

**08.1-13** PECULIARITIES OF THE STRUCTURE OF RARE EARTH INTERMETALLIC COMPOUNDS. By O.I. Bodak and E.I. Hladyshevsky, Chair of Inorganic Chemistry, Lvov State University, Lvov, USSR.

The known binary and ternary compounds with rare earths crystallize in 190 structure types (ST) and are connected by different relationships. They are systematized on the basis of common signs in related types and on the basis of possible structure transformations. 68 ST can be formed from 2- or 3-layer close packed structure types by various transformations; 56 are related in various ways to  $A_2B_2$  or contain its fragments. Relationships with binary ST are established for 51 of 78 ternary ones. The 20 derivative ternary superstructures are formed as a result of atomic ordering; 27 ternary ST are hybrids of more simple types; four are derived from binary by deformation, by partial substitution or by atomic/atomic-group redistribution. The crystal structures of 27 types were determined by us.

**08.1-14** POLYHEDRAL ATOMIC VOLUMES, VALENCE AND COORDINATION NUMBERS FOR THE EUROPIUM ARSENIDES. By F.L. Carter, Chem. Div., Naval Research Laboratory, Wash., D.C. 20375 and L.D. Calvert, Chem. Div., National Research Council of Canada, Ottawa, Canada.

The Polyhedral Atomic Volumes (PAVs), coordination numbers, and partial coordination number coefficients (PCNC) have been calculated (F.L. Carter, Acta Cryst. (1978) B34, 2962) for  $\text{Eu}_5\text{As}_3$ ,  $\text{Eu}_4\text{As}_3$ ,  $\text{Eu}_5\text{As}_4$ ,  $\text{Eu}_2\text{As}_2$ ,  $\text{Eu}_3\text{As}_4$ ,  $\text{Eu}_2\text{As}_3$  and  $\text{EuAs}_3$  as well as for  $\text{Eu}_4\text{As}_2\text{O}$  and  $\text{Eu}_3\text{As}_3\text{TaO}$ , all of whose structures have recently been accurately determined. Valences for these compounds were calculated via Pauling's metallic radii. These new data are used as a solid basis for sorting out the crystal chemistry and valence roles of both Eu and As. Europium in the pure arsenides is primarily divalent although we note some tendency toward trivalency. While the elemental volumes for Eu and As are 48.1 and 21.5  $\text{\AA}^3$  respectively in none of the above compounds are these volumes approached by either element. Thus Eu PAVs range from 35.1 to 42.5  $\text{\AA}^3$  while As PAVs vary from 15.7 to 19.7  $\text{\AA}^3$ . These PAVs are conveniently plotted using the PCNC which measure the relative importance of numbers and kinds of neighbors. Thus the importance of the As-As interaction as measured by PCNC for the above PAVs increase from <0.01 to 0.69. Europium trivalency is clearly seen in the  $\text{Eu}_4\text{As}_3$  structure (anti- $\text{Th}_3\text{P}_4$  type) where considerable d character is employed in Eu bonding. Assuming a covalent oxygen radius in  $\text{Eu}_4\text{As}_2\text{O}$  the PAVs of Eu1 and Eu2 are strikingly different, i.e., 31.1 and 41.8  $\text{\AA}^3$  respectively. This suggests that Eu has trivalent character; this could be tested via ESCA studies. The effect of the oxygen ionicity on the PAVs in  $\text{Eu}_4\text{As}_2\text{O}$  and  $\text{Eu}_3\text{As}_3\text{TaO}$  will be discussed at the conference.

