program *DIFABS* (Walker & Stuart, 1983) did not operate well with the data. The versions we used do not correctly handle indices over 50. So absorption corrections were performed using a modified version of *DATAP* (Coppens, Lieserowitz & Rabinovich, 1965) and the structure was refined using *SHELXL*93 (Sheldrick, 1993).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *CADAK* (Savariault, 1991*a*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TABPUB* (Savariault, 1991*b*).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$NbAs_2$

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Abstract

The structure of niobium diarsenide, $NbAs_2$, has been determined by single-crystal X-ray diffraction; it was found to crystallize with the $OsGe_2$ structure type.

Comment

The lattice parameters as well as the possible space groups of $NbAs_2$ were first reported in 1964 (Saini, Calvert & Taylor, 1964). A second study using the Guinier technique was performed in 1964 (Furuseth & Kjekshus, 1964*a*,*b*). In further investigations (Furuseth & Kjekshus, 1965), the crystal structure was solved in space group *C*2 using integrated intensities from Weissenberg photographs. Problems occurring during the refinement procedure were attributed to absorption effects. It was suggested by Pearson (1967, 1972) that $OsGe_2$ may be of the $NbAs_2$ type. A reinvestigation of a number of structures crystallizing with either the $OsGe_2$ or $NbAs_2$ structures showed that *C*2/*m* gives the best refinement results (Calvert, 1992). These structures may be classified in *C*2/*m* with $OsGe_2$ as the prototype structure (Calvert, 1992). Very recently, single crystals of $NbSb_2$ were reported to crystallize in space group *C*2/*m* with the $OsGe_2$ structure type (Rehr & Kauzlarich, 1994). To confirm that $NbAs_2$ also crystallizes with the $OsGe_2$ structure type, we refined our single-crystal data in both *C*2/*m* and *C*2. The final $R(F)$ and $wR(F)$ values were slightly lower for the *C*2/*m* refinement (3.03 and 2.88%) compared with those of the *C*2 refinement (3.13 and 3.12%). The positional parameters differ from those reported by Furuseth & Kjekshus (1964*b*, 1965). Consequently, the bond distances (Table 2) are also different from the values given in the previous contributions (Furuseth & Kjekshus, 1964*b*, 1965).

The Nb atom is in a triangular prism of six As atoms. Two other As atoms and one Nb atom lie outside the rectangular faces. Outside each of the triangular faces two, more distant, Nb atoms are located. Each As1 atom has a distorted square-pyramidal environment of five Nb atoms. One close As1 atom is located across the base of the pyramid. Each As2 atom is coordinated to three other As2 and three Nb atoms. The arrangement of the

As2 atoms leads to alternating short and long As2—As2 distances. The short As2—As2 distances can be regarded as covalent bonds.

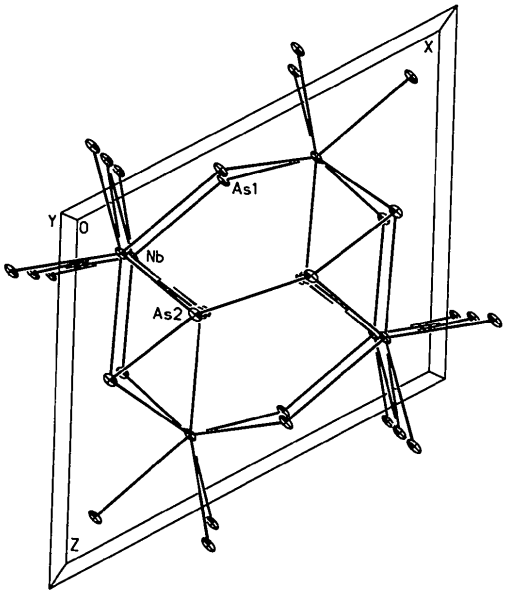

Fig. 1. The crystal structure of $NbAs_2$. Ellipsoids are drawn at the 70% probability level.

