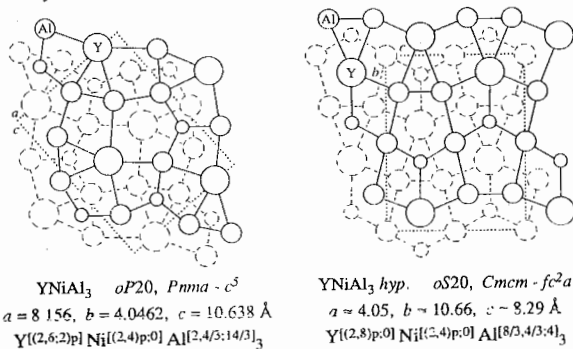contains one formula unit.The three silver atoms and five yttrium atoms occupy 8(c) positions with x = 0 and the twelve copper atoms occupy 12(d) positions with x = 0.135.
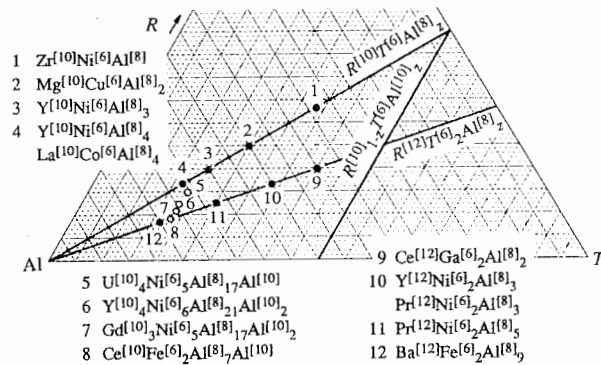
The 3 silver and 5 yttrium atoms have possibly statistic distribution in 8(c).This conjecture was verified by the intensity calculation. The structure consists of eight layers of atoms.Each layer of atoms is of the same kind,(Y and Ag may be included in the same category) and different kinds of atoms 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 YNiAl$_3$ (Gladyshevskii, R.E. & Parthé, E. (1992). *Acta Cryst.* C48, 229-232).



YNiAl$_3$   oP20, Pnma - c$^5$
$a = 8.156$, $b = 4.0462$, $c = 10.638$ Å
Y[(2,6:2)p] Ni[(2,4)p:0] Al[2,4/5:14/3]$_3$

YNiAl$_3$ hyp.   oS20, Cmcm - fc$^2$a
$a \approx 4.05$, $b \approx 10.66$, $c \approx 8.29$ 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 $R^{[12]}T^{[6]}_2Al^{[8]}_z$).



1   Zr[10]Ni[6]Al[8]
2   Mg[10]Cu[6]Al[8]$_2$
3   Y[10]Ni[6]Al[8]$_3$
4   Y[10]Ni[6]Al[8]$_4$
    La[10]Co[6]Al[8]$_4$

5   U[10]$_4$Ni[6]$_5$Al[8]$_{17}$Al[10]
6   Y[10]$_4$Ni[6]$_6$Al[8]$_{21}$Al[10]$_2$
7   Gd[10]$_3$Ni[6]$_5$Al[8]$_{17}$Al[10]$_2$
8   Ce[10]Fe[6]$_2$Al[8]$_7$Al[10]

9    Ce[12]Ga[6]$_2$Al[8]$_2$
10   Y[12]Ni[6]$_2$Al[8]$_3$
     Pr[12]Ni[6]$_2$Al[8]$_3$
11   Pr[12]Ni[6]$_2$Al[8]$_5$
12   Ba[12]Fe[6]$_2$Al[8]$_9$

