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Electron Microscopy and its Application to the Study of Incommensurately Modulated Compositionally and/or Displacively Flexible Phases

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Many crystalline phases behave as the text-books say they should *i.e* as three-dimensionally periodic objects characterized by well-defined stoichiometries, unit cells and space group symmetries. An ever-increasing number of compositionally and/or displacively flexible phases, however, do not fit into this category and are modulated in one form or another [1]. The nature of these modulation/s can be purely displacive in character, of either static or dynamic origin, or of mixed compositional and displacive character. An understanding of the local crystal chemistry of such flexible phases can not be had until these modulations are properly characterized. The ability of electron diffraction to reveal weak subtle features of reciprocal space from small local regions in conjunction with the capacity to image in various modes in real time with excellent spatial resolution and over a considerable range of temperature make the modern TEM an extremely powerful instrument for the study of many such modulated flexible phases.

Fig.1a, for example, shows a $<\bar{1},1,3>_p$ zone axis electron diffraction pattern (edp) of the ferroelectric α-polymorph of $K_3MoO_3F_3$. Indexation is with respect to the underlying elpasolite (or ordered perovskite) type parent structure. In addition to the existence of supercell reflections, note the presence of a spectacular and highly structured, previously unreported, diffuse intensity distribution related to local O/F ordering and associated structural relaxation. Likewise careful TEM investigation has revealed that there exist four quite distinct phase regions within the one previously reported $Co_{2-x}Se_2$, $0 \leq x \leq 0.5$, solid solution field. The second of these phase regions is a Co/vacancy ordered, (3+2)-d incommensurately modulated phase region, see, for example, the $<110>_p$ (p for the underlying *NiAs*/*CdI*$_2$ type parent structure) zone axis micro-diffraction pattern shown in Fig.1b. The presence of a multitude of higher order harmonic satellite reflections in the [001] zone axis edp of the incommensurately modulated $Ni_{6-x}Se_5$ solid solution phase (see Fig.1c) suggests a non-conservative interface modulated structure mechanism for the accommodation of non-stoichiometry in this system as is confirmed by the corresponding [001] HREM image (see Fig.1d).

Non-stoichiometry is not, however, the only known cause of structural flexibility. Many framework structures built out of corner-connected, essentially rigid polyhedral units are also inherently (displacively) flexible, particularly in their high temperature polymorphic forms. Fig.1e, for example, shows a $<\bar{1},1,0>$ zone axis edp of the high temperature polymorph of SiO_2-tridymite. The curved diffuse distribution in this edp traces out thermally excited, low energy RUM (Rigid Unit Mode) modes of distortion of this tetrahedral framework structure. On cooling, one or other of these RUM modes of distortion often condense out giving rise to a statically distorted, lower temperature polymorphic form. Fig.1f, for example, shows a $[-2,0,\sim 6.8]_p$ zone axis edp of the (3+2)-d incommensurately modulated, room temperature polymorph of the mineral fresnoite, $Ba_2TiSi_2O_8$. The weak incommensurate satellite reflections in Fig.1f arise from two such condensed RUM modes of distortion of the parent fresnoite framework structure.

[1] R.L.Withers, S.Schmid & J.G.Thompson, Prog. Solid St. Chem. **26** (1998) 1.

