determined by single crystal work [2,3]. Here we report the crystal structures of $Nb_{22}O_{54}$ and o-$Nb_{12}O_{29}$ determined by single crystal X-ray diffraction, with the choice of space group for