Poster

A tool for the analysis of the bond strength anisotropy and search for the low-periodic substructures in crystalline solids

Pavel. N. Zolotarev[1], Davide Campi[2], Davide M. Proserpio[1]

[1]Dipartimento di Chimica, Università degli studi di Milano, Via Golgi 19, 20133 Milano, Italy
[2]Department of Materials Science, Università degli Studi di Milano-Bicocca, Via R. Cozzi 55,

20125 Milano, Italy

pavel.zolotarev@unimi.it

The CrystalGraphAnalyzer [1] is a script designed to analyze the structural features of crystalline materials and identify low- dimensional substructures. The CrystalGraphAnalyzer takes cif file as input and initiates the analysis by constructing a graph representation of the crystal structure by computing the interatomic connectivity using the Voronoi algorithm. The constructed graph, referred to as the crystal graph, consists of nodes representing atoms and edges representing bonds between atoms. The interatomic bonds are characterized by the following descriptors used as weights of edges in the crystal graph: R - interatomic distance; SA - solid angle of the Voronoi-Dirichlet polyhedron face corresponding to an interatomic contact; BV - bond valence of the bond. Identification of low-dimensional substructures within the crystals is done by the iterative removal of the edges in crystal graph with weights less than a threshold value for a selected bond descriptor. After each edge removal iteration, the obtained fragment dimensionality is checked. The algorithm stops if the target dimensionality is reached. Next, the CrystalGraphAnalyzer computes several bond valence sums (BVS) and other quantities that characterize the bond strength and its distribution in the crystal structure, fragments identified and on interfragment borders: ***xbvs*** – fraction of bond valence sum in the fragment identified; ***mean_inter_bv*** – mean bond valence of contacts between fragments as a proxy for binding strength; ***inter_bvs_per_interface*** – bond valence sum per single fragment. The bond valence is applied here as a measure of a chemical bond strength, providing insights into the bonding characteristics of a crystal structure. Though it is not possible to directly relate the bond valence with the interatomic interaction energy, this bond descriptor is much better in reflecting the bond strength than the interatomic distance or solid angle as it implicitly takes into account atomic properties in addition to purely geometrical bond characteristics. Therefore, bond valence is a suitable proxy of bond strength that can be easily computed when screening large databases. In addition to fragment identification and BVS calculation, the CrystalGraphAnalyzer offers a method for estimating fragment charges. In summary, the CrystalGraphAnalyzer employs a step-by- step algorithmic approach to analyse crystal structures, encompassing low-dimensional fragments identification and estimation of their charge, bond strength anisotropy evaluation, dimensionality calculation.

Two-dimensional (2D) materials have emerged as promising candidates for next-generation electronic and optoelectronic applications [2], therefore, to test the script we decided to search for neutral 2-periodic substructures that can be easily exfoliated from their parent crystalline solids. The crystal structure data from the Inorganic Crystal Structure Database (ICSD) underwent a series of filtering steps, to ensure the selection of the highest-quality structures, namely, rejected were the structures with R_f exceeding 10%, structures with a number of atoms per unit cell more than 196, along with any disordered structures, as well as high-pressure and high- temperature phases. The final dataset contained 46678 inorganic compounds which underwent analysis with the CrystalGraphAnalyzer script. As a result, we obtained a list of 84 entries with ***mean_inter_bv*** and ***inter_bvs_per_interface*** values smaller than corresponding values for MoS_2, namely 0.021 and 0.062 units, respectively. The manual check revealed several promising structures different from the usual layered $M^{II/IV}X_2$, $M^{II}X$ and $M^{III}XY$-type compounds. These include zinc dicyanamide (ICSD refcode 122995), $Al_2Si_4O_{11}$ (201706), trifluoromethylsulfonates of copper (172335) and rubidium (171662), intermetallics CaMnGe (52758) and $LiSbO_2$ (262075) for which the exfoliation energy (0.32 $J \cdot m^{-2}$) has been estimated to be smaller than that for graphene [3].

[1] https://github.com/trioxane/StructureAnalyzer.

[2] Mounet, N., Gibertini, M., Schwaller, P., Campi, D., Merkys, A., Marrazzo, A., & Marzari, N. (2018). *Nature nanotechnology*, **13**, 246.

[3] Guan, S., Zhang, G., & Liu, C. (2021). *Nanoscale*, **13**, 19172.

Acknowledgements: We thank the MUR for the grant PRIN2020 "Nature Inspired Crystal Engineering (NICE)"