

Structural Phase Transition in Titanite, CaTiSiO_5 : A Raman Spectroscopic Study

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Abstract. The structural phase transition in titanite is correlated with a strong temperature dependence of Raman scattering cross sections and, to a somewhat lesser extent, with shifts of the phonon frequencies. Their quantitative temperature evolution in the low-symmetry phase ($P2_1/a$) is compatible with a nearly 2D Ising behaviour with $\beta \approx 0.12$ and $T_c = 497$ K. At temperatures above 860 K, the phonon signals agree with $A2/a$ symmetry but *not* in the temperature interval between 497 K and 860 K. In this temperature range new structural states give rise to additional phonon signals. A model based on mobile APBs between slabs of $P2_1/a$ material, first proposed by van Heurck et al. (1991), is in qualitative agreement with our experimental observations.

Introduction

The structural phase transition in titanite CaTiSiO_5 , was first described by Taylor and Brown (1976). Ghose et al. (1991) described the transition as symmetry breaking of the high temperature phase $A2/a$ to $P2_1/a$ with a critical point Z [i.e. $(0-1/2\ 1/2)$ in $A2/a$] on the surface of the Brillouinzone, although the appearance of intermediate structural states was not excluded. It is known that impurities modify the transition behaviour significantly (Mongiorgi and Riva di Sanseverino 1968, Speer and Gibbs 1976, Higgins and Ribbe 1976) and it is only since large single crystals are available that systematic studies of the transition mechanism became possible. The first quantitative study of thermodynamic properties of the order parameter was based on measurement of the optical birefringence by Bismayer et al. (1992) which found a critical exponent $\beta \approx 0.14$. This value is close to the theoretical value of $1/8$ of a 2D Ising system whereby the deviation of the experimental value from $1/8$ may be related to weak interlayer coupling in this essentially twodimensional structural transition. Although titanite is anti-ferroelectric in the $P2_1/a$ phase and might have

been expected to generate sufficient strain coupling to drive the system into a classic mean field limit (Marais et al. 1990, Salje 1990, Salje 1991), Ghose et al. (1991) reported extremely small values of the spontaneous strain. It is this small value of e_s which makes a short ranged Ising behaviour of titanite plausible. For this feature, titanite might be considered an "exotic" antiferroelectric which allows us to study a non-magnetic structural phase transition with weak order parameter-strain coupling; although further structural studies are needed to confirm this conjecture.

The non-classic behaviour of titanite is also reflected by the observation that the order parameter does not disappear at $T_c = 497$ K but that large excess tails are observed at temperatures between ca. 500 K and 860 K even for very pure, synthetic crystals (Bismayer et al. 1992). This observation is correlated with the formation of antiphase boundaries, APBs, at $T > T_c$, and is presumably independent of extrinsic defects. As we expect this order to be on a local rather than a macroscopic length scale, we undertook this spectroscopic study of the phonon Raman scattering to probe the local order parameters (Salje 1992, Bismayer 1990). The results of this study, as presented in this paper, confirm the existence of local order and allow us to quantify their thermodynamic properties.

Experimental

A titanite single crystal synthesized by the floating zone method (Tanaka et al. 1988) was used for the scattering experiments. The colourless, optically clear crystal was polished to a parallel epiped with the dimensions $3 \times 3 \times 4$ mm. Raman spectroscopical investigations were carried out with a spectrometer consisting of a 4W-Argon laser light source ($\lambda = 488$ nm) with continuously variable polarization direction. The beam was double focused on the sample mounted in a cryostat or a small furnace. The light scattered at 90° from the sample was focused on the entrance slit of a double monochromator and detected by a Peltier cooled photomultiplier attached to a photon counter. Line profile analysis was done on-line with a microcomputer using a fit procedure described by Bismayer et al. (1986).

