

Tableau 2. Distances interatomiques (Å) W—O dans les deux anions W<sub>12</sub>O<sub>42</sub>

Les écarts standards sont donnés entre parenthèses.

Premier anion			
W(2)—O(5)	1,95 (1)	W(3)—O(9)	1,70 (2)
W(2)—O(6)	1,72 (2)	W(3)—O(14)	2,23 (2)
W(2)—O(14)	1,91 (2)	W(3)—O(18)	1,95 (2)
W(2)—O(30)	1,84 (2)	W(3)—O(19)	1,95 (1)
W(2)—O(31)	2,28 (2)	W(3)—O(22)	2,35 (1)
W(2)—O(39)	2,07 (2)	W(3)—O(29)	1,75 (2)
W(5)—O(11)	1,75 (1)	W(7)—O(12)	1,98 (2)
W(5)—O(12)	1,86 (2)	W(7)—O(20)	1,94 (2)
W(5)—O(14)	2,23 (1)	W(7)—O(31)	2,26 (2)
W(5)—O(15)	1,73 (2)	W(7)—O(33)	1,77 (2)
W(5)—O(18)	1,91 (2)	W(7)—O(36)	1,85 (2)
W(5)—O(41)	2,20 (2)	W(7)—O(39)	1,85 (2)
W(8)—O(5)	2,00 (1)	W(9)—O(19)	1,93 (2)
W(8)—O(7)	1,76 (2)	W(9)—O(20)	1,90 (2)
W(8)—O(22)	1,88 (1)	W(9)—O(22)	2,26 (1)
W(8)—O(31)	2,26 (2)	W(9)—O(23)	1,79 (2)
W(8)—O(36)	2,14 (2)	W(9)—O(27)	1,75 (2)
W(8)—O(41)	1,80 (2)	W(9)—O(30)	2,18 (2)
Deuxième anion			
W(1)—O(1)	2,25 (1)	W(4)—O(10)	1,97 (2)
W(1)—O(10)	1,89 (2)	W(4)—O(13)	1,73 (2)
W(1)—O(34)	1,77 (1)	W(4)—O(17)	1,91 (2)
W(1)—O(35)	1,97 (2)	W(4)—O(21)	1,87 (1)
W(1)—O(37)	2,15 (1)	W(4)—O(24)	2,25 (2)
W(1)—O(38)	1,74 (2)	W(4)—O(25)	1,89 (2)
W(6)—O(1)	2,41 (2)	W(10)—O(3)	1,91 (2)
W(6)—O(2)	1,74 (2)	W(10)—O(4)	2,21 (2)
W(6)—O(3)	1,93 (2)	W(10)—O(16)	1,77 (2)
W(6)—O(35)	1,90 (1)	W(10)—O(17)	1,90 (2)
W(6)—O(40)	1,76 (2)	W(10)—O(32)	2,16 (1)
W(6)—O(32)	2,24 (1)	W(10)—O(42)	1,66 (3)
W(11)—O(24)	2,27 (2)	W(12)—O(1)	1,89 (2)
W(11)—O(25)	2,08 (2)	W(12)—O(4)	1,79 (2)
W(11)—O(26)	1,97 (2)	W(12)—O(8)	1,74 (2)
W(11)—O(28)	1,78 (2)	W(12)—O(21)	2,11 (1)
W(11)—O(32)	1,96 (1)	W(12)—O(24)	2,20 (1)
W(11)—O(37)	1,84 (1)	W(12)—O(26)	1,97 (2)

Tableau 3. Distances interatomiques (Å) NH<sub>4</sub>—O et NH<sub>4</sub>—H<sub>2</sub>O dans les polyèdres de coordination des ions ammonium

