Inorganic Chemistry

Communication

pubs.acs.org/IC

Bonding Preference of Carbon, Nitrogen, and Oxygen in Niobium-Based Rock-Salt Structures

Akira Miura,*[†] Takahiro Takei,[†] Nobuhiro Kumada,[†] Satoshi Wada,[‡] Eisuke Magome,[§]
Chikako Moriyoshi,[§] and Yoshihiro Kuroiwa[§]

[†]Center for Crystal Science and Technology, University of Yamanashi, Miyamae 7-32 Kofu 400-8511 Japan, [‡]Interdisciplinary Graduated School of Medicine and Engineering, University of Yamanashi, 4−4−37 Takeda, Kofu 400−8510 Japan, [§]Department of Physical Science, Hiroshima University, Kagamiyama, Higashihiroshima, Hiroshima 739-8526, Japan

Supporting Information

ABSTRACT: Carbon, nitrogen, and oxygen are essential components in solid-state materials. However, understanding their preference on the bonding to metals has not been straightforward. Here, niobium carbide, nitride, and oxide with simple rock-salt-based structures were analyzed by first-principles calculations and synchrotron X-ray diffraction. We found that an increase in the atomic number from carbon to oxygen formed fewer and shorter bonds to metals with better hybridization of atomic orbitals. This can provide a simple guiding principle for understanding the bonding and designing carbides, nitrides, oxides, and mixed-anion compounds.

There is no doubt that carbon, nitrogen, and oxygen govern the chemical bonds to metals in crystal structures, and recent advances in mixed-anion chemistry are accelerated based on the concept of controlling the chemical bonds between metals and these light elements.[1] However, the preferences to chemically combine atoms are still controverted. Anion exchange often causes unexpected structural changes, and understanding the covalency and ionicity in carbide/nitride/oxide is not straightforward. Hence, a detailed investigation of the simple compounds should provide clues to a better understanding of the chemical bonding. The rock-salt structure is one of the simplest structures with formulary 1:1 compounds, and we can find many carbides, nitrides, and oxides. This work focuses on three niobium-based rock-salt NbX (X = C, N, O). NbC and NbN have six-coordinated Nb−C and Nb−N bonds, respectively,[2,3] while NbO shows a rock-salt structure with one-fourth of the ordered vacancies at both the Nb and O sites (Figure 1).[4] As a result, Nb and O have four-coordination and form square planes. Experimentally obtained NbC and NbN are most likely somewhat far from perfect stoichiometric rock-salt structures, but ordered vacancies have not been reported in NbC and NbN. This unique ordered structure cannot be explained by simple ionic models based on coulombic interactions because the system prefers more a densely packed structure.[5] In addition, ionic models make it difficult to understand the bonding preference because the oxidation states of niobium in NbC/NbN/NbO are not clear and the ionic radii of Nb^{2+} and C^{4-} are not generally known.

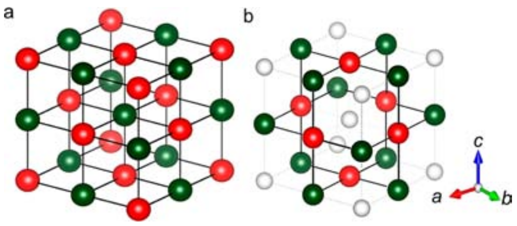

Figure 1. Crystal structures of (a) six-coordinated NbC and NbN and (b) four-coordinated NbO. Green and red spheres represent Nb and C/N/O, respectively. White spheres represent ordered vacancies.

There are a number of publications about NbX compounds.[6] Onwuagba and Sundararajan calculate the density of states (DOS) of six-coordinated NbX (X = C, N, O) and conclude that an increase in the atomic number from carbon to oxygen induces less hybridization of the atomic orbitals between Nb and X.[7] Burdett and Hughbanks explain the origin of the ordered vacancies in NbO by both Nb−O and Nb−Nb bonds via theoretical calculations.[5] Electron-density analysis by X-ray diffraction is a powerful tool to visualize chemical bonding. Electron-density distributions in NbC are visualized by single-crystal diffraction via Mo Kα and Ag Kα radiation.[2] However, errors from Fourier synthesis cannot be ignored for further discussion. Experimental evidence by synchrotron X-ray diffraction is required for a better understanding of the chemical-bonding character.

