

Inorganic and Mineral Compounds

MS08.00.01 SYSTEMATIC CRYSTAL CHEMISTRY VIA CRITICAL NETS ON ORBIFOLDS. Carroll K. Johnson, Michael N. Burnett, Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6197, USA.

Our Crystallographic Orbifold Atlas illustrates space-group topology by showing asymmetric units of space groups wrapped up to form closed spaces, called Euclidean 3-orbifolds, which have singular sets corresponding to the Wyckoff sites. The "Gaussian density" for a crystal structure, based on overlapping Gaussian density functions centered on atomic sites, has a critical-net representation with critical points joined by density gradient-flow separatrices. Crystal-structure critical nets, wrapped into the corresponding space-group orbifolds, form "Crystal Orbifold Morse Functions (COMFs)" with the singular set of the space group acting as a template for the critical net. COMFs provides a new approach for classifying both crystal structures and space groups.

For simple crystal structures, each component of the critical net, which includes (a) peaks, (b) passes, (c) pales, and (d) pits, as well as (ab), (bc), and (cd) separatrices, plus the (da) steepest gradient paths, corresponds to a classical crystallographic lattice complex. This geometric arrangement of lattice complexes provides the global characteristics needed to characterize and classify crystal structure families using only the asymmetric units of the unit cells wrapped up as COMFs. Morse functions on orbifolds have unique topological characteristics which currently are not well characterized in the mathematical topology literature.

Crystallographers have long bemoaned the fact that traditional space-group nomenclature is more a hindrance than a help in classification requiring systematic symmetry breaking. We are trying to derive a more structurally related space-group classification based on the imbedding properties of a basis set of simple COMFs into space group orbifolds. This classification also will incorporate space-group/subgroup relationships as given by the color Shubnikov groups represented as color orbifolds.

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MS08.00.02 A PRIORI PREDICTION OF CRYSTAL STRUCTURE. I.D. Brown, Brockhouse Institute of Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1.

The structures of a number of inorganic solids can be predicted from a knowledge of only their chemical formula, by assuming that the solid will adopt the highest symmetry structure that is consistent with the chemical constraints. The atoms of the formula unit are used to find the highest symmetry bond graph (connectivity table) that gives the expected coordination numbers around each cation, and this graph is used to determine the highest possible point symmetries of the atoms. The space groups are then systematically searched to find those whose special positions match in number and symmetry the atoms in the formula unit. Further screening eliminates those space groups whose topology cannot accommodate the bond graph or whose geometry cannot accommodate the predicted bond lengths.

Bond graphs can be reliably constructed providing the atomic environments are regular and the total number of bonds is not too large. Special tables allow the high symmetry space groups to be rapidly screened for a match between the numbers and symmetries of the atoms and those of the special positions. The structure is determined if a successful candidate space group of cubic, tetragonal or trigonal symmetry exists, otherwise the structure has orthorhombic or lower symmetry and requires a different prediction technique. For some compounds it is only possible to generate a high symmetry structure by straining the bonds (e.g. perovskites). In these cases, the lowering of symmetry that relaxes the strains can often be predicted. The compounds NaCl, CsCl, ZnS, ZnO, CaF₂, TiO₂, SrTiO₃, MgSiO₃ and CaCrF₅ will be used to illustrate the method.

MS08.00.03 PRINCIPLES OF STRUCTURAL FORMATION FOR INORGANIC COMPOUNDS WITH HEAVY ATOMS. S.V. Borisov, Institute of Inorganic Chemistry, Novosibirsk, Russia

We have considered the most abundant structure types of heavy-metal fluorides (about 50 types), binary and more complex Nb (Ta) oxides with the commonly occurring cation stoichiometry 1:1, 1:2, 1:3 (about 40 types), and as many structure types of tungstates and molybdates. For the most cases, it was found that: (1) the heavy atoms (cations) are located in the vicinity of crystallographic planes with $d(hkl)$ in the 2,5-3,5Å range forming the dense nets close to the ideal 3₆, 4₄, 3₆+3₃⁴² nets; (2) the points of intersection of these planes form a sublattice whose nodes are occupied by the cations, and sometimes by the large Cl⁻; (3) the geometry of the cation sublattices is close to that of one of three types, i.e., the F type (the ABC close packing) - about 45% of all the structures, the I type (a body - centered cubic sublattice) - 30%, and the AA type (a hexagonal one-layer sublattice, in which the basis plane is split into two planes whose filled nodes complement each other) - 25%; (4) a set of the close-filled cation planes, specific to each sublattice type (with the special geometry of the cation nets), is retained even with the sublattice parameters deviating from the ideal values. The stable tendency toward an ordering of heavy and related atoms is indicative of decreasing a number of atomic degrees of freedom in the structure and can be explained in terms of a novel crystalline state concept. According to this concept, a crystal is considered as an atomic system controlled by self-consistent sets of standing elastic waves related to crystallographic planes (Borisov S.V., J.Struct.Chem., 1992, V.33, N6, pp.871-877). The data on structure considerations have been published in J.Struct. Chem. in 1994 and 1995; a summary of our results will be published *ibid* in 1996. We have the unique set of the CAS-PAN programme (Bliznyuk N.A., Borisov S.V., J.Struct.Chem., 1992, V.33, N2, pp.284-304).

MS08.00.04 A PROCEDURE FOR THE CLASSIFICATION OF NONORGANIC CRYSTAL STRUCTURES. Hans Burzlaff, Lehrst. für Kristallographie, Inst. f. Angewandte Physik, Universität Erlangen, Bismarckstr. 10, D-91054 Erlangen, Germany, Yuri Malinovsky, Institute of Crystallography of the Russian Academy of Sciences, Leninsky Prospekt 59, 117333 Moscow, Russia

After the discussion of the historical background (Ewald, P.P., Hermann, C., 1931; Pearson, W.B., 1967, 1972; Parthe', E. 1990) and of the properties of structural descriptors the concept of mappings is applied to establish and quantify geometrical relationships among crystal structures (Burzlaff, H., Rothammel, W. 1992; Malinovsky, Y, Burzlaff, H., Rothammel, W., 1993). Mappings that lead to relationships are called similarity operators (Bertaut, F.E., 1983) Thus all structures belonging to the same structure type can be collected, e.g. from the data of a data bank by suitable similarity operators. Moreover, different structure types may be grouped to structure families using the same technique.

A procedure is described how a similarity operator can be computed for a pair of structures if a relationship is present. An economical labelling scheme for structure types is proposed using modified Pearson symbols suitable for a classification scheme of inorganic structures to structure types and structure families. The method will be demonstrated using the crystal structures of the Lovozerite and the pyroxene family.

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