Modulated molecular crystals: Incommensurate, high Z' forms and their variation as function of temperature and stress

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Modulated crystal structures consist of a basic structure that possesses 3D space group symmetry, while the constituents of the basic unit cell are modulated by a periodic deformation/modulation.[1] Depending on whether the modulation wave vector, q, is rational or irrational with respect to the basic lattice, they are termed as commensurately or incommensurately modulated structures, respectively. The (3+d)D superspace approach (d = 1,2,3) is employed to recover periodicity of the diffraction patterns and crystal structures of incommensurately modulated crystals (can be applied to commensurate cases too). 3D Sections perpendicular to the internal higher dimension(s) describe crystal structures in real space that vary as function of the phase of the modulation.[1]

Following a brief discussion on the advantages of the superspace approach in understanding phase relations in molecular crystals[2], phase transitions, modulated phases, properties and origin of modulation with respect to intra/intermolecular interactions of the following systems will be discussed:

Case 1: Trimethyltin hydroxide exhibits a discontinuous switching of commensurate modulations below [$q_{T<Tc}$ = (0,0,1/2)] and above [$q_{T>Tc}$ = (0,0,3/8)] its phase transition temperature ($T_c \approx 176$ K) with similar basic lattices.[3,4]

Case 2: Λ–cobalt sepulchrate trinitrate undergoes phase transitions from classical 3D periodic to incommensurately modulated at T_{c1} = 133 K, from incommensurately modulated to incommensurately modulated at T_{c2} = 107 K and further to commensurately modulated at T_{c3} = 98 K [q = (1/6,0,0)].[5]

Case 3: Upon cooling, biphenyl carboxy protected L-phenylalaninate undergoes a phase transition at T_c = 124 K from classical 3D periodic to commensurately modulated [q = (1/2,0,1/2)]. The crystals exhibit anomaly of their fluorescence emission intensity at T_c.

Case 4: Trifluoroborane trimethylamine molecules are highly globular and crystallize in space group R3m. The crystals are plastically bendable, ductile and can be pressed and deformed into thin films with development of a 2D modulation [$q_1 \approx$ (1/2,0,0), $q_2 \approx$ (0,1/2,0)] described in (3+2)D superspace.[6]

Case 5: Isoniazid crystals are stiff (elastic modulus, E ~ 30 GPa) while that of 3,4-dimethylbenzoic acid are soft (E ~ 5 GPa). The crystal structure of the 1:1 cocrystal is incommensurately modulated [q ≈ (0.05,0,1/4)]. The modulation remains incommensurate down to T = 100 K that originates due to competition between energetically soft and hard intermolecular forces.

[1] van Smaalen, S. (2012). “Incommensurate Crystallography”, Oxford University Press, Oxford.

[2] Schoenleber, A. (2011). Z. Kristallogr. 226, 499–517. 10.1524/zkri.2011.1372

[3] Dey, S. et. al. (2016). Z. Kristallogr. 231, 427–434. 10.1515/zkri-2016-1952

[4] Dey, S. et. al. (2018). Cryst. Growth Des. 18, 1394–1400. 10.1021/acs.cgd.7b01295

[5] Dey, S. et. al. (2016). Acta Crystallogr. B 72, 372–380. 10.1107/S2052520616005503

[6] Mondal, A. et. al. (2020). Angew. Chem. Int. Ed. 10.1002/anie.202001060

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