In this work, we investigated the effect of carbon, nitrogen, and oxygen on rock-salt-based NbX structures via first-principles calculations and synchrotron X-ray diffraction. Both computational and experimental results demonstrate that an increase in the atomic number causes shorter and fewer bonds between Nb and X with enhanced hybridization between Nb 4d and X 2p orbitals.

First, we performed computational calculations to examine the bonding features of Nb−X (X = C, N, O) with a six-coordinated rock-salt structure (0% vacancies), a four-coordinated NbO structure (25% vacancies), and intermediate structures having the same amount of Nb and X vacancies. Figure 2a shows the relationship between the concentration of the vacancy and the refined average distance between Nb and X. The bond lengths in six-coordinated NbC and NbN and four-coordinated NbO are close to the experimental values[2−4] (Table S1 in the Supporting

Received: April 4, 2013
Published: August 12, 2013

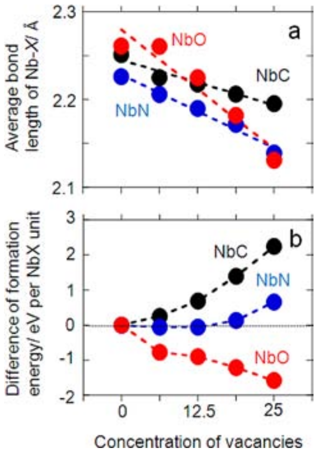

Figure 2. (a) Average bond length of Nb−X and (b) formation energy difference of rock-salt-based NbX (X = C, N, O) with various vacancy concentrations of the same amount of Nb and X calculated by the Vienna ab initio simulation package (VASP) code. Zero energy is set to the six-coordinated rock-salt structures. Dotted lines are eye guides.

Information, SI). NbX with vacant concentration between 6.25 and 17.75% shows local distortion after the refinement (Figures S1 and S2 in the SI). The average bond length of all three NbX structures tends to reduce with increasing concentrations of the vacancies. The slope of the bond length versus concentration of the vacancies from 0 to 25% shows the steepest drop in NbO, less in NbN and the least in NbC. Thus, an increase in the atomic number from carbon to oxygen tends to enhance the reduction rate of the bond length by introducing vacancies. Figure 2b shows the relationship between the concentrations of the vacancies and the formation energies of the rock-salt-based structures. In the case of carbide, no vacancy model is the most stable. On the other hand, oxide with 25% ordered vacancies is thermodynamically favorable. These predictions agree with the experimental results.[2,4] The formation energies of NbN with vacancies up to 12.5% are comparable, and the structures with more vacancies are unfavorable. This result on the Nb−N bond can be interpreted as the intermediate feature between the six-coordinated Nb−C and four-coordinated Nb−O bonds and indicates that the introduction of vacancies into NbN is not thermodynamically difficult. Nonetheless, an increase in the vacancy reduces the number of bonding. Hence, we propose the concept that fewer and shorter bonding is thermodynamically favorable with increasing atomic number from carbon to oxygen.

