

08.1-13 FACTORS WHICH INFLUENCE THE STRUCTURE OF INTERMETALLIC COMPOUNDS. By K. Girgis, Inst. f. Krist. u. Petrgr. ETHZ, Zürich, Switzerland.

1. Thermodynamic Factors:

Rajasekharan & Girgis (Phys. Rev. (1983) B27, 909) show that, notwithstanding the isotropic nature of Miedema's semiempirical theory for the heat of formation ΔH of intermetallic compounds, and contrary to the present view in literature, the parameters Φ^* , n_{WS} used to predict the sign of ΔH , can contribute quantitatively to our understanding of structural phenomena. We found that the structure of an intermetallic compound is dependent on its heat of formation. A clear separation on a map using these two factors is achieved between $MgCu_2$ and $SiCr_3$ structure types. The total exclusion of $SiCr_3$ -type phases from the 250 binary systems in which Laves phases occur and that of Laves phases from the 87 binary systems with $SiCr_3$ -type phases will be represented. Different examples will be shown.

2. Geometrical Factors:

2.1. Atomic radii and atomic volumes

The interatomic distance, d_{AB} , designates the shortest distance between atom A and atom B, which depends on all lattice constants. The concentration weighted mean atomic radius, R , is equal to $(m.R_A + n.R_B)/(m+n)$ for the compound $A_m B_n$, where one takes always $m \leq n$. Very high correlation factors have been found, e.g., 37 structure types exhibit correlation factors in the range 0.99 to 1.00.

A similar correlation has been found between the volume of the unit cell V_{uc} , and the concentration

weighted mean atomic volume, \bar{V} , which is defined by $\bar{V} = (m.V_A + n.V_B)/(m+n)$ for an $A_m B_n$ compound where V_A and V_B are the atomic volumes of elements A and B respectively.

2.2. Space Filling Factor:

The ratios c/a , b/a and the generalized space filling factor are found to be in narrow ranges for all representatives of a structure type. In certain cases of pronounced scatter of axial ratios, the structure family may be subdivided. The space filling range for Si_3W_5 type is 0.75 to 0.76. The mean space filling of 700 compounds of different structure types is 0.74 ± 0.04 ; (0.74 for ccp or hcp). This demonstrates the close packing in the structure of intermetallic compounds. (Villars & Girgis, Z. Metallk. (1982) 73, 455).

3. Electron Configuration:

There is a correlation between the position of an element in the periodic table (s-, p-, d-, f-element) and its equipoint position in the structure; e.g. in the case of Si_3W_5 type (I4/mmm) the point positions 4a and 8h are occupied by the p-elements, while the 4b and 16k are occupied by d- or f-elements. The ratio of p- to d-(f-) elements is always 3:5 and never 5:3.

4. Electronegativity:

It has been found that the electronegativity difference in intermetallic compounds is smaller than 0.8. Examples showing this effect in correlation with other factors will be represented.

08.1-14 SYMMETRY GROUPS IN STRUCTURE TYPE ASSIGNMENT AND CLASSIFICATION. By M. O. Figueiredo, Centro de Cristalografia e Mineralogia, I.I.C.T., Alameda Afonso Henriques, 41 - 4^a E, 1000 Lisboa, Portugal.

Any crystal structure must conform with one of the 230 three-dimensional, three-periodic space groups, which will characterize its real, crystallographic symmetry. However, space-group symmetry alone is not enough to discriminate the crystal-structure type (STP). Further improvements in STP assignment and classification should be attained by considering i) non-crystallographic symmetry operations, ii) coloured symmetry groups, and iii) symmetry groups with continuous dimensions (G_n^t , where t stands for the translations, or dimensions remaining periodic, in a n -dimensional space). The geometry and dimensionality of the structural units (Lima-de-Faria & Figueiredo, J. Solid St. Chem. (1976) 16, 7) could be appropriately specified, and important structural processes - like the condensation of groups, chains, sheets and frameworks out of the corresponding isopoint (same space group) atomic arrays, and the polymerization of groups into chains and/or sheets up to frameworks - would become apparent. As illustrative examples, two low-symmetry space groups ($C2/m$ and $C2/c$) are examined in connection with four representative types of silicate structures: pyroxenes/amphiboles, micas and feldspars/coesite.

08.1-15 POLYMERIZATION OF ANIONS IN ANHYDROUS BORATES. N.I. Leonyuk, Department of Geology, Moscow State University, Moscow, USSR.

Polyborates account for over 35% of all the anhydrous borates studied structurally. More than 50 varieties of polyanions are known. In polyanions, BO_3 -triangles and BO_4 -tetrahedra form relatively compact groupings that take, usually, the shape of single and double rings. Polymerization trends characterized by the n_B/n_O ratio have been analysed depending on the value of $N = N_{M_x O_y} : N_{B_2 O_3}$, the size of M-cation and its charge. With decreasing N-criterion, the n_B/n_O ratio increases and anions get more polymerized: isolated BO_3 - and BO_4 -anions are replaced with pyrogroups, then with chain- or circular-type polyanions and, ultimately, with laminar and framework ones. As the N-factor goes down, the share of BO_4 -tetrahedra at first grows and then diminishes. More often their maximum number equal to that of triangles is recorded when $N=1/2$. Larger size of cations contributes to the polymerization as well, if less noticeably. On the other hand, growth of their charges brings about a counter-effect. Similarly to crystals, melts and glasses are also characterized by more intensive polymerization as $B_2 O_3$ concentration rises. As polymerization intensifies and the number of "free" bonds are, therefore, reduced, the interaction between the anionic motives and cations becomes weaker.