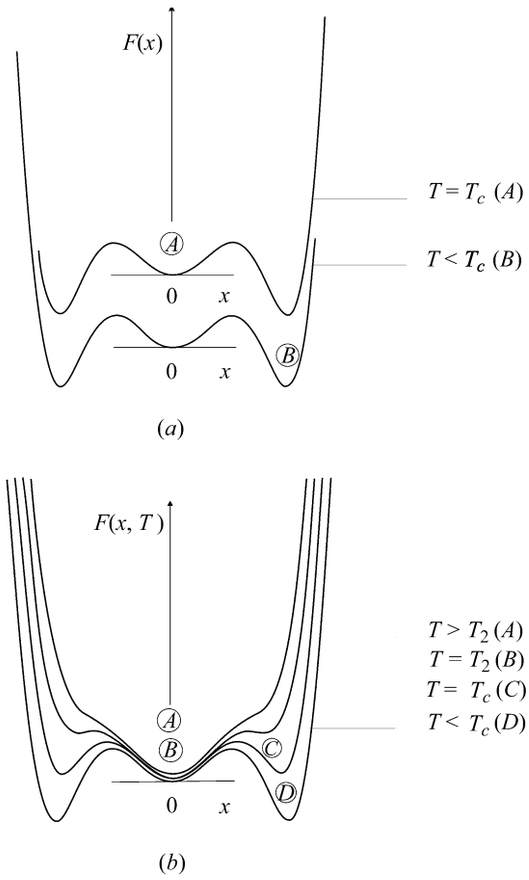

Fig. 3.1.5.17. Double-well models [circled letters show the time-averaged expectation values of the position $x(T)$ of the order parameter at each temperature]. (*a*) For purely order–disorder systems, the depth and separation of the wells is temperature-independent; only the thermal populations change, due to either true quantum-mechanical tunnelling (which only occurs for H or D ions) or thermally activated hopping (for heavier ions). (*b*) For purely displacive systems, all the temperature dependence is in the relative depths of the potential wells. [For mixed systems, such as KH_2PO_4, both well depth(s) and thermal populations change with temperature.]

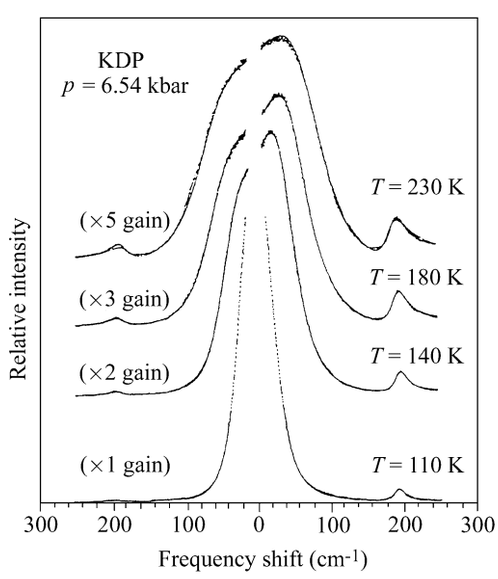

Fig. 3.1.5.18. Pressure dependence of the 'soft' optical phonon branch Raman spectra in potassium dihydrogen phosphate (after Peercy, 1975*b*), showing the displacive character of the phase transition [purely order–disorder phase transitions cannot exhibit propagating (underdamped) soft modes].

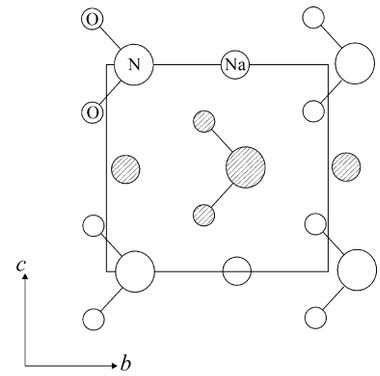

Fig. 3.1.5.19. Structure of sodium nitrite, $NaNO_2$. The molecularly bonded NO_2 ions are shaped like little boomerangs. At high temperatures they are randomly oriented, pointing up or down along the polar b axis. At low temperatures they are (almost) all pointed in the same direction ($+b$ or $-b$ domains). Over a small range of intermediate temperatures their directions have a wave-like 'incommensurate' modulation with a repeat length L that is not an integral multiple of the lattice constant b.

The difficulty comes in recognizing that the normal-mode coordinate x corresponding to the soft mode in this case involves protons (H ions) and K and P ions. Therefore, the free-energy description (as in Fig. 3.1.5.17) will have partly displacive character and partly order–disorder. If the transition were purely displacive (as in TSCC, discussed above), all the important temperature changes would be in the shape of the free energy $F(x)$ with temperature T. Whereas if the transition were purely order–disorder (as in $NaNO_2$, discussed below), the shape of the free-energy curves $F(x)$ would be quite independent of T; only the relative populations of the two sides of the double well would be T-dependent. KDP is intermediate between these descriptions. Strictly, it is 'displacive' in the sense that its normal mode is a propagating mode, shown in Fig. 3.1.5.18 by Peercy's pressure-dependence Raman studies (Peercy, 1975*a*,*b*). If it were truly order–disorder, the mode would be a Debye relaxation with a spectral peak at zero frequency, independent of pressure or temperature. Only the width and intensity would depend upon these parameters.

As a final note on KDP, this material exhibits at ambient pressure and zero applied electric field a phase transition that is very slightly discontinuous. Application of modest pressure or field produces a truly continuous transition. That is, the tricritical point is easily accessible [at a critical field of $6\ \mathrm{kV\ cm^{-1}}$, according to Western *et al.* (1978)].

3.1.5.2.11. *Sodium nitrite, $NaNO_2$*

Sodium nitrite exhibits a purely order–disorder transition and has been chosen for discussion to contrast with the systems in the sections above, which are largely displacive. The mechanism of its transition dynamics is remarkably simple and is illustrated in Fig. 3.1.5.19. There is a linear array of Na and N ions. At low temperatures, the arrow-shaped NO_2 ions (within each domain) point in the same direction; whereas above the Curie temperature they point in random directions with no long-range order. The flopping over of an NO_2 ion is a highly nonlinear response. Therefore the response function (spectrum) associated with this NO_2 flip-flop mode will consist of two parts: a high-frequency peak that looks like a conventional phonon response (lightly damped Lorentzian), plus a low-frequency Debye relaxation ('central mode' peaking at zero frequency). Most of the temperature dependence for this mode will be associated with the Debye spectrum. The spectrum of sodium nitrite is shown in Fig. 3.1.5.20.

Particularly interesting is its phase diagram, relating structure(s) to temperature and 'conjugate' field applied along the