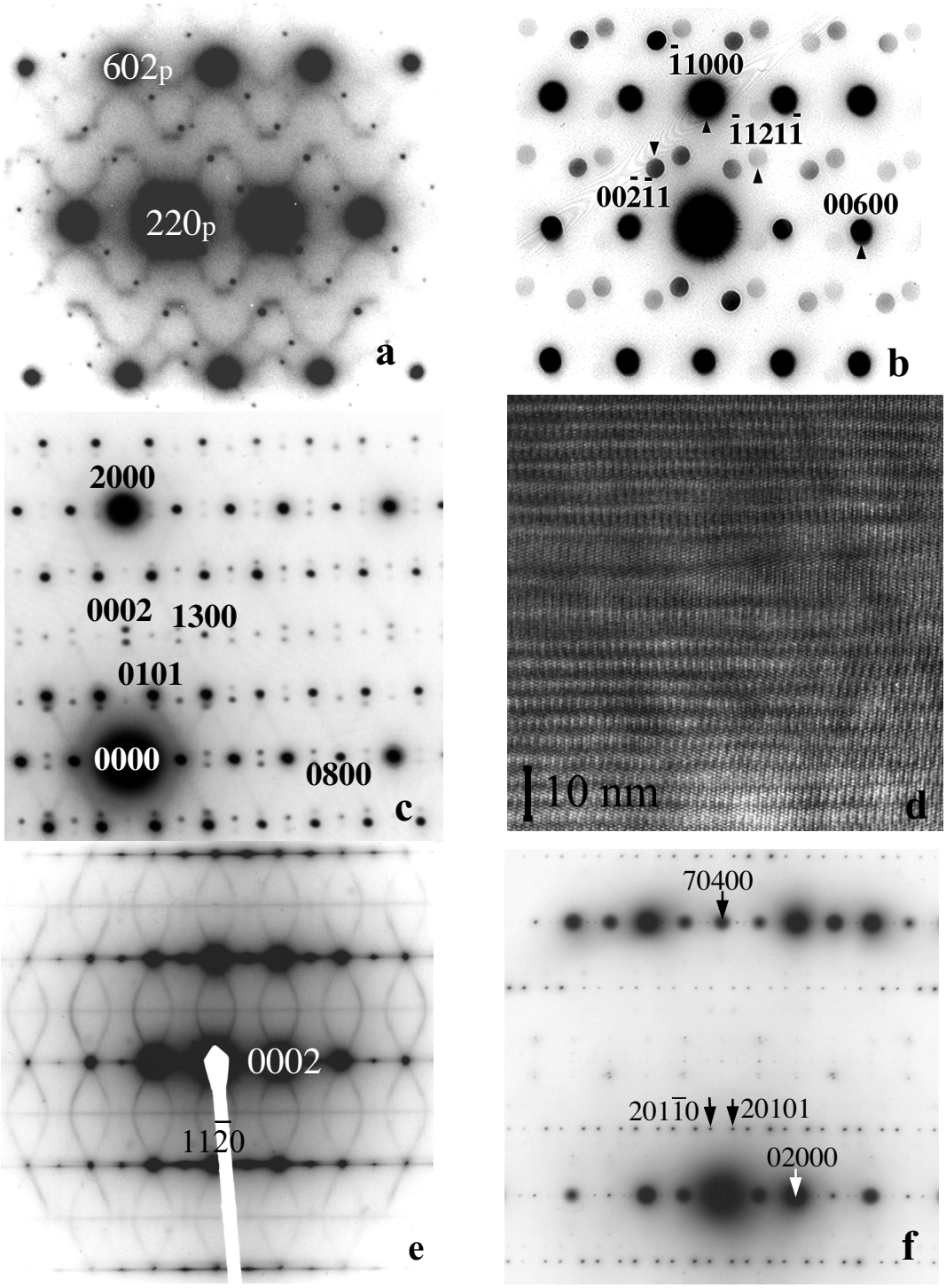

Fig.1 (a) a <–1,1,3>$_p$ zone axis edp of $K_3MoO_3F_3$. Indexation is with respect to the underlying elpasolite type parent structure, (b) a <110>$_p$ micro-diffraction pattern of an incommensurately modulated phase in the $Co_{2-x}Se_2$ system, (c) an [001] zone axis edp of the incommensurately modulated $Ni_{6-x}Se_5$ solid solution phase along with the corresponding HREM image in (d), (e) a <–1,1,0> zone axis edp of the high temperature polymorph of SiO_2-tridymite and (f) a [-2,0,~6.8]$_p$ zone axis edp of the incommensurately modulated, room temperature polymorph of the mineral fresnoite, $Ba_2TiSi_2O_8$.

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