Experimental

During our investigation of the quarternary system Tl–Nb–Se–As we obtained $NbAs_2$ as black needles. The elements in the ratio 0.8:6:7:1 (Tl:Nb:Se:As) were placed in a quartz ampoule and sealed under vacuum. The mixture was heated to 1273 K (100 K h^{-1}) for six weeks and cooled to room temperature by quenching the ampoule in water. Crystals of $NbAs_2$ were obtained in addition to different niobium selenides.

Crystal data

$NbAs_2$
M_r = 242.8
Monoclinic
$C2/m$
a = 9.368 (2) Å
b = 3.396 (1) Å
c = 7.799 (3) Å
β = 119.42 (1)°
V = 216.1 (1) Å^3
Z = 4
D_x = 7.460 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 26 reflections
θ = 10.3–18.1°
μ = 35.479 mm^{-1}
T = 295 K
Needle
0.14 × 0.02 × 0.015 mm
Black

Data collection

Stoe AED II diffractometer
$\omega/2\theta$ scans
294 observed reflections [$F > 4\sigma(F)$]
Absorption correction: refined from ΔF (*XEMP* in *SHELXTL-Plus*; Sheldrick, 1991)
T_{min} = 0.530, T_{max} = 0.623
664 measured reflections
364 independent reflections
R_{int} = 0.0235
θ_{max} = 30°
$h = -12 \rightarrow 0$
$k = -4 \rightarrow 4$
$l = -9 \rightarrow 10$
4 standard reflections
frequency: 120 min
intensity decay: <0.5%

Refinement

Refinement on F
R = 0.0303
wR = 0.0363
S = 0.9536
292 reflections
20 parameters
$w = 1/[\sigma^2(F) + 0.001F^2]$
$(\Delta/\sigma)_{max} \leq 0.001$
$\Delta\rho_{max}$ = 2.84 e Å^{-3}
$\Delta\rho_{min}$ = −3.25 e Å^{-3}
Extinction correction: $F^* = F(1 + 0.002\chi F^2/\sin\theta)^{-1/4}$
Extinction coefficient: χ = 0.0014 (3)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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}
Nb	0.1574 (1)	0	0.1965 (1)	0.003 (1)
As1	0.4059 (1)	0	0.1084 (1)	0.004 (1)
As2	0.3600 (1)	1/2	0.4720 (1)	0.004 (1)

Table 2. *Selected distancess* (Å)

Nb—As1		2.731 (2)	Nb—Nb		3.034 (1)
Nb—As1	×2	2.705 (1)	As1—As1		2.983 (3)
Nb—As2		2.669 (2)	As2—As2		2.439 (2)
Nb—Nb	×2	3.396 (1)	As1—As1	×2	3.069 (2)
Nb—As2	×2	2.664 (1)	As2—As2	×2	2.864 (2)
Nb—As1	×2	2.739 (1)			

The *SHELXTL-Plus* package (Sheldrick, 1991) was used for crystallographic computations.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$NaM^{II}Zr_2F_{11}$ (M^{II} = Mn, Fe, Co, Ni, Zn) Fluorides

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Abstract

The structures of $NaMnZr_2F_{11}$ (sodium manganese undecafluorodizirconate), $NaFeZr_2F_{11}$, $NaCoZr_2F_{11}$, $NaNiZr_2F_{11}$ and $NaZnZr_2F_{11}$ have been refined from single-crystal X-ray diffraction data. These compounds are isostructural with $AgPdZr_2F_{11}$. They are characterized by isolated compressed octahedra, which are slightly tetragonally distorted, surrounding the divalent cations of the first-row transition metals. Attempts at the growth of single crystals of divalent chromium (d^4) and copper (d^9) failed, probably because these cations are unstable as a result of the Jahn–Teller effect.

