

08-Inorganic and Mineralogical Crystallography

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MS-08.01.08

THE RELATIONSHIP BETWEEN CRYSTAL STRUCTURE AND PHYSICAL PROPERTIES IN INORGANIC CRYSTALS

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There is an increasing search for new crystalline materials for many applications. Therefore, the understanding of the relationship between crystal structure and physical properties is becoming ever more relevant, particularly because it forms the scientific foundation for the prediction of the new technologically-important crystals of the future.

In this talk, a review will be given of the relationship between physical properties and crystal structure. We will consider how analysis of crystal structure can be of benefit to materials research and technology and, therefore, how the crystallographer can also benefit from this relationship. The major emphasis will be placed on non-centrosymmetric crystal structures and the relation of these with polar or chiral physical properties such as the piezoelectric and electrooptic effects or optical rotation, but we will also consider the much-neglected relationship between structure and simple linear properties such as refractive index. Some examples of this from our own research on crystals of the potassium titanyl phosphate, KTiOPO_4 , family of nonlinear optical crystals will be given; for example, the questions of how useful lasing ions can be introduced into KTiOPO_4 itself and how the isostructural analogue KTiOAsO_4 can be modified so that it is useful for second-harmonic generation.

Further to the straight-forward relationship between structure and naturally-occurring physical properties in crystals, it is important to recognize the current emphasis on the modification of well-characterised and established crystals. These modifications produce subtly-altered materials that have been perfected for a given function. This has long been the case in the area of semiconductor research but these ideas are now spreading in an analogous way into the realms of optical materials and dielectrics. In particular, we shall discuss the phenomenon of periodic domain inversion in polar crystals and also address the growing phenomenon of composite materials that are designed to incorporate the desirable features of more than one component; for example, inorganic-organic composites for nonlinear optical and photoelectric applications will be described.

PS-08.01.09 THE ROLE OF LONE PAIR ELECTRONS IN THE BOND-VALENCE APPROACH FOR Sb(III)-CHALCOGEN COMPOUNDS. By X. Wang* and F. Liebau, Mineralogisches Institut der Universität Kiel, Germany.

One of the basic assumptions of the bond-valence model is the valence sum rule: $V_i = \sum s_{ij}$ (1). Here, V_i is the atomic valence of atom i and s_{ij} refers to the bond valences of the chemical bonds around atom i . The bond valence s_{ij} is assumed to be a monotonic function of bond length d_{ij} and can be approximated by the empirical equation $s_{ij} = \exp[(r_0 - d_{ij})/B]$ (2), where r_0 and B are bond valence parameters and can be calculated from (1) and (2) (Brown, I.D. 1992, Acta Cryst. B48, 553-572). Assuming that V_i is equal to the formal valence (oxidation number), Brown and Altermatt (1985, Acta Cryst. B41, 244-247) found that for most bonds, B can be set equal to 0.37 Å. They tabulated r_0 for most of the common bonds. These r_0 are widely used and usually considered as constants.

According to Brown (1992), in most cases, structures in which the bonding is distorted by electronic effects, as through the presence of lone pair electrons, do not violate the valence sum rule. However, during studies of Sb(III)-chalcogen compounds we found that for some accurately determined $[\text{Sb(III)}\text{S}_n]$ groups the sums of bond valences of the bonds around Sb(III) calculated from (2) are much higher than 3 (the formal valence of Sb), if the bond valence parameters of Brown and Altermatt (1985) are used. Further studies disclosed that for those $[\text{Sb(III)}\text{X}_n]$ groups with $\text{X}=\text{S}, \text{Se}$, which can be considered as $[\text{SbX}_3\text{E}]$ tetrahedra ($\text{E}=\text{electron lone pair}$) complemented by 0 to 4 additional X ions with weaker Sb-X bonds, the calculated individual r_0 values are inversely correlated with the average of the X-Sb-X angles of the $[\text{SbX}_3\text{E}]$ tetrahedra (Fig. 1) rather than being constant. Since so calculated r_0 is equal to the average bond length in a $[\text{SbX}_3]^{3-}$ symmetrical trigonal pyramid, the fact that the solid squares representing the X-Sb-X bond angles and Sb-X bond lengths (with bond valence 1.25 v.u.) of the symmetrical $[\text{Sb(V)}\text{X}_4]^{3-}$ tetrahedra fall on the correlation trends in Fig. 1, indicates that the effective valence of Sb of the $[\text{SbX}_3]^{3-}$ pyramids approaches $1.25 \times 3 = 3.75$ v.u. as the average X-Sb-X angle increases. Therefore, if we treat Sb(III) in $[\text{SbX}_3]^{3-}$ pyramids as $[\text{Sb(V)E}]$ and E as an anion, then Sb(V)-E has a "bond" valence between 2 and 1.25 v.u. depending on the X-Sb-X angles, which might be considered as a measure of sp^3 hybridization.