**08.1-15** DEFINITIONS AND USE FOR COORDINATION NUMBERS AND POLYHEDRAL ATOMIC VOLUMES. By F. L. Carter and D. Weber, Chemistry Division, Naval Research Laboratory, Washington, DC 20375

The concept of coordination number CN is central to most discussions of crystal chemistry systematics, however only recently has this concept been mathematically generalized (F. L. Carter, Acta Cryst. (1978) B34, 2962). This generalization adds to the flexibility of the concept, perhaps to an undesired extent. Thus one may define coordination numbers based on bond energies, bond orders, overlap integrals, as well as geometrical quantities such as solid angles. This paper compares various coordination number definitions with each other, including those of G. O. Brunner (Acta Cryst. (1977) A33, 226), and M. O'Keeffe (Acta Cryst. (1979) A35, 772). In addition the definition of atomic volume is considered as an extension of the Wigner-Seitz or Voronoi cell. Four methods of calculating polyhedral atomic volumes for structures of different sized atoms are now in use and will be compared; these include the radical plane dissection of W. Fischer, E. Koch, and E. Hellner (N. Jb. Miner. Mh., 1971, 227).

Finally the usefulness of this author's version of CN and the related concepts of partial CN and partial coordination number coefficient, which provides a numerical estimate of the relative importance of various neighbor interactions, is illustrated with examples. These include a determination of valence states for rare earths in some complex 'Vernier' halides, the effective charges of sulfur in nitrogen and phosphorous compounds, and the dramatic volume contraction of the rare earth intermetallics with first row transition elements.

**08.1-16** NEW PHASES IN THE Li-Ge-SYSTEM:  $\text{Li}_7\text{Ge}_{12}$ ,  $\text{Li}_{12}\text{Ge}_7$ ,  $\text{Li}_{14}\text{Ge}_6$ . By A. Grüttner, R. Nesper and H.G.v.Schnering, Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany.

A new investigation of the Li-Si-System (1) established, in contrast to former investigations, four well defined phases:  $\text{Li}_{12}\text{Si}_7$  (2),  $\text{Li}_{14}\text{Si}_6$  (1),  $\text{Li}_{13}\text{Si}_4$  and  $\text{Li}_{20}\text{Si}_5$ .  $\text{Li}_{20}\text{Si}_5$  replaces  $\text{Li}_{22}\text{Si}_5$  (3) (F4 3 m; four special Li positions of the " $\text{Li}_{22}\text{Si}_5$ " structure are not occupied). These results initialized the re-investigation of the system Li-Ge. The existence of  $\text{LiGe}$ ,  $\text{Li}_9\text{Ge}_4$  and  $\text{Li}_{15}\text{Ge}_4$  is confirmed,  $\text{Li}_{20}\text{Ge}_5$  probably too. Additionally the phase diagram is characterized by 3 new compounds  $\text{Li}_7\text{Ge}_{12}$ ,  $\text{Li}_{12}\text{Ge}_7$  and  $\text{Li}_{14}\text{Ge}_6$ .  $\text{Li}_{12}\text{Ge}_7$  and  $\text{Li}_{14}\text{Ge}_6$  are isotypic with the corresponding Si-compounds.  $\text{Li}_7\text{Ge}_{12}$  is a completely new type structure. It crystallizes with well sharpened platelets of metallic luster. The sample is sensitive to air and humidity and has to be handled under inert conditions. It melts at 290 K incongruently.  $\text{Li}_7\text{Ge}_{12}$  crystallizes as orthorhombic with  $a=15.418 \text{ \AA}$ ,  $b=11.583 \text{ \AA}$  and  $c=8.055 \text{ \AA}$ . It is characterized by two dimensional Germanium layers,  $\text{Ge}_{12}^{7-}$  inbetween the Li-cations are intercalated.  $\text{Li}_7\text{Ge}_{12}$  is a diamagnetic semiconductor and belongs to the Zintl-phases.

- 1) H.G.v.Schnering, R.Nesper, K-F.Tebbe, J.Curda Z.f.Metallkde, 71, 357 (1980)
- 2) H.G.v.Schnering, R.Nesper, J.Curda, K-F.Tebbe Angew.Chemie, Int.Ed. 19, 1033 (1980)
- 3) To be published.