

3.1. STRUCTURAL PHASE TRANSITIONS

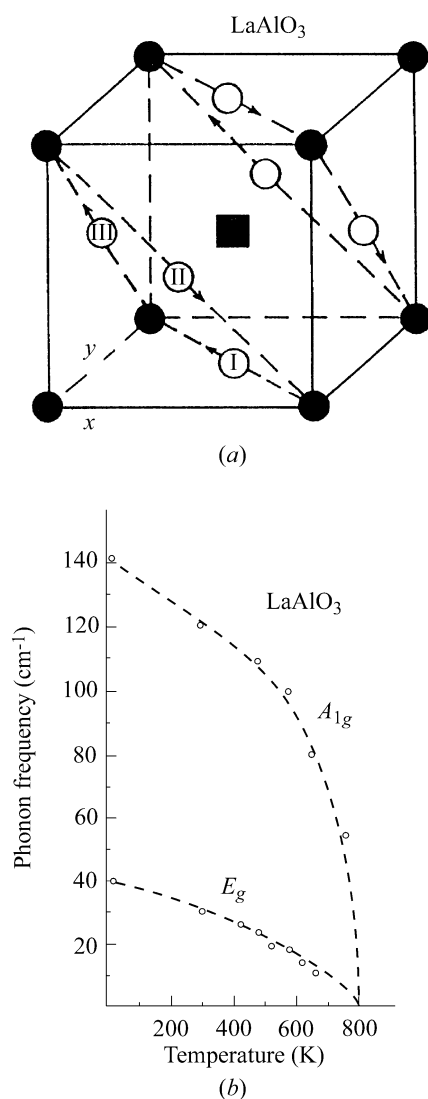


Fig. 3.1.5.8. (a) Structure of lanthanum aluminate above (undistorted) and below (arrows) its cubic-rhombohedral phase transition near 840 K. As in strontium titanate (Figs. 3.1.5.4–3.1.5.7), there is a nearly rigid rotation of oxygen octahedra (the oxygen ions actually remain on the cube faces); however, in the lanthanide aluminates ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$) the rotation is about a cube [111] body diagonal, so that the resulting structure is rhombohedral, rather than tetragonal. The primitive unit cell doubles along the cubic [111] axis; domains will form with the unique axis along all originally equivalent body diagonals of the cubic lattice. (b) Optical phonon frequencies versus temperature in lanthanum aluminate.

group and the size of the primitive cell wrong. The latter error has many serious implications for solid-state physicists: For example, certain electronic transitions from valence to conduction bands are actually ‘direct’ (involving no change in wavevector) but would have erroneously been described as ‘indirect’ with the structure proposed by Lytle. More serious errors of interpretation arose with the microscopic mechanisms of ultrasonic loss proposed by Cowley based upon Lytle’s erroneous structure.

The determination of the correct structure of strontium titanate (Fig. 3.1.5.4) was actually made *via* EPR studies (Unoki & Sakudo, 1967) and confirmed *via* Raman spectroscopy (Fleury *et al.*, 1968). The presence of ‘extra’ $q = 0$ optical phonon peaks in the Raman spectra below T_0 (Fig. 3.1.5.6) is simple and unmistakable evidence of unit-cell multiplication. The fact that two optical phonon branches have frequencies that decrease continuously to zero (Fig. 3.1.5.7) as the transition temperature is approached from below shows further that the transition is ‘displacive’, that is, that the structures are perfectly ordered both above and below the transition temperature. This is a classic example of Cochran’s soft-mode theory discussed above.

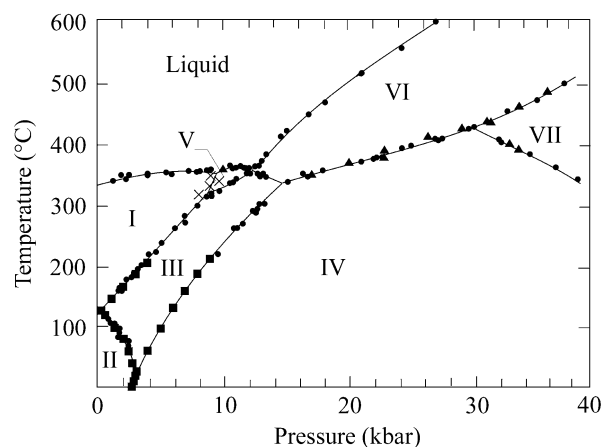


Fig. 3.1.5.9. Phase diagram of potassium nitrate, KNO_3 .