NH <sub>4</sub> (1)—O(1)	2,99 (3)	NH <sub>4</sub> (2)—O(4)	3,05 (3)
—O(2)	3,00 (3)	—O(9)	2,91 (3)
—O(8)	2,99 (3)	—O(10)	3,17 (3)
—O(10)	3,05 (3)	—O(15)	2,96 (3)
—O(11)	2,74 (3)	—O(17)	3,03 (3)
—O(13)	2,99 (3)	—O(18)	3,44 (3)
—O(21)	3,19 (3)	—O(37)	3,07 (3)
—O(34)	2,92 (3)	—O(38)	2,95 (3)
—O(34)	2,86 (3)	—O(42)	2,91 (4)
NH <sub>4</sub> (3)—O(19)	3,20 (3)	NH <sub>4</sub> (4)—O(7)	2,88 (3)
—O(23)	3,02 (3)	—O(8)	3,04 (3)
—O(28)	2,79 (3)	—O(11)	2,96 (3)
—O(29)	2,96 (3)	—O(18)	3,08 (3)
—O(W4)	3,08 (3)	—O(34)	3,14 (3)
—O(W7)	2,92 (4)	—O(38)	3,08 (3)
—O(W10)	2,79 (4)	—O(W2)	3,05 (3)
		—O(W3)	3,02 (4)
NH <sub>4</sub> (5)—O(3)	2,84 (3)	NH <sub>4</sub> (6)—O(7)	3,05 (3)
—O(8)	2,89 (3)	—O(7)	2,90 (3)
—O(11)	3,06 (3)	—O(22)	3,31 (3)
—O(12)	3,40 (3)	—O(23)	3,11 (3)
—O(27)	3,02 (3)	—O(29)	2,99 (3)
—O(30)	2,99 (3)	—O(W2)	3,27 (3)
—O(41)	2,98 (3)	—O(W3)	3,11 (3)
		—O(W3)	2,87 (3)
		—O(W7)	2,94 (4)

## Références

- ALLMANN, R. (1971). *Acta Cryst.* **B27**, 1393–1404.  
 D'AMOUR, H. & ALLMANN, R. (1973). *Z. Kristallogr.* **138**, 5–18.  
 MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN. A Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. de York, Angleterre, et Louvain, Belgique.

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## Structure and Order Parameter of an A15-Type Niobium Germanium Single Crystal

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**Abstract.** Nb<sub>3</sub>Ge<sub>0.8</sub>Nb<sub>0.2</sub>, cubic, *Pm3n*, *a* = 5·1692 (8) Å. Single-crystal diffractometry was carried out using Ag K $\alpha$  radiation. The  $\sin \theta/\lambda$  cut off was at 1·6 Å<sup>-1</sup>. The results of the refinements of site occupation, extinction and thermal parameters are discussed. Final *R* = 3·4% for 122 reflections and six parameters.

**Introduction.** The majority of crystal structure investigations on superconductors has been carried out on polycrystalline materials. Single crystals are in general better suited for characterizing a given compound and we have therefore started experiments for growing single crystals of superconducting intermetallic compounds.

The A15 structure of space group  $Pm\bar{3}n$  is nominally of stoichiometry  $A_3B$  with the  $A$  atoms in 6(c) and the  $B$  atoms in 2(a) sites. In the Nb–Ge system the A15 structure is well established but the phase with the stoichiometric composition is unstable. References to the literature on this aspect are given, e.g., by Cox, Moehlecke, Sweedler, Newkirk & Valencia (1976) and by Rasmussen (1977).

We have succeeded in obtaining single crystals of  $Nb_{3+y}Ge_{1-y}$  with  $0.2 \leq y \leq 0.43$ . Crystals  $0.1 \text{ mm}^3$  were obtained by floating zone melting of  $Nb_3Ge$  mixtures (Rasmussen, 1977). Several samples were analyzed by X-ray fluorescence (Vicente & Rasmussen, 1978). The crystals were examined by Weissenberg and precession methods with graphite-monochromated  $Cu K\alpha$  and  $Mo K\alpha$  radiations, respectively. We eliminated contamination of  $\lambda/2$  radiations by running the X-ray tubes at 16 and 34 kV, respectively. Crystals of composition near  $Nb_6Ge$  contained domains of Nb structure as evidenced by reflections extraneous to the A15 structure on Weissenberg photographs, whereas the crystals of  $Nb_5Ge$  and  $Nb_4Ge$  stoichiometry proved to be single phased. Intensities were collected for several crystals with monochromated  $Mo K\alpha$  radiation and automatic diffractometers, one being a computer-steered Supper-type instrument (Kryger, 1975), the other a Picker FACS-I system. One crystal of composition  $Nb_4Ge$  was measured with the Picker diffractometer and  $Ag K\alpha$  radiation. Intensities were in this case measured out to  $\sin \theta/\lambda = 1.6 \text{ \AA}^{-1}$ . Although refinements were carried out on all data sets only the results from the latter measurements are reported here.