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 ~ 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 $\beta$ 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. B, 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.
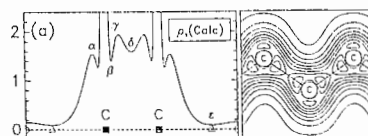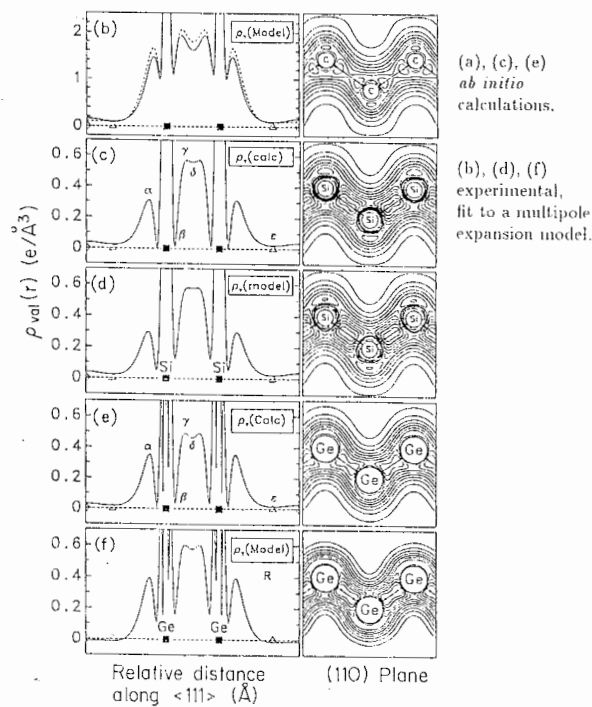


Figure 1. Valence charge density along the bond (left) and the (110) plane (right).

(a), (c), (e)
*ab initio*
calculations.

(b), (d), (f)
experimental,
fit to a multipole
expansion model.

$\rho_{val}(r)$ (e/Å³)

Relative distance
along <111> (Å)

(110) Plane

additional Bi-O bonds complete the coordination [one oxo-oxygen atom with Bi-O = 2.48(2) Å and three oxygen atoms belonging to the arsenate tetrahedra with Bi-O from 2.70(1) Å to 2.94(2) Å. The arsenate tetrahedra are as usual (average $<$As-O$>$ = 1.70 Å). The two oxo-oxygen atoms are coordinated to two Bi and to two Cu atoms (short Cu-O bonds). The hydrogen bond lengths of the water molecule (site symmetry 2) are 2.87(2) Å, the angle $O \cdots O_w \cdots O$ is 70.5(7)°; in addition the $O_w$ atom is coordinated to two Na atoms resulting in a tetrahedral environment.

The compound shows a pronounced layer structure parallel (001) with predominant interconnections parallel [010]: Considering only the nearest neighbour environments, $BiO_3$ units are connected *via* oxo-oxygen atom corners to infinite chains and the $CuO_4$ squares to ribbons parallel [010]. These chains and ribbons share common O-O edges to form layers parallel (001). Including the additional Bi-O bonds into the connection scheme, Bi chains are maintained; in contrast, considering $Cu^{[4+1]}$ and $Cu^{[4+2]}$ coordination results in layers solely formed by the copper coordination polyhedra. The arsenate tetrahedra are branched to these complex layers. The layers are interconnected by the sodium atoms and by the water molecule; $NaO_6$ polyhedra share common edges with neighboured $NaO_6$ polyhedra and $CuO_4$ squares.

Structural work on the isotypic compound $K_2Cu_3Bi_2O_4(AsO_4)_2 \cdot H_2O$ is in progress. This compound was obtained as one of the byproducts from systematic experiments to synthesize the mineral mixite, $BiCu_6(OH)_6(AsO_4)_3 \cdot 3H_2O$, under hydrothermal conditions (*R. Miletich* and *J. Zemann*, Aufschluß 44, 1993, 17-21).

## PS-08.01.13 THE CRYSTAL STRUCTURE OF THE NEW SYNTHETIC COMPOUND $Na_2Cu_3Bi_2O_4(AsO_4)_2 \cdot H_2O$.

By H. Effenberger and R. Miletich, Institut für Mineralogie und Kristallographie, Universität Wien, Vienna, Austria.