3.1.5.2.4. Lanthanum aluminate, LaAlO_3

A structural distortion related to that in strontium titanate is exhibited in lanthanum aluminate at approximately 840 K. As in strontium titanate, the distortion consists primarily of a nearly rigid rotation of oxygen octahedra. However, in the lanthanide aluminates (including NdAlO_3 and PrAlO_3) the rotation is about the [111] body diagonal(s) of the prototype cubic structure. The rotation, shown in Fig. 3.1.5.8, is out-of-phase in adjacent cubic unit cells, analogous to that in strontium titanate.

Historically, this phase transition and indeed the structure of lanthanum aluminate were incorrectly characterized by X-ray crystallography (Geller & Bala, 1956) and correctly assigned by Scott (1969) and Scott & Remeika (1970) *via* Raman spectroscopy. The causes were as in the case of strontium titanate, namely that it is difficult to assess small, nearly rigid rotations of light ions in twinned specimens. In the case of lanthanum aluminate, Geller and Bala incorrectly determined the space group to be $R\bar{3}m$ (D_{3d}^5), rather than the correct $R\bar{3}2/c$ (D_{3d}^6) shown in Fig. 3.1.5.8, and they had the size of the primitive unit cell as one formula group rather than two.

3.1.5.2.5. Potassium nitrate, KNO_3

Potassium nitrate has a rather simple phase diagram, reproduced in Fig. 3.1.5.9. Two different structures and space groups were proposed for the ambient temperature phase I: Shinnaka (1962) proposed D_{3d}^6 ($R\bar{3}2/c$) with two formula groups per primitive cell ($Z = 2$), whereas Tahvonen (1947) proposed D_{3d}^5 ($R\bar{3}m$) with one formula group per primitive cell. In fact, both are wrong. The correct space group is that of Nimmo & Lucas (1973): D_{3d}^6 ($R\bar{3}2/c$) with one formula group per primitive cell. Again, Raman spectroscopy of phonons shows that the Tahvonen structure predicts approximately twice as many spectral lines as can be observed. Balkanski *et al.* (1969) tried creatively but unsuccessfully to account for their spectra in terms of Tahvonen’s space-group symmetry assignment for this crystal; later Scott & Pouligny (1988) showed that all spectra were compatible with the symmetry assigned by Nimmo and Lucas. In this case, in contrast to the perovskites strontium titanate and lanthanum aluminate, the confusion regarding space-group symmetry arose from the large degree of structural disorder found in phase I of KNO_3 . The structures of phases II and III are unambiguous and are, respectively, aragonite D_{2h}^{16} ($Pnma$) with $Z = 4$ and C_{3v}^5 ($R3m$) with $Z = 1$.

3.1.5.2.6. Lanthanum pentaphosphate

The lanthanide pentaphosphates ($\text{La}, \text{Pr}, \text{Nd}$ and $\text{TbP}_5\text{O}_{14}$) consist of linked ribbons of PO_4 tetrahedra. In each material a structural phase transition occurs from a high-temperature D_{2h}^7 ($Pncm$) point-group symmetry orthorhombic phase to a C_{2h}

3. PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

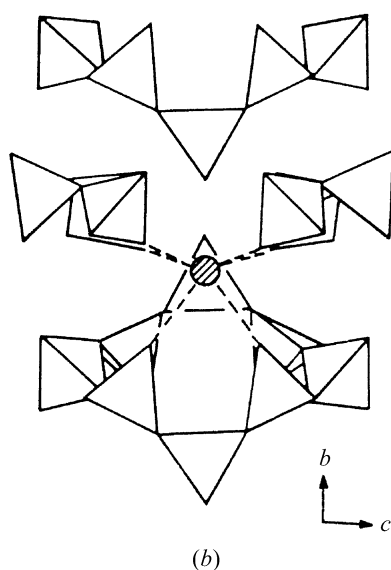
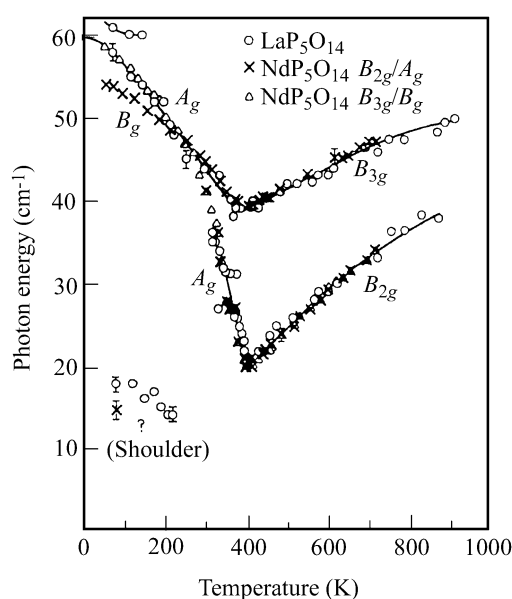


Fig. 3.1.5.10. (a) 'Soft' optical phonon frequency *versus* temperature in $\text{LaP}_5\text{O}_{14}$, showing displacive character of the phase transition. Large acousto-optic interaction prevents the optical phonon frequency from reaching zero at the transition temperature, despite the second-order character of the transition. (b) Lanthanum pentaphosphate structure, showing linked 'ribbons' of phosphate tetrahedra.