The crystal used was irregularly shaped. It can approximately be described as being limited by the planes (001), (110), ( $\bar{3}\bar{3}1$ ) and their centrosymmetric counterparts. The data were corrected for absorption, and symmetry-related reflections averaged. Reflections which deviated by more than three standard deviations from each other were discarded leaving 122 independent reflections for refinement.

The lattice parameter was determined on the four-circle diffractometer. The reflections 880,  $\bar{8}\bar{8}0$  and 088 were measured by Bond's (1960) method. The results were averaged over the three reflections and over the  $\alpha_1$  and  $\alpha_2$  radiations, yielding  $a = 5.1692(8) \text{ \AA}$  [ $\lambda(Ag K\alpha_1) = 0.559363$ ,  $\lambda(K\alpha_2) = 0.563775 \text{ \AA}$ ].

**Discussion.** For the ideal A15 structure,  $A_3B$ , the structure factors\* may for convenience be arranged in the following categories:

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34384 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CHI 2HU, England.

(I)  $h + k + l = 2n + 1$ , with contributions from  $A$  atoms only, and

(II)  $h + k + l = 2n$ , with contributions from  $A$  and  $B$  atoms.

In category (I) the following types of reflections are extinguished:  $h = 2n + 1, k = 2n + 1, l = 2n + 1$ ;  $h = 4n, k = 4n, l = 2n + 1$ ;  $h = 4n + 2, k = 4n + 2, l = 2n + 1$ . The reflections with  $h = 4n + 2, k = 4n, l = 2n + 1$  are generally strong with  $F(hkl) = 4f_A$ .

Category (II) reflections yield the following structure factors:  $F = 2(f_B - f_A)$  for  $h$  and  $k = 2n + 1, l = 4n$  and for  $h$  and  $k = 4n + 2, l = 4n$ ;  $F = 2(f_B + f_A)$  for  $h = k = 2n + 1, l = 4n + 2$ ;  $F = 2f_B \pm 6f_A$  for the rest.

Deviations from the ideal structure may be caused by disorder, by non-stoichiometry or by both. A model assuming random distribution of  $A$  and  $B$  atoms on the 6(c) and 2(a) sites would lead to extinction of reflections of type  $h = k = 2n + 1, l = 4n$ . These reflections were, however, clearly visible on the photographs and easily measurable on the diffractometer, also after off-setting of the goniometer arcs to avoid Renninger effects. Another extreme model we could discard is one which assumes an ordered arrangement of excess Nb atoms on the 2(a) sites and of the Ge atoms. If, for example, the Nb atoms preferentially occupied (0,0,0) and the Ge atoms ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ), reflections with  $h + k + l = 2n + 1$ , which are completely extinguished in the ideal structure, would be measurable. We did in fact observe such reflections both on overexposed precession photographs and from diffractometer measurements. They disappeared, however, from the precession photographs both when the precession angle was changed and at a  $1^\circ$  off-setting of the  $\varphi$  angle. The intensities of those reflections were reduced below threshold when the goniometer arcs were off-set a few degrees to avoid having a crystallographic axis parallel to the  $\varphi$  axis of the diffractometer. Thus these forbidden reflections were caused by multiple diffraction and could be discarded. The structure was refined by a full-matrix least-squares procedure. The scattering factors were from *International Tables for X-ray Crystallography* (1974) appropriately corrected for dispersion. Neutral atoms were assumed.

For an A15-type compound of general composition  $A_{1-\beta}B_\beta$  the Bragg–Williams long-range order is defined by two parameters:

$$S_a = \frac{r_a - (1 - \beta)}{\beta}; \quad S_b = \frac{r_b - \beta}{1 - \beta},$$

where  $r_a$  is the fraction of  $a$  sites occupied by  $A$  atoms and  $r_b$  the fraction of  $b$  sites occupied by  $B$  atoms (Flükiger & Staudenmann, 1976). Cox *et al.* (1976) write these expressions as

$$S_A = 1 - \frac{4x}{3(1-y)}; \quad S_B = 1 - \frac{4(x+y)}{3+y}$$

for a generalized composition  $(A_{3-x}B_x)(B_{1-x-y}A_{x+y})$  where  $x$  is a measure of the order parameter and  $y$  represents the deviation from stoichiometry. The two expressions are identical when  $r_a = 1 - x/3$ ,  $r_b = 1 - (x + y)$ , and  $y = 1 - 4\beta$ . The order parameters are functionally related by  $S_b = [3\beta/(1 - \beta)] S_a$ . Analysis of the X-ray reflections yields one order parameter only, e.g. as a site-occupation factor, and it is therefore not possible to determine both the degree of order and the stoichiometry from the X-ray data alone, unless the scale factor and the Debye–Waller factors can be determined independently.

