MS27-1-1 Behaviour of Occupied and Void Space in Molecular Crystal Structures at High Pressure
#MS27-1-1

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Abstract
We report a Monte Carlo algorithm for calculation of occupied ("network") and unoccupied ("void") space in crystal structures.[1] The variation of the volumes of the voids and the network of intermolecular contacts with pressure sensitively reveals discontinuities associated with first- and second-order phase transitions, providing insights into the effect of compression (and, in principle, other external stimuli) at a level between those observed in individual contact distances and the overall unit cell dimensions. The method is shown to be especially useful for the correlation of high-pressure crystallographic and spectroscopic data, illustrated for naphthalene, where a phase transition previously detected by vibrational spectroscopy, and debated in the literature for over 80 years, has been revealed unambiguously in crystallographic data for the first time. Premonitory behaviour before a phase transition and crystal collapse at the end of a compression series has also been detected. The network and void volumes for 129 high-pressure studies taken from the Cambridge Structural Database (CSD)[2] were fitted to equation of state to show that networks typically have bulk moduli between 40 and 150 GPa, while those of voids fall into a much smaller range, 2–5 GPa. These figures are shown to reproduce the narrow range of overall bulk moduli of molecular solids (ca. 5–20 GPa). The program, called CellVol, has been written in Python using the CSD Python API and can be run through the command line or through the Cambridge Crystallographic Data Centre's Mercury interface.[3] The in situ use of the program shall also be demonstrated by presenting recent results from a high pressure study on glyphosate and the immediate appearance of phase behaviour when compared to classical methods discussed.

References
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