

08.1-1 ELECTRON TRANSITIONS, LEADING TO POLYMORPHIC TRANSITIONS. NEW CLASSIFICATION OF POLYMORPHIC TRANSITIONS BASED ON ELECTRON ENERGY CHANGES OF THE ATOMS OR IONS OF THE CRYSTAL. By Y. Shopov, dep. of Atomic Physics, Physical faculty, University of Sofia, Sofia, Bulgaria.

A dependence between the electron configuration of each of the composing atoms or ions and the crystal lattice parameters has been found. It is of the form:

$$a, b \text{ or } c = f(1/|Z_e - K|) = f(1/|\Psi_e|^2)$$

where Z_e - electron effective charge (after Slater) of the atom at the outmost electron level, K - electron interaction constant, specific for each atom or ion, $|\Psi_e|^2$ - electron density at the atomic nucleus.

This dependence agrees with experimental data for electron configurations and crystal structures of polymorphic modification and its transitions.

The obtained dependence leads to the following law of polymorphic structures: - Each electron transition into a new basic stable electron configuration leads to a polymorphic transition. The reverse is not always true.

A new approach to the polymorphic transitions investigation is suggested. It permits the prediction of new polymorphic forms and establishes the conditions for their existence from the possible electron configurations of the crystal composing atoms or ions. A new polymorphic transitions classification system revealing transitions causes is offered on the base of discovered law.

08.1-2 CRYSTAL CHEMISTRY OF OXYGEN COORDINATED Cu^{2+} . By W. Eysel, K.-H. Breuer and U. Lambert, Mineralogisch-Petrographisches Institut der Universität, Im Neuenheimer Feld 236, D-6900 Heidelberg 1, Germany.

The crystal chemistry of oxygen coordinated Cu^{2+} (including also OH^- and H_2O as ligands) is discussed with particular emphasis on silicates and germanates. For Cu^{2+} various coordination polyhedra are known: Elongated octahedron CuO_{4+2} , steep tetragonal pyramid CuO_{4+1} , square CuO_4 , tetrahedron CuO_4 and elongated trigonal bipyramid CuO_{3+2} . Type, shape and distortions of these polyhedra are caused by both, the Jahn-Teller effect and the accompanying atoms.

Due to the special bonding requirements of Cu^{2+} many structures are unique without possibilities of Cu-substitution. Thus CuGeO_3 (Völlenknecht et al., Mh. Chem. 98, 1352, 1967) is the only structure with einer-Einfachkette among silicates and germanates. If known crystal structures are hosts for Cu^{2+} , they are usually distorted, e.g. the spinel type (Reinen, Struct. Bond. 7, 114, 1970) and the extremely deformed pyroxene $\text{CaCuGe}_2\text{O}_6$ (Breuer et al., ECM-8, Liège 1983).

For the most frequent elongated octahedron, the variation of shape and size will be demonstrated using 30 well refined structures. The copper "ion" is characterized as a rotational ellipsoid with varying dimensions.

08.1-3 EMPIRICAL BOND LENGTH RELATIONS FOR OXYGEN COMPOUNDS

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In oxides of many elements, irrespective of their oxidation state, bond lengths are correlated empirically with bond valences (M. Trömel, Z. Krist. (1983) 162, 224; Acta Cryst. (1983) B39, 664). Relations of this kind apply not only to crystalline compounds, but also to molecules in the gas phase.

The C(IV)-O bond-length-bond-strength parameters (I. D. Brown, K. K. Wu, Acta Cryst. (1976) B32, 1957) apply well to all oxidation states of inorganic carbon. Bond lengths in most organic compounds, however, are significantly longer.

Considerably longer bonds than expected are found in several unstable molecules (PO , S_2O_2 , SO , ClO) which are known from spectroscopic investigations only. The exceptionally long Cl-O bond in ClO_2 may be due to a similar effect.

Secondary bonding (N. W. Alcock, Adv. Inorg. Chem. Radiochem. (1972) 15, 1) is of importance in oxygen coordination around heavy main group elements in lower oxidation states, e.g. Te(IV), I(III), or I(V). For these arrangements, which are regarded as 'open' coordinations, rather long bonds have to be taken into account. For $s = (R_1/R)^N$ (where s = bond valence and R = atomic distance), the following parameters were obtained by preliminary evaluations, including distances $\leq 4 \text{ \AA}$:

	Te	I	Xe
$R_1 (\text{Å})$	1.93	1.95	1.94
N	4.9	5.1	6.2

08.1-4 THE MOST POPULOUS OF ALL STRUCTURE TYPES - THE BaAl_4 STRUCTURE. W. B. Pearson, Dept. Physics, University of Waterloo, Waterloo, Ont. Canada, N2L 3G1.

The BaAl_4 (ThCu_2Si_2) t110 structure MN_2X_2 ($a = 4.566$, $c = 11.278 \text{ \AA}$, $I4/mmm$, $M 2(a) 000; N 4(d) 00z; X 4(e) 00z$; z ideal = 0.375) appears to be the most populous of all structure types, since some 400 phases are reported therewith. In addition several "splitted" varieties derived from BaAl_4 are known, although there are no known derivatives where Ba is replaced by a dumbbell of atoms as in the CaCu_5 structure. Eight different groups of phases can be discerned depending on whether the most important interatomic distances are shorter or longer than the appropriate radius sums. However only two significantly different structural arrangements emerge: those in which the [001] X-X dumbbell distances are shorter than D_X (for CN 12) and the lesser group of phases in which they are longer by anything up to 2 \AA . Here we consider only the major group of phases with [001] X-X dumbbells.

z values have been determined for 140 phases. These show that the N-X distances are remarkably constant relative to the appropriate radius sums (also to a slightly lesser extent are the [001] X-X distances), despite the great variety of axial ratios and diameters of the component atoms that range from 3.18 to 5.09 \AA for M, 1.76 to 3.33 \AA for N and 1.96 to 3.60 \AA for X.

