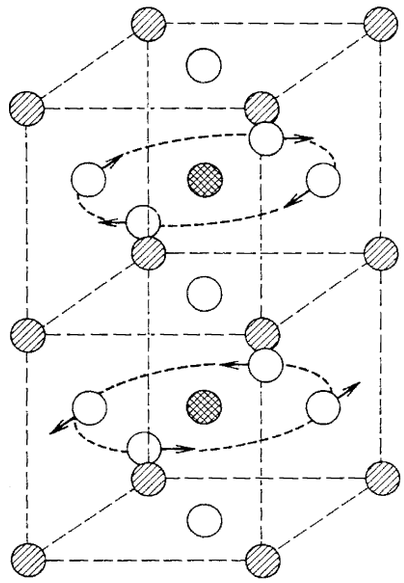

Fig. 3.1.5.4. Structure of strontium titanate above (undisplaced ions) and below (arrows) its anti-ferrodistortive phase transition at *ca.* 105 K. Below this temperature, the cubic primitive cell undergoes a tetragonal distortion and also doubles along the [001] cubic axis (domains will form along [100], [010] and [001] of the original cubic lattice). The ionic displacements approximate a rigid rotation of oxygen octahedra, out-of-phase in adjacent unit cells, except that the oxygens actually remain on the cube faces, so that a very small Ti—O bond elongation occurs.

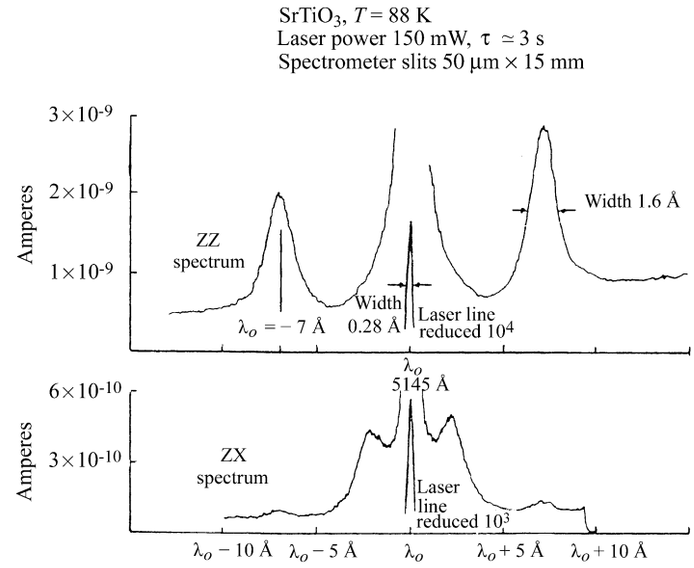

Fig. 3.1.5.6. Raman spectra of strontium titanate below its cubic–tetragonal phase transition temperature. These features disappear totally above the phase transition temperature, thereby providing a vivid indication of a rather subtle phase transition.

the second greatest amount of attention of this family over the past thirty years. It also provides a textbook example of how optical spectroscopy can complement traditional X-ray crystallographic techniques for structural determination.

Fig. 3.1.5.4 shows the structure of strontium titanate above and below the temperature ($T_0 = 105$ K) of a non-ferroelectric phase transition. Note that there is an out-of-phase distortion of oxygen ions in adjacent primitive unit cells (referred to the single formula group ABO_3 in the high-temperature phase). This out-of-phase displacement approximates a rigid rotation of oxygen octahedra about a [100], [010] or [001] cube axis, except that the oxygens actually remain in the plane of the cube faces. We note three qualitative aspects of this distortion: Firstly, it doubles the primitive unit cell from one formula group to two; this will approximately double the number of optical phonons of very long wavelength ($q = 0$) permitted in infrared and/or Raman spectroscopy. Secondly, it makes the gross crystal class tetragonal, rather than cubic (although in specimens cooled through the transition temperature in the absence of external stress, we might expect a random collection of domains with tetragonal axes along the original [100], [010], [001] cube axes, which will give macroscopic cubic properties to the multidomain aggregate). Thirdly, the transition is perfectly continuous, as shown in Fig. 3.1.5.5, where the rotation angle of the oxygen octahedra about the cube axis is plotted *versus* temperature.

Fig. 3.1.5.4 does not correspond at all to the structure inferred earlier from X-ray crystallographic techniques (Lytle, 1964). The very small, nearly rigid rotation of light ions (oxygens) in multidomain specimens caused the X-ray study to overlook the primary characteristic of the phase transition and to register instead only the unmistakable change in the c/a ratio from unity. Thus, the X-ray study correctly inferred the cubic–tetragonal characteristic of the phase transition but it got both the space

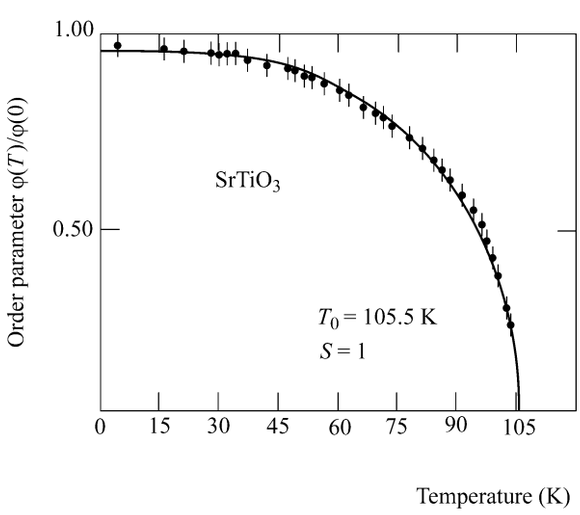

Fig. 3.1.5.5. Rotation angle *versus* temperature for the oxygen octahedron distortion below 105 K in strontium titanate described in Fig. 3.1.5.4. The solid curve is a mean-field least-squares fit to an $S = 1$ Brillouin function.

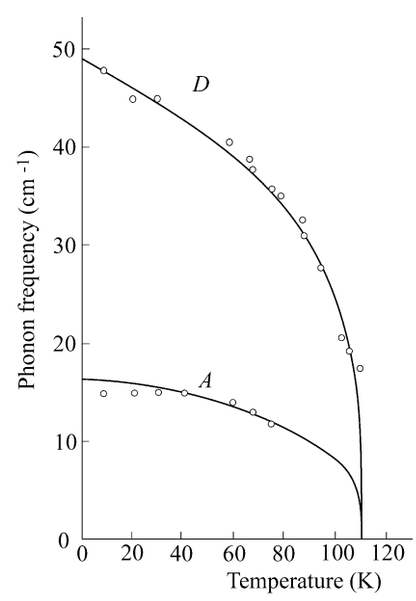

Fig. 3.1.5.7. Temperature dependence of phonon branches observed in the Raman spectra of tetragonal strontium titanate.