Different energy levels of C/N/O 2p orbitals and bonding distances should affect hybridization between the Nb 4d and X 2p orbitals. This is confirmed by the partial DOS (pDOS) and negative crystal orbital Hamilton population (COHP) of NbX with/without 25% ordered vacancies (Figures S3 and S4 in the SI). All of the NbX structures exhibited dominant contributions of Nb 4d and X 2p orbitals near the Fermi level. An increase in the atomic number from carbon to oxygen gave a large bandwidth for both coordinations.[7] COHP plots showed orbital mixing of the Nb 4d−X 2p and Nb 4d−Nb 4d orbitals. Table 1 summarizes the negative integrated COHP (−ICOHP). In the structure without the vacancy, the values of Nb 4d−X 2p decrease with increasing atomic number from carbon to oxygen, which indicates that an increase in the atomic number brings about less stable bonding between Nb 4d and X 2p.[7] On the other hand, an increase in the vacancy concentration enhances the value of −ICOHP, and most enhancements are found in four-coordinated NbO. Because little antibonding lies below the Fermi level (Figure S4 in the SI), more stable bonds suggest better hybridization between Nb 4d and O 2p atomic orbitals and compensate for the energy loss for less bonding owing to ordered vacancies. Importantly, the value of the Nb 4d−Nb 4d interaction in four-coordinated NbO is larger than others (Table 1), which agrees with the finding of Burdett and Hughbanks.[5] Therefore, the most enhanced overlap of the Nb 4d−X 2p and Nb 4d−Nb 4d orbitals in the oxide is the explanation for the four-coordinated structure with one-fourth of the ordered vacancies.

Table 1. −ICOHP of Nb 4d−X 2p and Nb 4d−Nb 4d Interactions in Rock-Salt NbX (X = C, N, O) with 0% and 25% Ordered Vacancies Calculated by the All-Electron Scalar-Relativistic *TB-LMTO-ASA* Program Code (eV bond^{-1})[a]

	−ICOHP			
	Nb 4d−X 2p		Nb 4d−Nb 4d	
compound	0% vacancy	25% vacancy	0% vacancy	25% vacancy
NbC	1.33 (7.98)	1.56 (6.24)	0.12 (1.44)	0.13 (1.04)
NbN	1.21 (7.26)	1.58 (6.32)	0.13 (1.56)	0.14 (1.12)
NbO	0.94 (5.64)	1.42 (5.68)	0.14 (1.68)	0.21 (1.68)

[a] Those values per atom are shown in parentheses (eV atom^{-1}).

Next, we carried out crystal structure analyses by synchrotron powder X-ray diffraction. Chemical analyses suggested that NbC (Nb/C = 1.02) and NbO (Nb/O = 1.00) were almost 1:1 compounds. These NbC and NbO structures can be refined by the Rietveld method with the single-phase models of six- and four-coordinated rock-salt structures, respectively (Table S2 in the SI). The refined lattice parameters of six-coordinated NbC and four-coordinated NbO are 4.47208(2) and 4.21165(1) Å, respectively, which are close to the reported values of NbX.[2,4] While the refinement of six-coordinated NbC was performed with isothermal displacement parameters, the thermal displacements for four-coordinated NbO were conducted with anisothermal displacement parameters. Larger displacement parameters of niobium and oxygen toward the ordered vacancies were found in NbO (Figure S6 in the SI). The refinement of NbN was complicated. Chemical analysis suggests nitrogen vacancies and the existence of oxygen (Nb:N:O = 1.00:0.86:0.04). After the refinement, approximately 2 mass % of the NbO_2 phase was detected as an impurity phase. More importantly, the peaks of NbN at high angle split into two peaks (Figure S7 in the SI) and cannot be refined well using the single-phase model with cubic symmetry. The double cubic phase model of $NbN_{0.86}$ with slightly different lattice parameters (ca. 0.04%) improved the refinement (Table S2 in the SI). It would be most likely that precise X-ray diffraction could detect evidence of the phase separation with tiny differences of the lattice parameters. Additionally, approximately a few times larger thermal displacement parameters of niobium were found compared with those of constituent atoms in NbC and NbO. It is quite natural to consider that this large value and phase separations are caused by relatively high concentrations of nitrogen vacancies.

