Flexible local crystal chemistry and its (modulated) consequences

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There exists an extraordinarily broad range of compositionally and/or displacively flexible "modulated" crystalline materials (displacively flexible framework structures, materials susceptible to Fermi surface driven structural instabilities, substitutionally disordered solid solutions *etc*) whose reciprocal spaces at one temperature or the other exhibit either sharp satellite reflections and/or highly structured diffuse intensity distributions accompanying the strong Bragg reflections of an underlying, well-defined average structure. The existence of such additional scattering reflects strong local crystal chemical "rules" underlying, for example, the correlated rotations of neighbouring polyhedra in flexible framework structures, the local distribution of dopant ions in substitutionally disordered systems or the correlated displacements of neighbouring ions induced by temperature-dependent, charge density wave (CDW) type structural instabilities. The local crystal chemistry as well as the associated physico-chemical properties of such flexible phases can not be understood until such modulations are recognized and properly taken into account. The results of recent structural investigations of some flexible framework structures [1], of O/F ordering in transition metal oxyfluorides [2] and of the low temperature Kondo effect in ThAsSe [3] will be used to highlight these different types of local flexibility and their structural consequences.

[1] Liu Y., Withers R.L., *J. Solid State Chem.*, 2003, **172**, 431. [2] Brink F.J., Norén L., Withers R.L., *J. Solid State Chem.*, 2004, **177**, 2177. [3] Withers R.L., Vincent R., Schoenes J., *J. Solid State Chem.*, 2004, **177**, 701.

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