Comment

Compounds of the general formula $NaM^{II}Zr_2F_{11}$ can be divided into two very different structure types according to the nature of the divalent cation, M^{2+}. For a divalent cation of the second transition series, such as Pd^{2+} or Ag^{2+}, a three-dimensional layered structure with triclinic space group $P\bar{1}$ has been observed (Müller, 1987). In this structure type, the Pd^{2+} ions have regular octahedral coordination, whereas the F-atom environment about Ag^{2+} is pseudotetragonally elongated. It can be inferred that the distortion of the Ag^{2+} octahedra is Jahn–Teller induced. A slightly less distorted variant of this structure type has been observed for $AgPdZr_2F_{11}$, which crystallizes in the monoclinic space group $C2/m$ (Müller, 1987). Here, the Pd^{2+} ion also has regular octahedral coordination. We report herein the structures of a series of fluorides with general formula $NaM^{II}Zr_2F_{11}$ (M^{II} = Mn, Fe, Co, Ni, Zn) which are closely related to that of $AgPdZr_2F_{11}$. In these compounds, the divalent cations are in slightly compressed octahedra. Assuming that the Jahn–Teller effect may operate in $NaM^{II}Zr_2F_{11}$ compounds since such a strong effect has already been observed for Ag^{2+} in $NaAgZr_2F_{11}$, the lack of representatives for Cr^{2+} (d^4) and Cu^{2+} (d^9), for which a strong Jahn–Teller effect could be expected, may be interpreted as due to such an effect being stronger for divalent cations of the first transition row than for Ag^{2+}, leading to unstable structures. For the Co^{2+} compounds the stabilization of the high-spin state is related to the weak crystal field generally induced by an F-atom environment.

The Zr^{IV} ions are located in corner-linked *trans* chains of $(Zr_2F_{12})^{4-}$ binuclear units comprising pairs of edge-sharing pentagonal bipyramids. The Na^+ and M^{2+} ions are ordered within chains of edge-linked polyhedra, made up of alternating hexagonal bipyramids and octahedra. Both types of chains are joined by sharing corners and edges, resulting in layers as illustrated in Fig. 1. These layers are perpendicular to [201] and are further linked to form a three-dimensional framework by sharing corners. The layers are stacked along [201] in the sequence A,B,C,D,E and are related by a translation in such a way that one layer is displaced relative to the other by $\frac{1}{2}\mathbf{b} - \frac{1}{4}\mathbf{c}$ so that an additional Na–Zr–M^{II}–Zr ordering occurs within the corner-linked *trans* chains of composition $(NaM^{II}Zr_2F_{24})_n^{13n-}$, extended along [201].

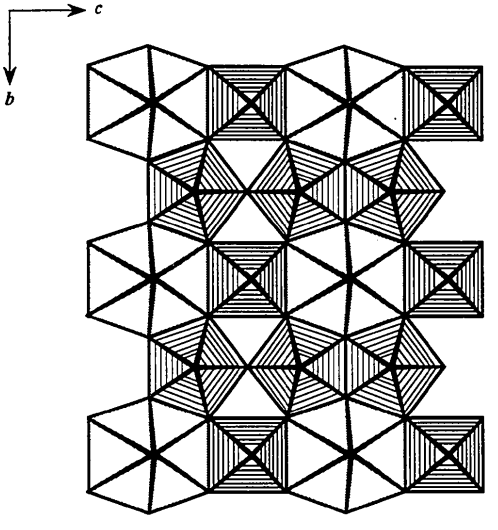

Fig. 1. Polyhedral layer showing the linkage between octahedra (M^{II}), pentagonal bipyramids (Zr) and hexagonal bipyramids (Na).

Experimental

Single crystals of $NaMnZr_2F_{11}$ were obtained by heating a stoichiometric mixture of the dried binary fluorides at 1073 K for 2 d in a sealed platinum tube followed by slow cooling to room temperature at 4 K h^{-1}. For the other $NaM^{II}Zr_2F_{11}$ fluorides (M^{II} = Fe, Co, Ni, Zn), single crystals were obtained by heating stoichiometric mixtures of the dried starting fluorides to 1073 K in sealed platinum tubes, as above, but once this temperature had been reached the samples were allowed to cool slowly to 913 K at 4 K h^{-1}. The temperature

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