The electron-density distributions of six-coordinated NbC and four-coordinated NbO were experimentally visualized via the maximum-entropy method (MEM) (Figure 3). While the electron clouds in six-coordinated NbC are rather isolated, those of four-coordinated NbO are well overlapped; the minimum electron densities between NbC and NbO are 0.78

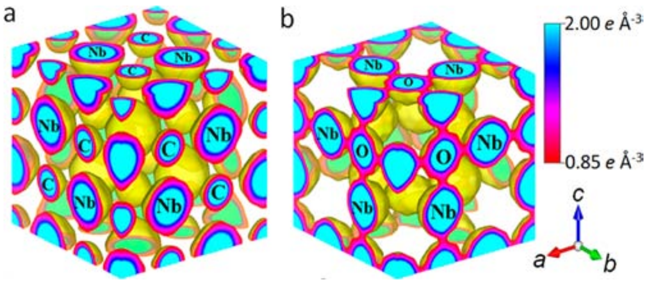

Figure 3. 3D electron-density distributions at room temperature of (a) NbC and (b) NbO deduced by the MEM from synchrotron X-ray diffraction data. The equidensity surface level of 0.85 e $Å^{-3}$ is drawn in yellow. 2D electron-density distributions from 0.85 to 2.0 e $Å^{-3}$ are exhibited by the gradient from red to light blue on the cross sections.

and 1.06 $Å^{-3}$, respectively. This is clear evidence for enhanced hybridization between Nb 4d and O 2p orbitals in four-coordinated NbO, which agrees with the theoretical prediction.

Both theoretical and experimental results suggest that an increase in the atomic number from carbon to oxygen prefers fewer and shorter bonds with more hybridization. Our finding of bonding with C/N/O is also useful for understanding the bonding feature in mixed-anion compounds, such as oxynitrides. An example is found in TaON, which is crystallized in the monoclinic system with different crystallographic sites of nitrogen and oxygen.[8,9] In this structure, nitrogen forms NTa_4 tetragons, while oxygen forms OTa_3 triangles.[9] The mean bond lengths of Ta−N and Ta−O are 2.114 and 2.065 Å, respectively.[9] The average value of the minimum electron density of the Ta−N bond (0.84 $Å^{-3}$) is lower than that of the Ta−O bond (0.96 $Å^{-3}$).[9] Thus, the bonding number, length, and electron density in TaON show the same trends as those of the rock-salt-based NbX compounds, although these crystal structures are entirely different. When one compares these findings with other examples, such as SrO and HgO and AlF_3 and $AlBr_3$,[10] lower bonding numbers in NbO, HgO, and $AlBr_3$ give better hybridization of the atomic orbitals. Nonetheless, their bonding distances cannot be understood in a simple manner because they rely on not only the bonding number but also occupied electron shells of these components. Another interesting finding in this study is the relatively high tolerance by vacancies in NbN. While theoretical results indicate the NbN phase with a high tolerance of both niobium and nitrogen vacancies (Figure 2b), experimental results show NbN with vacancies of only nitrogen. Although there are different vacancies, the origin of these vacancies may be attributed to the intermediate bonding feature in NbN, which locates between six-coordinated NbC and four-coordinated NbO. The tolerance of vacancies affords a variety of rock-salt-based niobium nitrides, including NbN with slightly different lattice parameters,[11] carbonitrides,[12] and oxinitrides.[13] Exact control of the composition, vacancies, and crystal structure in NbN-based materials implies challenging problems but can be essential in controlling their properties.