A publication on semi-quantitative calculation of effective valences of Sb(III) in chalcogenides is in preparation.

Support from the DFG is gratefully acknowledged.

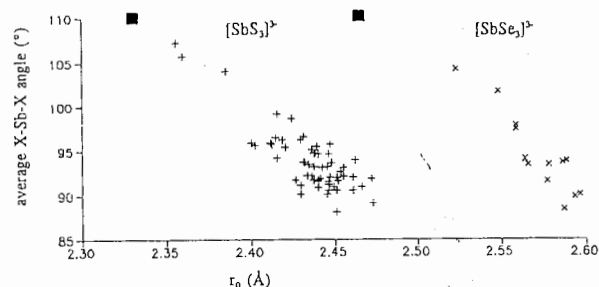


Fig.1 Correlation between r_0 and average X-Sb-X angles of $[\text{SbX}_3]^{3-}$ pyramids. For $[\text{Sb(V)}\text{X}_4]^{3-}$ tetrahedra the average experimental Sb-X bond lengths are plotted instead of r_0 and are represented by solid squares.

PS-08.01.10 THE CRYSTAL STRUCTURE OF $\text{Ag}_3\text{Cu}_{12}\text{Y}_5$, A NEW TERNARY COMPOUND. By L.M. Zeng*, D.X. Li and Y.H. Zhuang, Department of Physics, Guangxi University, Nanning 530004, China.

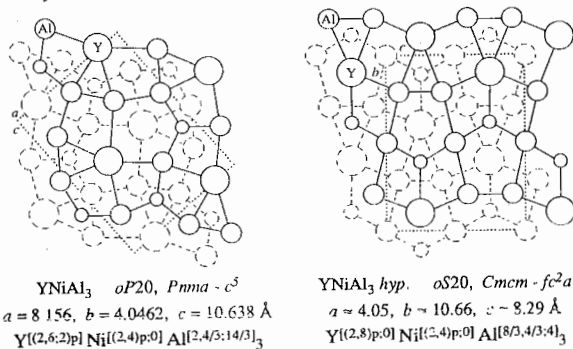
A new ternary compound has been found in our recent investigation of the 500°C isothermal section of Ag-Cu-Y system. The new phase, which is $\text{Ag}_3\text{Cu}_{12}\text{Y}_5$, has a limited solid solubility. The compositional range is 23-27at.% Y, 9-19at.% Ag and 68-54at.% Cu. The structure of the compound $\text{Ag}_3\text{Cu}_{12}\text{Y}_5$ was determined by X-ray powder diffraction data (Cu K α radiation, $\lambda = 1.54178$ Å). The new phase has a cubic structure of $\beta\text{-Mn}$ (A13) type with $a = 7.127(4)$ Å at 25°C. The space group is $\text{O}^7\text{-P4}_32$ with $V = 362.0(7)$ Å³, $D_x = 7.02$ gcm⁻³. Each unit cell

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 $x = 0.135$.

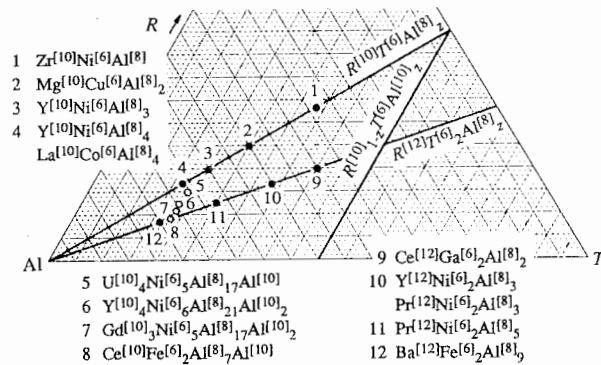
The 3 silver and 5 yttrium atoms have possibly statistic distribution in 8(c). This conjecture was verified by the intensity calculation. The structure consists of eight layers of atoms. Each layer of atoms is of the same kind, (Y and Ag may be included in the same category) and different kinds of atoms 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).



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 $R^{(10)7}Al^{(8)}_2$ and $R^{(12)7}Al^{(8)}_2$).



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 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.

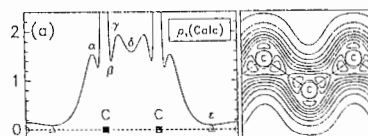


Figure 1. Valence charge density along the bond (left) and the (110) plane (right).