Looking at 10 almost complete series of MN_2X_2 phases with M = rare earth, N = Mn, Fe, Co, Ni, Cu and X = Si, Ge, and for each changing M while keeping N and X constant, we find (where d_{i-j} is the calculated interatomic distance between the i and j components):

- i) $R_M + R_N - d_{M-N}$ = constant for the Mn phases of Si and Ge
- ii) $R_M + R_X - d_{M-X}$ = constant for the Fe, Co, Ni and Cu phases of Si and Ge

iii) $R_N - R_X - d_{N-X}$ values for all N and X phases lie in a very narrow band, but with different slopes versus D_M : these averaging -0.46 for Mn, -0.38 for Co and -0.35 for Fe, Ni and Cu phases.

These results indicate that the relative cell dimensions are controlled by M-N or M-X contacts within the di-capped hexagon tetragonal prism about M (Fig. 1) as the M component is changed, whereas the overall size of a and c are such as to best satisfy the N-X distances (for CN 5) of the square pyramid framework (Fig. 2) (and to a lesser extent the [001] X-X dumbbell distances), this framework being the basis of the structure's stability. In addition, a and c are not independently variable in that they must provide an equitable unit-cell volume.

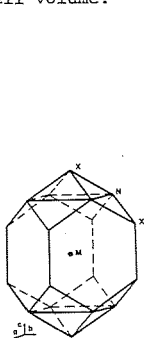
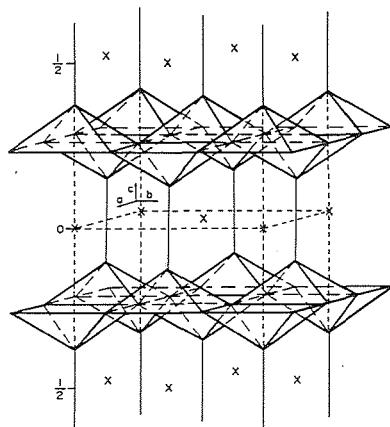


Fig. 1

Fig. 2 b.. 00% $P_{222} [5py_{4e}] + F$ framework.

08.1-5 TOWARDS A GRAMMAR OF INORGANIC STRUCTURE. By Alan L. MACKAY, Dept. of Crystallography, Birkbeck College, London and Jacek KLINOWSKI, Dept of Physical Chemistry, University of Cambridge.

Pauling's Rules are only the first level of a hierarchic grammar of structure. The rules have been very successful for describing the immediate surroundings of atoms, especially if they are symmetrical, but they are less useful for handling large-scale structures, where cooperative movement may occur and large blocks, approaching crystallites in size, adjust themselves into position like colloidal crystals under electrostatic forces. HRTEM, SEM and XRD have recently provided information on "syntax" - these higher levels of structure. It is shown that hierarchisation minimises complexity and increases probability of formation. Complex silicates and lyotropic structures both parallel minimal surfaces (and can be modelled as membranes rather than lines of force). The concept of curved sheets can be extended in dimensionality to the distortion of polyhedra, leading to explanations of Loewenstein's Rule and such orderings in silicates, now being revealed by NMR. Through Delone's formalism, it becomes possible to treat ordered and disordered structures similarly. Also transformations of sheets to frameworks (such as kaolin to ultramarine) can be expressed in catastrophe theory terms.

08.1-6 COMPLEX TRANSITION METAL BORATES By H. Behm, Institut für Kristallographie, Universität Karlsruhe, D-7500 Karlsruhe, Germany. In the course of a systematic investigation of transition metal borates various chelate-complexes were synthesized. The crystal structures of several of these compounds have been completely determined; in other cases at least the complex borate anions could be identified. These chelates represent a novel type of borate which were not considered in former systematic classifications. The most important features of these complex borates are presented here and are discussed with the intention of predicting further hypothetical complex ions.

1. Borates can build up mono- or polynuclear chelates with transition metals.
2. Size, shape and topology of the borate molecules are fundamentally influenced by the coordination number and coordination polyhedron of the transition metal ion.
3. In mononuclear complexes the nuclei are coordinated to oxygen atoms which are either bonded to two boron atoms or to one boron atom and one hydrogen atom, but never to terminal oxygen atoms. In polynuclear complexes the bridging ligands are terminal oxygen atoms or oxide ions.
4. Additional coordinations may occur to ligands not belonging to the borate complex.
5. A satisfactory charge balance, as required by Pauling's rules, can be obtained by using the following charges for the ligand atoms: $O^{2-} = -2$, $\text{>B-O} = -1$, $\text{=B-O} = -1/2$, $\text{>B-O} = -1/4$ and $\text{>B-OH} = -1/4$.
6. Ring-like complexes must contain at least eight boron atoms.

Examples of ring-like mono-, di- and tetra-nuclear chelates are found in the compounds:
 a) $K_6[UO_2(B_{16}O_{24}(OH)_8)] \cdot 12H_2O$ (in press)
 b) $Na_6[Cu_2(B_{16}O_{24}(OH)_{10})] \cdot 12H_2O$ (A.C.1983,C39)
 c) $Na_5Cu_{0.5}[Cu_4O(B_{20}O_{32}(OH)_8)] \cdot 26H_2O$ (in press)
 These ring-like complexes can be regarded as being derived from a simple cyclic B_8O_8 unit. Neighbouring tetrahedral boron atoms may be connected by additional BO_3 groups. In the polynuclear chelates the B_8O_8 unit may be widened by insertion of BO_2 units. With this method new hypothetical complex anions can be generated. The stability of such complexes must then be checked by experiment.