In conclusion, studies of first-principles calculations and X-ray diffraction for rock-salt-based NbX (X = C, N, O) reveal that an increase in the atomic number from carbon to oxygen prefers fewer and shorter bonding. NbC shows the six-coordinated rock-salt structure with relatively long bonds and NbO the four-coordinated rock-salt structure with relatively short bonds. Six-coordinated NbC exhibits less overlap of the Nb 4d and C 2p orbitals compared with four-coordinated NbO. We theorize that NbN contains a high concentration of vacancies in the six-coordinated rock-salt structure owing to the intermediate bonding feature between Nb 4d and N 2p. These investigations unravel a fundamental problem in the bonding chemistry and provide the concept for a better understanding of the bonding and design of oxides, nitrides, carbides, and mixed-anion compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and calculation methods, crystal structures optimized by the *VASP* code, histograms of bond length, lattice parameters of NbX, total and partial DOS, COHP plots, Rietveld refinement profiles and refined parameters of NbX (X = C, N, O), Oak Ridge thermal ellipsoid plot drawing (99% thermal ellipsoids) of NbO, and split diffraction peak of the NbN phase. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: amiura@yamanashi.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The synchrotron radiation experiments were performed at SPring-8 with approval of the Japan Synchrotron Radiation Research Institute (JASRI: Proposal Nos. 2012B1781 and 2012B0084).

■ REFERENCES

(1) (a) Yang, M.; Oró-Solé, J.; Rodgers, J. A.; Jorge, A. B.; Fuertes, A.; Attfield, J. P. *Nat. Chem.* **2011**, *3* (1), 47−52. (b) Tsujimoto, Y.; Yamaura, K.; Takayama-Muromachi, E. *Appl. Sci.* **2012**, *2* (1), 206−219. (c) Kobayashi, Y.; Hernandez, O. J.; Sakaguchi, T.; Yajima, T.; Roisnel, T.; Tsujimoto, Y.; Morita, M.; Noda, Y.; Mogami, Y.; Kitada, A.; Ohkura, M.; Hosokawa, S.; Li, Z.; Hayashi, K.; Kusano, Y.; Kim, J. e.; Tsuji, N.; Fujiwara, A.; Matsushita, Y.; Yoshimura, K.; Takegoshi, K.; Inoue, M.; Takano, M.; Kageyama, H. *Nat. Mater.* **2012**, *11* (6), 507−511. (d) Kamihara, Y.; Watanabe, T.; Hirano, M.; Hosono, H. *J. Am. Chem. Soc.* **2008**, *130* (11), 3296−3297.

(2) Will, G.; Platzbecker, R. *Z. Anorg. Allg. Chem.* **2001**, *627* (9), 2207−2210.

(3) Christensen, A. N. *Acta Chem. Scand.* **1977**, *31a*, 77−78.

(4) Bowman, A. L.; Wallace, T. C.; Yarnell, J. L.; Wenzel, R. G. *Acta Crystallogr.* **1966**, *21* (5), 843.

(5) Burdett, J. K.; Hughbanks, T. *J. Am. Chem. Soc.* **1984**, *106* (11), 3101−3113.

(6) Neckel, A. *Int. J. Quantum Chem.* **1983**, *23* (4), 1317−1353.

(7) Onwuagba, B. N.; Sundararajan, V. *Phys. Status Solidi B* **1995**, *190* (2), 393−399.

(8) (a) Brauer, G.; Weidlein, J.; Strähle, J. *Z. Anorg. Allg. Chem.* **1966**, *348* (5−6), 298−308. (b) Brauer, G.; Weidlein, J. R. *Angew. Chem., Int. Ed. Engl.* **1965**, *4* (10), 875−875.

(9) Yashima, M.; Lee, Y.; Domen, K. *Chem. Mater.* **2007**, *19* (3), 588−593.

(10) West, A. R. *Solid State Chemistry and Its Applications*; John Wiley & Sons: New York, 1984; p 223.

(11) Linde, A. V.; Marin-Ayral, R. M.; Granier, D.; Bosc-Rouessac, F.; Grachev, V. V. *Mater. Res. Bull.* **2009**, *44* (5), 1025−1030.

(12) Christensen, A. N.; Fregerslev, S. *Acta Chem. Scand.* **1977**, *31a*, 861−868.

(13) Ohashi, Y.; Motohashi, T.; Masubuchi, Y.; Moriga, T.; Murai, K.; Kikkawa, S. *J. Solid State Chem.* **2011**, *184* (8), 2061−2065.