08-Inorganic and Mineralogical Crystallography

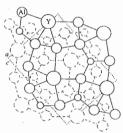
contains one formula unit. The three silver atoms and five yttrium atoms occupy 8(c) positions with x = 0 and the twelve copper atoms occupy 12(d) positions with x = 0.135.

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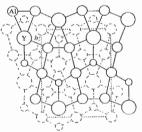
The 3 silver and 5 yttrium atoms have possibly statistic distribution in 8(c). This conjecture was verified by the intensity calculation. The structure consists of eight layers of atoms. Each layer of atoms is of the same kind, (Y and Ag may be included in the same category) and different kinds of atoms of different layers pack alternatively. for copper, each layer has 3 atoms and for yttrium (or silver), 2 atoms. The nearest distances between Cu and Y(or Ag), Y and Ag are 2.87 Å and 3.09 Å respectively. The nearest distances between Cu and Cu are 2.57 Å, which is very near the value (2.56 Å) of the interatomic distances in pure copper.

PS-08.01.11 TWO - LAYER STRUCTURES: COORDINATION AND STOICHIOMETRY. By R.E. Gladyshevskii, K. Cenzual and E. Parthé*, Laboratoire de Cristallographie, Université de Genève, Switzerland.

A large number of inorganic crystal structures with at least one short translation period are built up of two alternating atomic layers where the atoms of each layer are located above and below the centres of the polygons formed by the atoms in the neighbouring layers. Such structures can be decomposed into interpenetrating, centred straight prisms with equatorial mirror plane. For different combinations of elements, different prisms are expected. For a given composition it is then possible to derive the most probable average coordination numbers and individual coordinations of the atoms (Gladyshevskii, R.E., Cenzual, K. & Parthé, E. (1992). J. Solid State Chem. 100. 9-15). Combining interpenetrating prisms, hypothetical atom arrangements may be designed for particular structure families. For example, the hypothetical structure shown below is built up of the same kinds of prism as the known structure of YNiAl₃ (Gladyshevskii, R.E. & Parthé, E. (1992). Acta Cryst. C48, 229-232).

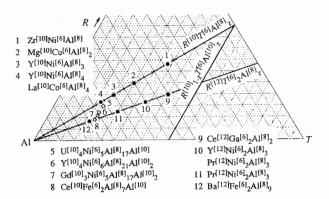


YNiAl₃ oP20, Pnma · c⁵ $a = 8 \ 156$, b = 4.0462, c = 10.638 Å Y[(2,6:2)p] Ni[(2,4)p:0] A[(2,4/5:14/3)]₃



YNiAl₃ hyp. oS20, Cmcm - fc^2a $a \approx 4.05$, $b \approx 10.66$, $c \approx 8.29$ Å Y[(2,8)p:0] Ni[(2,4)p:0] Al[8/3,4/3;4]₃

For ternary rare (alkaline) earth - transition metal - {B, Al, Ga, In} compounds alone some 60 two-layer structure types are known. It can be seen from the diagram below that in aluminides the transition metal atoms preferentially centre trigonal prisms (of composition R_2Al_4 or Al_6) and the rare-earth metal atoms pentagonal or hexagonal prisms. The stoichiometries of compounds where each component centres a particular kind of prism are to be found on straight lines in the ternary diagram (for aluminides $R^{\{10\}}T^{\{6\}}Al^{\{8\}}_z$ and $R^{\{12\}}T^{\{6\}}_2Al^{\{8\}}_z$).



In the corresponding ternary borides larger (heptagonal or octagonal) prisms must also be taken into consideration for the rare-earth metal atoms, whereas trigonal prisms are preferred by the small boron atoms. In gallides and indides the polyhedra around the constituting atoms are similar to those observed for aluminides, but in the case of gallides both gallium and transition metal atoms can be found inside trigonal and larger prisms.

A detailed report of this work will be submitted to J. Alloys Comp.

PS-08.01.12 NOVEL BONDING EFFECTS IN DIAMOND-STRUCTURE CRYSTALS: A HIGH-ACCURACY STUDY OF SILICON, GERMANIUM AND DIAMOND. By M. Deutsch*, Physics Department, Bar-Ilan University, Ramat-Gan 52900, Israel, Z.W. Lu and A. Zunger, National Renewable Energy Laboratory, Golden, CO 80401, U.S.A.

Using multipole expansion formalism and recent high-accuracy x-ray structure factors, a detailed, millielectron level accuracy description of the charge distribution in crystalline silicon, germanium and diamond is obtained.

For silicon (Deutsch, M., Phys. Rev. B, 1992, 45, 646) an 0.5% expansion of the core L shell is detected for the first time, in addition to the known $\sim 6\%$ one of the valence M shell. A non rigid thermal motion of the atom is also found, with the valence charge vibrating with a much smaller amplitude than the core. The postulated anharmonic force constant β is found to be twofold smaller than expected. We obtain an R factor of 0.036%, half of the best previous value. The final goodness-of-fit $GoF\approx 1$, indicates that the model exhausts the accuracy of the measured data. For germanium we find a valence shell expansion of 4.5%, a $\beta>0$ in good agreement with neutron measurements, a clear indication of relativistic effects, and no indications for a non-rigid thermal motion. Here $R{=}0.19\%$ with $GoF\approx 1$. For diamond, where only low accuracy data is available, we find no valence shell expansion, and a qualitatively different bonding charge distribution than that of Si and Ge. Detailed distributions of the total, valence and deformation charge densities obtained from the fits will be presented and discussed.

We also carried out detailed ab-initio calculations, using an accurate implementation of the density functional formalism (Lu, Z.W. and Zunger, A., Acta Cryst. A, 1992, 48, 545; Lu, Z. W., Zunger, A., and Deutsch, M., Phys. Rev. B., in press). Detailed total, valence, and deformation charge density maps were derived for the three crystals. The effects of high-momentum components (currently outside the range of the high-precision measurements) on these maps were also studied. The calculations are found to be in a remarkably good agreement with experiment. In particular, we obtain a 2-5 fold improvement in R over previous calculations for silicon. A comparison of the static valence charge distribution derived from experiment through the multipole expansion model and the ab-initio calculations is shown in Fig. 1, indicating very good agreement for all three crystals. Directions and possibilities for further progress will be discussed.

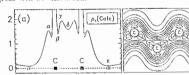


Figure 1. Valence charge density along the bond (left) and the (110) plane (right).