We refined a site-occupation factor for the  $A$  atoms assuming  $y = 0.25$ ,  $0.20$  and zero. Other parameters refined were anisotropic temperature vibration parameters for the  $A$  atoms, scale factor, an overall temperature factor parameter and an extinction parameter. The site-occupation parameter is highly correlated with the scale factor. It refines to  $1.003$  for  $y = 0.25$  and to  $0.993$  for  $y = 0.20$ . The vibration parameters are also practically the same for the two  $y$  values. The extinction is moderate, as minimum transmission is 75%.  $R$  for both  $y$  values is 3.4% for 122 independent reflections and six parameters. Table 1 shows the parameters obtained for the stoichiometry  $Nb_3Ge_{0.8}Nb_{0.2}$ .

The temperature vibration parameters are physically meaningful considering the high melting point (2273 K) of the compound. The smallest vibration amplitude of the Nb atoms is in the direction of the shortest Nb–Nb

Table 1. Atomic coordinates, thermal parameters ( $\text{\AA}^2$ ) and site-occupation factor of  $Nb_3Ge_{0.8}Nb_{0.2}$

	$x$	$y$	$z$	$U_{11} \times 10^4$	$U_{33} \times 10^4$	Occupation factor
Nb	0	$\frac{1}{3}$	$\frac{1}{4}$	63 (5)	40 (4)	0.993 (6)
Ge	0	0	0	57 (2)		0.80
Nb	0	0	0	57		0.20

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## Neutron Diffraction Study of Sodium Bromide Dihydrate\*

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**Abstract.**  $NaBr \cdot 2H_2O$ , monoclinic,  $P2_1/c$ ,  $a = 6.575(2)$ ,  $b = 10.456(5)$ ,  $c = 6.776(2)$   $\text{\AA}$ ,  $\beta =$

bond as would be expected. The order parameter for the Nb atoms on the  $A$  sites is 1 within experimental uncertainty. The order parameter  $S_B$  is thus 0.75.  $S_B$  does not, however, really measure the kind of ordering of the  $B$  sites which would decrease the cubic symmetry to tetragonal in the case of a complete ordering of the atoms on the  $B$  sites. As mentioned above no indication of partial ordering on the  $B$  sites has been observed. This observation agrees with our results for the ternary compound  $V_6GaSb$  (Rasmussen & Hazell, 1978) which has the A15 structure with V atoms completely occupying the  $A$  sites and with random distribution of Ga and Sb on the  $B$  sites.

Refinements of data from other single-phase samples prepared from floating zone melting of Nb and Ge are essentially in agreement with the results reported here. These data were taken over a more limited range of  $\sin \theta/\lambda$  and not corrected for systematic errors to the same extent as the data taken with Ag  $K\alpha$  radiation.

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### References

- BOND, W. L. (1960). *Acta Cryst.* **13**, 814–818.  
 COX, D. E., MOEHLECKE, S., SWEEDLER, A. R., NEWKIRK, L. R. & VALENCIA, F. A. (1976). *Superconductivity in d- and f-Band Metals*, edited by D. H. DOUGLASS, pp. 461–487. New York: Plenum.  
 FLÜRIGER, R. & STAUDENMANN, J. L. (1976). *J. Less-Common Met.* **50**, 253–273.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 KRYGER, L. (1975). Thesis. Univ. of Aarhus, Denmark.  
 RASMUSSEN, S. E. (1977). *Acta Chem. Scand. Ser. A*, **31**, 79–82.  
 RASMUSSEN, S. E. & HAZELL, R. G. (1978). *Acta Chem. Scand. Ser. A*, **32**, 785–788.  
 VICENTE, V. A. & RASMUSSEN, S. E. (1978). *X-Ray Spectrom.* **7**, 5–8.

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$113.38(2)^\circ$ ,  $Z = 4$ . The structure has been determined from single-crystal neutron diffraction data at 295 K. Each water molecule is tetrahedrally coordinated by two  $Na^+$  ions and two  $Br^-$  ions. The  $O-H \cdots Br^-$  bonds involving  $H_2O(1)$  are similar in