INORGANIC COMPOUNDS

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The μ-Phase of $Co_{6.3}Nb_{6.7}$

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Abstract

The rhombohedral structure of the μ-phase $Co_{6.30}Nb_{6.70}$, space group $R\bar{3}m$, Pearson symbol *hR*39, was refined from X-ray diffraction data of an obverse–reverse twinned crystal. The Co atoms have distorted icosahedral environments, the Nb atoms have coordination numbers 12, 14, 15 and 16, and configurations typical for Frank–Kasper phases. The structure is quantitatively analysed in terms of the dihedral angles and ranges of the edge lengths of the distorted tetrahedra. It is shown that the derived mean values hardly differ from those calculated for other representatives of tetrahedrally close-packed structure types.

Comment

The structure of a phase of nominal composition CoNb was first determined by Shurin, Kripyakevich & Gladyshevskii (1965) by means of X-ray powder photographs and was found to be isotypic with the μ-phase Fe_7W_6 (Arnfelt & Westgren, 1935). The μ-phases belong to the family of the Frank–Kasper (FK) phases (Frank & Kasper, 1958, 1959), the structures of which exhibit only triangulated coordination polyhedra of coordination numbers (CN) 14, 15 and/or 16 in addition to those of CN 12. The polyhedra interpenetrate unambiguously and completely, thus forming a specific close packing of slightly distorted tetrahedra. The structures of μ-phases comprise 12-, 14-, 15- and 16-fold coordinated atoms in the ratio 7:2:2:2.

Until now only a few μ-phases have been structurally characterized by single crystal X-ray diffraction methods. Structural parameters of Fe_7W_6 and Co_7Mo_6 (Forsyth & D'Alte da Veiga, 1962), for example, were determined from integrated intensities of Weissenberg photographs. Here we report structural parameters for μ-$Co_{6.30}Nb_{6.70\,(7)}$ (Table 1) determined from the intensities from a twinned crystal, the fractions of the volume being 0.954 (2) and 0.046.

The rhombohedral structure is composed of five crystallographically distinct atoms, the primary coordinations of which are shown in Fig. 1. In accord with the relative size of the atoms, the Co atoms are exclusively 12-fold coordinated. The second icosahedrally coordinated site at the origin of the cell is occupied by 70 (7)% Nb and 30% Co. The mean distances (⟨ ⟩) reflect the different atom sizes and coordination numbers (*cf.* Table 2): Co1 (CN 12) ⟨2.649 Å⟩, Nb/Co (CN 12) ⟨2.664 Å⟩, Nb1 (CN 15) ⟨2.906 Å⟩, Nb2 (CN 16) ⟨2.879 Å⟩, Nb3 (CN 14) ⟨2.854 Å⟩. The seemingly unexpected greater distance for Nb1 (CN 15) compared with that for Nb2 (CN 16) correlates with the frequency of the smaller Co atoms in the primary coordination spheres. The suspiciously high isotropic displacement parameter of Nb2 seems not to be associated with a partial substitution of Co for Nb, but is rather a result of the space available for the highly coordinated Nb2. This is concluded from an independent refinement of both parameters, occupancy [0.99 (2)] and displacement [U_{eq} = 0.0077 (6) Å] do not obviously interfere. The shortest Nb—Nb distance [2.543 (3) Å] is found between two Nb3 atoms (CN 14) arranged along the threefold axis of symmetry (see Fig. 2).

