

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
$R_1 (\text{\AA})$	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 ($a = 4.566$, $c = 11.278 \text{ \AA}$, $I4/mmm$, $M 2(a) 000; N 4(d) 0\frac{1}{2}; X 4(e) 00z$; 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