Hydrothermal syntheses in the system $Na_2O$-$CuO$-$Bi_2O_3$-$As_2O_5$-$H_2O$ at 503 K in teflon lined stainless steel autoclaves produced dark green crystals of the compound $Na_2Cu_3Bi_2O_4(AsO_4)_2 \cdot H_2O$. They proved to be monoclinic, the space group is C2: $a$ = 9.716(1) Å, $b$ = 5.203(1) Å, $c$ = 13.362(2) Å, $\beta$ = 115.03(1)°. The lamellar crystals are elongated parallel to [010] and flattened parallel (100). The crystal structure was investigated from single crystal X-ray data: STOE four-circle diffractometer, graphite monochromatized MoKα radiation, $2\vartheta \leq 60°$, peak scan width 0.78° in $2\vartheta/\omega$ mode, scan speed 0.015 to 0.030° per second. 3585 reflections ($\pm h \pm k \pm l$) have been measured, after averaging ($R_i$ = 0.031) a unique data set of 1787 reflections was obtained, 1683 with $F_o \geq 3\sigma_F$ (Friedel pairs were kept separated due to perceptible anomal dispersion effects). The structure was solved from a Patterson map and from subsequent Fourier summations. The refinement yielded R = 0.037 and wR = 0.038, w = $0.720/\sigma_F^2$ (program SHELX-76).

The sodium atom has six ligands with 2.28(1) Å $\leq$ Na-O $\leq$ 2.96(1) Å in an distorted octahedral coordination. The two Cu atoms (site symmetries 2 and 1) are [4+2] and [4+1] coordinated forming a tetragonal dipyramid and a tetragonal pyramid, respectively [short Cu-O from 1.92(1) Å to 1.98(2) Å, additional bonds 2.49(1) Å and 2.51(1) Å]. The Bi atom has three short Bi-O bonds to oxo-oxygen atoms [2.18(1) Å to 2.21(1) Å] forming a trigonal pyramid; four

## PS-08.01.14 A CRYSTAL STRUCTURE OF $Di$-$\mu_4$-(carbonato-O,O,O',O')-tetrakis[diammineplatinum(II)] Nitrate Trihydrate.

By Shih-Chi Chang[*a], J. R. Ruble[c], H. K. Mahtani[b], P. B. Stein[b], [a]Department of Physics, [b]Department of Chemistry, Duquesne University, Pittsburgh, PA 15282 ; [c]Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260.

We report on a minority product identified during an investigation of "platinum 2'-deoxyuridine blue". Cis-diamminediaquaplatinum(II) was allowed to react with 2'-deoxyuridine for several hours at -40°C under aerobic conditions, addition of $NaNO_3$ and incubation at ~0°C.

Most crystals from the above reaction are blue and appear as dendritic aggregates of thin flakes. The crystallinity is of poor quality and unsuitable for X-ray diffraction work. However, a few thin colorless transparent plates with dimensions about 0.2x0.15x0.04mm were observed and selected for study. The crystallographic data is summarized as: a=11.324 b=12.151 c=10.926 α=103.792 β=111.266 γ=75.845 space group=P1 Z=2 R=0.039 $R_w$=0.041. The ORTEP drawing shows the $[Pt_4(NH_3)_8(\mu_4$-$CO_3)_2]^{4+}$ cation with nearly $D_{2d}$ point symmetry and a square arrangement of the four Pt atoms. The absence of 2'-deoxyuridine and



the occurrence of carbonate coordination is noted. Carbonate ions, which are picked up from the air as $CO_2$, are known to be present in similar reactions (Lippert B., J. Clin. Hemat. Oncol. 7, 26-50). This is the first reported crystal structure of $\mu_4$-$CO_3$ coordination with Pt(II) metal species. It is also the first example of a L2,M4 carbonato complex.