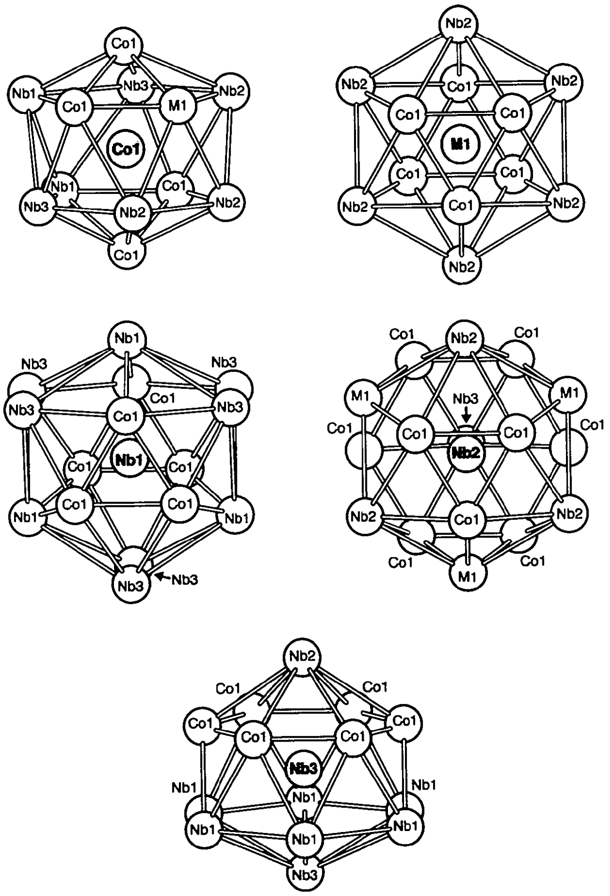

Fig. 1. Triangulated coordination polyhedra about the five crystallographically distinct atoms.

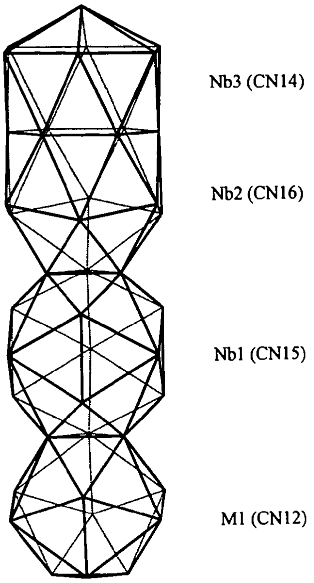

Fig. 2. Sequence of face-sharing coordination polyhedra along the threefold axis of symmetry; range $-0.09 < z < 0.56$, inversion at $z = 0, \frac{1}{2}$ reproduces the sequence.

In addition, the structure was analysed with respect to the dihedral angles θ and deviations (E) of the six edge lengths from the mean value of each single tetrahedron for all 222 tetrahedra (per cell), in order to measure the distortion of the structure relative to a fictitious, impossible structure built up of regular tetrahedra. Table 3 lists dihedral angles $\theta_{m,p}$ and error parameters E_p averaged for each distinct coordination polyhedron of the structure. Table 4 compares the overall mean value with that of other prominent Frank–Kasper phases. Two conclusions are drawn: (i) in accord with the statement of Shoemaker & Shoemaker (1986), the mean dihedral angles differ less than 0.1° from the ideal dihedral angle [$\cos^{-1}(1/3) = 70.529°$] for the listed FK phases; (ii) the error parameters E of tetrahedrally close-packed FK phases do not differ significantly and fall in the range 0.060–0.066.

Experimental

Plate-like crystals of $Co_{6.3}Nb_{6.7}$ were selected from a sample which was prepared from the metals and $Nb_{1.2}S_2$. In a first step the compressed mixture was arc-melted in an argon atmosphere on a water-cooled copper plate with the use of a non-consumable tungsten electrode; subsequently, the crushed button was heated in a sealed molybdenum crucible for 7 d at 1570 K.

Crystal data

$Co_{6.30}Nb_{6.70}$
$M_r = 993.75$
Rhombohedral
$R\bar{3}m$
$a = 4.904\ (1)$ Å
$c = 26.186\ (10)$ Å
$V = 545.4\ (2)$ Å^3
$Z = 3$
$D_x = 9.077$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.4$–$25.3°$
$\mu = 23.55$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.050 × 0.050 × 0.015 mm
Silver lustre

Data collection

(* indicates values for the larger domain of the twin)

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans
$T_{min} = 0.859$, $T_{max} = 0.999$
3889 (2149*) measured reflections
469* independent reflections

198* observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.116$
$\theta_{max} = 32.9°$
$h = -6 \rightarrow 6$
$k = -6 \rightarrow 6$
$l = 0 \rightarrow 39$
3 standard reflections
frequency: 130 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0286$
$wR(F^2) = 0.081$
$S = 1.076$
198 reflections
21 parameters
$w = 1/[\sigma^2(F_o^2) - 10P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 4.50$ e Å^{-3}
$\Delta\rho_{min} = -3.17$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0024 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co1	0.1687 (4)	$1-x$	0.92317 (6)	0.0048 (6)
$M1$*	0	0	0	0.0062 (14)
Nb1	0	0	0.16583 (11)	0.0035 (6)
Nb2	0	0	0.34789 (9)	0.0081 (7)
Nb3	0	0	0.45145 (8)	0.0034 (8)

* $M1$ = 70 (7)% Nb, 30% Co.

