

Crystals under pressure: their compression and intermolecular forces

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The compressibility of crystals depends on their structure and interactions [1]. Intuitively, this interdependence can be summed up by relating the stronger interactions with the weaker effect of pressure and *vice versa*. However, the multitude of shapes and sizes of molecules/ions, the variety of types of interactions and their possible arrangements leads to the myriad of crystal structures of different compressibilities. These compressibilities are characteristic for different classes of materials and determine their behaviour under the extreme conditions in the interior of Earth and other planets [2-4], during the technological processes, *e.g.* for pharmaceutical formulation and explosives [5-7], photovoltaics [8], sensors [9] and other applications.

The interest in the compressibility measurements is fuelled by the development, low cost and easy access to the equipment capable of the compressibility measurements in crystallographic and X-ray diffraction laboratories. Presently, the diamond-anvil cell (DAC) has become a standard attachment of in-house single-crystal diffractometers, not to mention the general-users community access to the high-pressure beamlines widely available in synchrotrons, spallation sources, nuclear reactors and other large facilities [10].

Every year reveals new aspects and potentials of the high-pressure research. It is particularly useful for the crystallographers investigating the molecular aggregation, intermolecular interactions and properties of crystals, as all they can be significantly altered under high pressure. For decades, the compressibility of crystals has continued to be an exceptionally engaging example of the structure-properties relations, often leading to counterintuitive behaviour of various types of crystals [11-15]. Their interplay with the intermolecular interactions in crystals will be presented:

- [1] Prewitt, Ch. T.; Downs, R. T. (1998). Chapter 9: High-Pressure Crystal Chemistry. *Ultrahigh Pressure Mineralogy: Physics and Chemistry of the Earth's Deep Interior*, edited by R. J. Hemley, Berlin, Boston: De Gruyter, pp. 283-318.
- [2] Pushcharovsky, D.; Bindi, L. (2025). Secrets from the Depths of Space and Earth: Unraveling Newly Discovered High-Pressure Polymorphs in Meteorites and Diamond Inclusions. *Minerals* **15**, 144.
- [3] Tshauer, O. (2019). High-pressure minerals. *Am. Mineralogist* **104**, 1701.
- [4] Mao, H-k.; Hemley, R. (2007). The high-pressure dimension in earth and planetary science. *PNAS* **104**, 9114.
- [5] Fabbiani, F.P.A.; Pulham, C.R. (2006) High-pressure studies of pharmaceutical compounds and energetic materials. *Chem. Soc. Rev.* **35**, 932.
- [6] Feng, Y., Hao, H., Chen, Y., Wang, N., Wang, T., & Huang, X. (2022). Enhancement of Crystallization Process of the Organic Pharmaceutical Molecules through High Pressure. *Crystals*, **12** 432.
- [7] Boldyreva, E.V., Shakhtshneider, T.P., Ahsbahs, H. et al. Effect of High Pressure on the Polymorphs of Paracetamol. (2002). *J. Therm. Analysis Calorimetry* **68**, 437.
- [8] Szafranski, M.; Katrusiak, A. (2017). Photovoltaic Hybrid Perovskites under Pressure. *J. Phys. Chem. Lett.* **8**, 2496.
- [9] Runowski, M.; Sobczak, S.; Marciniak, J.; Bukalska, I.; Lis, S.; Katrusiak, A. (2019). Gold Nanorods as a High-Pressure Sensor of Phase Transitions and Refractive-Index Gauge. *Nanoscale* **11**, 8718.
- [10] Katrusiak, A. (2019). Lab in a DAC - High-Pressure Crystal Chemistry in a Diamond-Anvil Cell. *Acta Crystallogr. B* **75**, 918.
- [11] Cai, W.; He, J.; Li, W.; Katrusiak, A. (2014). Anomalous Compression of a Weakly CH...O Bonded Nonlinear Optical Molecular Crystal. *J. Mater. Chem. C* **2**, 6471.
- [12] Cai, W.; Katrusiak, A. (2014). Giant Negative Linear Compression Positively Coupled to Massive Thermal Expansion in a Metal-Organic Framework. *Nat. Commun.* **5**, 4337.
- [13] Cai, W.; Gładysiak, A.; Anioła, M.; Smith, V. J.; Barbour, L. J.; Katrusiak, A. (2015). Giant Negative Area Compressibility Tuneable in a Soft Porous Framework Material. *J. Am. Chem. Soc.* **137**, 9296.
- [14] Anioła, M.; Katrusiak, A.; Kia, R. (2012). Negative Linear Compression and Expanding NH...N Bonds in an Imidazoline Compound. *CrystEngComm* **14**, 6424.
- [15] Zieliński, W.; Katrusiak, A. (2014). Colossal Monotonic Response to Hydrostatic Pressure in Molecular Crystal Induced by a Chemical Modification. *Cryst. Growth Des.* **14**, 4247.
- [16] Roszak, K.; Katrusiak, A. (2023). Low-Density Preference of the Ambient and High-Pressure Polymorphs of DL-Menthol. *IUCrJ* **10**, 341.