Negative X-ray expansion in cadmium cyanide

Chloe S. Coates[1,2], Claire A. Murray[3], Hanna L. B. Boström[4], Emily M. Reynolds[5] and Andrew L. Goodwin[2]

[1]Department of Chemistry, Cambridge, U. K, CB2 1EW, [2]Inorganic Chemistry Laboratory, Oxford, U. K., OX1 3QR, [3]Diamond Light Source, Didcot, Oxfordshire OX11 0DE, U. K. [4]Nanochemistry Department, Max Planck Institute for Solid State Research, Stuttgart, Germany, 70569 [5]ISIS Facility, Didcot, Oxfordshire, U. K., OX11 0QX.
cc2084@cam.ac.uk

That X-rays can affect the structure, and therefore functionality, of materials is well established. In macromolecular crystallography, the phenomenology of 'radiation damage' is a mature and important field.[1] Conversely, discussions about radiation damage in small molecule crystallography are rarer and only starting to be identified.[2] X-ray-induced effects are somewhat less well studied in conventional inorganic systems, despite being implicated in a number of interesting phenomena. Examples include decomposition, conductivity enhancement, colour changes, spin-crossover, charge transfer, cell-parameter changes, crystallisation, and amorphisation. [3–5]

Cadmium cyanide, $Cd(CN)_2$, is a flexible coordination polymer best studied for its strong and isotropic negative thermal expansion (NTE) effect. In this talk I will show that this NTE is actually X-ray exposure dependent: $Cd(CN)_2$ contracts not only on heating but also on irradiation by X-rays.[6]

This behaviour contrasts that observed in other beam-sensitive materials, for which X-ray exposure drives lattice expansion. We call this effect 'negative X-ray expansion' (NXE) and suggest its origin involves an interaction between X-rays and cyanide 'flips'; in particular, we rule out local heating as a possible mechanism.[7] Irradiation also affects the nature of a low-temperature phase transition. Our analysis resolves discrepancies in NTE coefficients reported previously on the basis of X-ray diffraction measurements, and we establish the 'true' NTE behaviour of $Cd(CN)_2$ across the temperature range 150–750 K. The interplay between irradiation and mechanical response in $Cd(CN)_2$ highlights the potential for exploiting X-ray exposure in the design of functional materials.

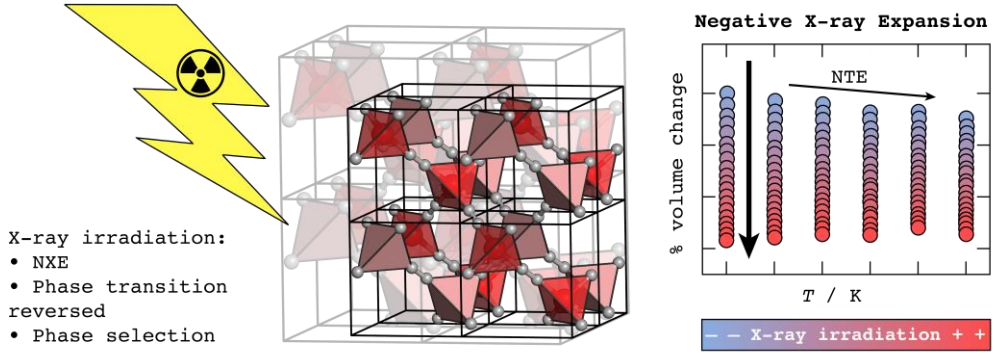

Figure 1. X-ray irradiation of cubic coordination polymer $Cd(CN)_2$ leads to unit-cell contraction and phase transition selectivity.

[1] E. F. Garman (2010) Acta Cryst. D 66, 339–351.
[2] J. Christensen, P. N. Horton, C. S. Bury, J. L. Dickerson, H. Taberman, E. F. Garman and S. J. Coles (2019) IUCrJ, 6, 703–713
[3] V. Kiryukhin, D. Casa, J. P. Hill, B. Keimer, A. Vigliante, Y. Tomioka and Y. Tokura (1997), Nature, 386, 813–815.
[4] H. Ishibashi, T. Y. Koo, Y. S. Hor, A. Borissov, P. G. Radaelli, Y. Horibe, S.-W. Cheong and V. Kiryukhin (2002), Phys. Rev. B 66, 144424
[5] M. Tu et al., (2021) Nat. Mater. 20, 93–99
[6] C. S. Coates, C. A. Murray, H. L. B. Boström, E. M. Reynolds and A. L. Goodwin (2021) Mater. Horiz.
[7] C. S. Coates et al. (2021) Nat. Commun. 12, 2272

Keywords: radiation damage; negative X-ray expansion; negative thermal expansion; phase transitions