Table 2. *Selected geometric parameters* (Å, °)

Co1—Co1	2.422 (3)	× 2	Nb3—Nb3	2.543 (3)	
Co1—$M1$	2.470 (2)		Nb3—Co1	2.680 (2)	× 6
Co1—Co1	2.482 (3)	× 2	Nb3—Nb2	2.712 (3)	
Co1—Nb3	2.680 (2)	× 2	Nb3—Nb1	3.095 (1)	× 3
Co1—Nb1	2.736 (3)		Nb3—Nb1	3.113 (1)	× 3
Co1—Nb1	2.756 (3)		$M1$—Co1	2.470 (2)	× 6
Co1—Nb2	2.772 (2)		$M1$—Nb2	2.8571 (5)	× 6
Co1—Nb2	2.945 (2)	× 2	Nb2—Nb3	2.712 (3)	
Nb1—Co1	2.736 (3)	× 3	Nb2—Co1	2.772 (3)	× 3
Nb1—Co1	2.756 (3)	× 3	Nb2—$M1$	2.8571 (5)	× 3
Nb1—Nb1	2.8319 (5)	× 3	Nb2—Nb2	2.932 (1)	× 3
Nb1—Nb3	3.095 (1)	× 3	Nb2—Co1	2.945 (2)	× 6
Nb1—Nb3	3.113 (1)	× 3			

Table 3. *Coordination number* CN, *values of the local error parameter* E_p, *the local average dihedral angles* $\theta_{m,p}$ *and the minimum and maximum dihedral angle of the tetrahedra in the five distinct coordination polyhedra*

	CN	E_p	$\theta_{m,p}$ (°)	$\theta_{\min}$ (°)	$\theta_{\max}$ (°)
Co1	12	0.0623	70.571	59.288	79.972
*M*1	12	0.0596	70.567	60.319	77.132
Nb1	15	0.0649	70.515	54.748	79.972
Nb2	16	0.0634	70.536	59.288	77.132
Nb3	14	0.0663	70.486	54.748	79.972

Table 4. *Values for the error parameter E and the average dihedral angle* θ_m *of selected Frank–Kasper phases*

Phase	Type	$E \times 10^{-2}$	θ_m (°)
Cr_3Si^a	A15	0.0631	70.435
$Al_3Zr_4{}^b$	Z	0.0612	70.500
$Fe_7W_6{}^c$	μ	0.0658	70.540
$Co_{6.30}Nb_{6.70}$	μ	0.0633	70.540
Cu_2Mg^d	C15	0.0621	70.588

Calculations are based on crystal data as reported by (*a*) Boren (1933); (*b*) Wilson, Thomas & Spooner (1960); (*c*) Arnfelt & Westgren (1935), and (*d*) Laves & Witte (1935).

The quality of the crystal was checked by precession photographs (Mo $K\alpha$). The structure of the observe–reverse twinned crystal was refined with the program *SHELXL*93 (Sheldrick, 1993). The geometrical analyses of the tetrahedral close (german: *dicht*) packed structures were performed with the program *TDP* (Wagner, 1994). The error parameters *E* were calculated using the algorithm of Brandon, Chieh, Pearson & Riley (1975).

Data collection: CAD-4 software. Cell refinement: CAD-4 software. Data reduction: *SDP* (Frenz, 1978). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SCHAKAL* (Keller, 1992).

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Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1106). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Novel Semiconducting Perovskite-Related Phase: $Sr_5Nb_5O_{17}$

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Abstract

The structure of strontium niobium oxide, $Sr_5Nb_5O_{17}$, prepared by the floating-zone melting technique, has been determined by single-crystal X-ray analysis. The structure contains distorted perovskite-type slabs parallel to (100) formed from five NbO_6 octahedra and Sr atoms. The Nb—O distances range from 1.89 (2) to 2.10 (2) Å for Nb1, from 1.809 (5) to 2.282 (6) Å for Nb2, and from 1.851 (6) to 2.167 (6) Å for Nb3. The NbO_6 conformations are (4+1+1) distorted. Sr2 and Sr3 are coordinated by 12 O atoms with Sr—O distances in the range 2.64 (1) to 3.04 (1) Å for Sr2 and 2.50 (1) to 3.06 (1) Å for Sr3. Sr1, placed near the boundary of the slab, is irregularly coordinated by five O atoms in the same slab and two O atoms in the neighbouring slab [Sr—O 2.46 (1) to 2.915 (6) Å] and by a further three O atoms at long coordination distances [3.345 (8) to 3.544 (9) Å]. The title compound is isotypic with $La_5Ti_5O_{17}$ and both structures belong to the homologous

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