($P2_1/c$) monoclinic phase. The macroscopic order parameter for this transition is simply the monoclinic angle φ , or more precisely ($\varphi - 90^\circ$). In this family of materials, the X-ray crystallography was unambiguous in its determination of space-group symmetries and required no complementary optical information. However, the Raman studies (Fox *et al.*, 1976) provided two useful pieces of structural information. First, as shown in Fig. 3.1.5.10, they showed that the phase transition is entirely displacive, with no disorder in the high-symmetry phase; second, they showed that there is a microscopic order parameter that in mean field is proportional to the frequency of a 'soft' optical phonon of long wavelength ($q = 0$). This microscopic order parameter is in fact the eigenvector of that soft mode (normal coordinate), which approximates a rigid rotation of phosphate tetrahedra.

3.1.5.2.7. Barium manganese tetrafluoride

BaMnF_4 is an unusual material whose room-temperature structure is illustrated in Fig. 3.1.5.11(a). It consists of MnF_6 octahedra, linked by two shared corners along the polar a axis,

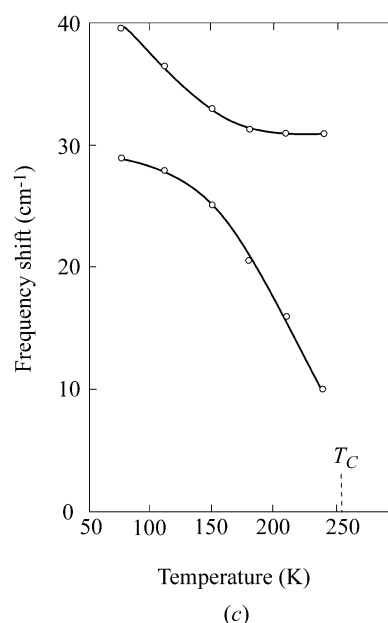
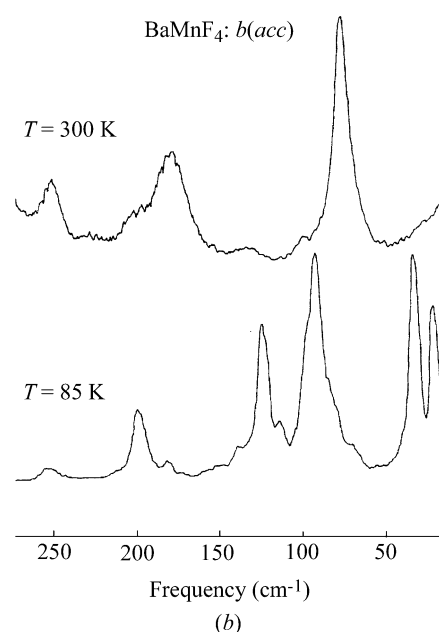
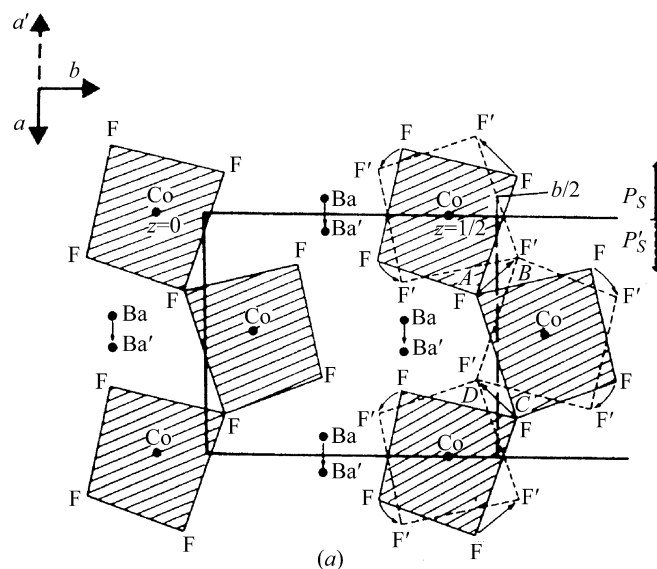


Fig. 3.1.5.11. (a) Structure of barium metal fluoride BaMF_4 ($M = \text{Co, Mn, Mg, Zn, Ni}$) at ambient temperature (300 K). (b) Raman spectroscopy of barium manganese fluoride above and below its structural phase transition temperature, ca. 251 K. (c) Temperature dependence of lower energy phonons in (b).