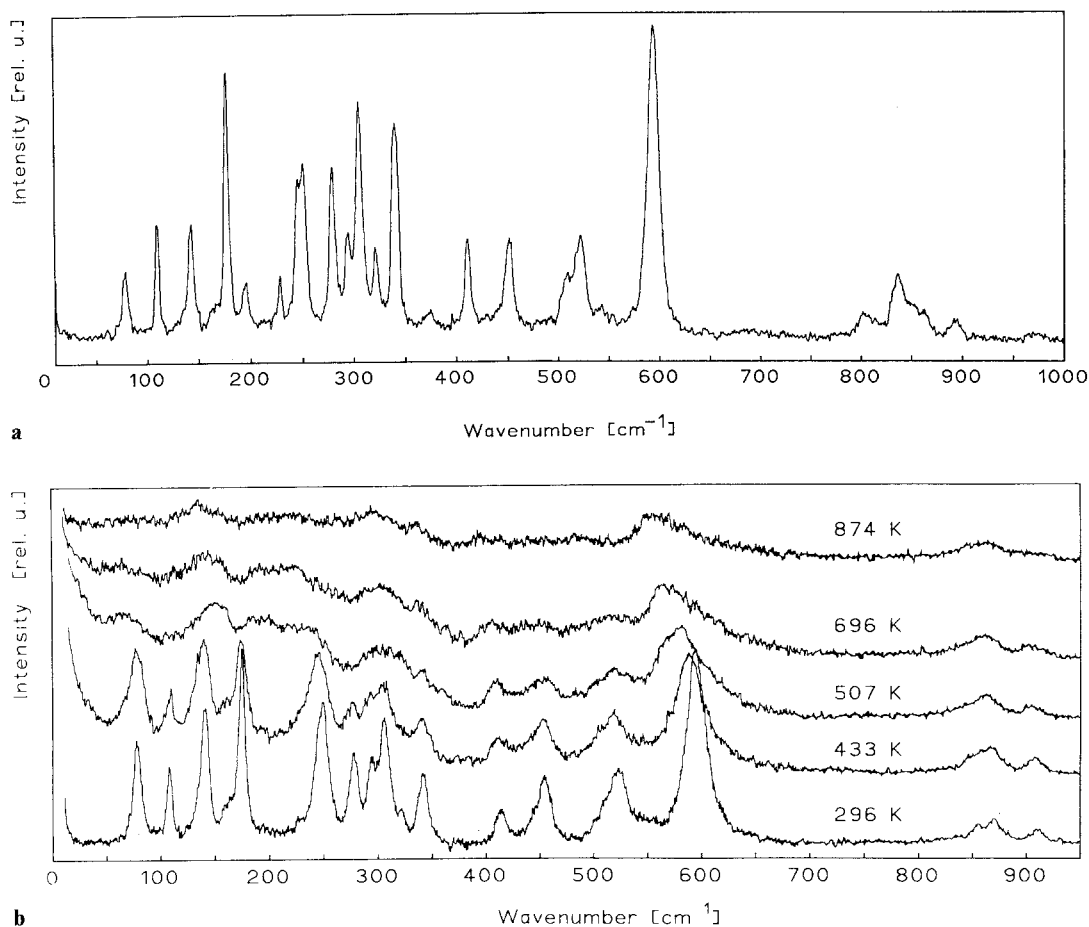


Fig. 1. **a** Raman spectrum of titanite at 110 K in diagonal polarisation (slit 2.4 cm^{-1}). The peak positions of the most prominent lines are listed in Table 1. **b** Unpolarised first-order Raman spectrum of titanite at room temperature, 433 K, 407 K, 696 K, and 874 K

Table 1. Frequencies of the most prominent Raman signals of titanite at 110 K [units cm^{-1} , intensities are scaled vw, w, s, vs in increasing strength]. Strong depolarisation prevented the full $A_g - B_g$ symmetry analysis. Room temperature assignments by Griffith (1969) are given for comparison.

Frequencies	Int.	Frequencies	Int.	Assignment
78.3	s	374	w	
109.6	s	412	s	ν_4
136	vw	447	vw	
142.5	s	452.5	s	ν_4
165	vw	508	s	
177	vs	522	s	ν_4
195	s	543	w	
229	s	594	vs	
246	s	690	vw	
251	s	802	w	
279	s	836	s	ν_1
294	s	851	w	
305.6	vs	863	w	ν_3
321	s	895	w	ν_3
340.5	vs	972	vw	

Results

Titanite shows an intense first order Raman spectrum at room temperature and below (Fig. 1). The positions of the most prominent peaks are listed in Table 1. The

line widths of all phonon peaks are approximately 10 cm^{-1} at room temperature which is a typical value for weak thermal anharmonicity. The spectra change dramatically with increasing temperature: most peak intensities decrease while the apparent line widths increase. For some lines (e.g. near 405 cm^{-1}) this line broadening at $T > T_c$ is due to additional phonon signals which appear at frequencies close to those of the phonon peaks which are in the $P2_1/a$ phase. At $T > 860 \text{ K}$, several lines disappear. The peak intensities of the individual modes show strong temperature dependencies. Typical examples for 4 lines near 414 cm^{-1} , 455 cm^{-1} , 522 cm^{-1} and 595 cm^{-1} are shown in Figs. 2 and 3.

With increasing temperature the scattering intensities decrease strongly and some disappear at an extrapolated temperature of ca. 497 K (Figs. 7–10). This temperature agrees well with the extrapolated T_c of earlier experiments (Bismayer et al. 1992). At $T_c < T < 860 \text{ K}$, the intensities still decrease to an approximately constant value at $T > 860 \text{ K}$. In case of the 455 cm^{-1} mode, this value is zero so that the observed intensity is directly related to the structural modification generated by the phase transition.

Integrated cross sections which include the effect of the spectral anharmonicities (i.e. line widths) show a weaker temperature dependence (Fig. 4). The shifts of the phonon frequencies (Figs. 5, 6) show similar temperature dependencies as the peak intensities.

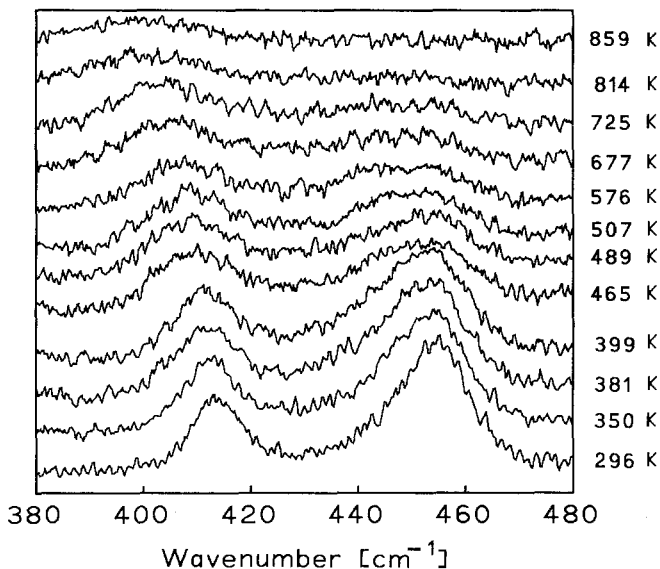


Fig. 2. A_g -Raman spectrum between 380 cm^{-1} and 480 cm^{-1} at different temperatures. Weak additional signals near 400 cm^{-1} appear at $T \geq 489\text{ K}$

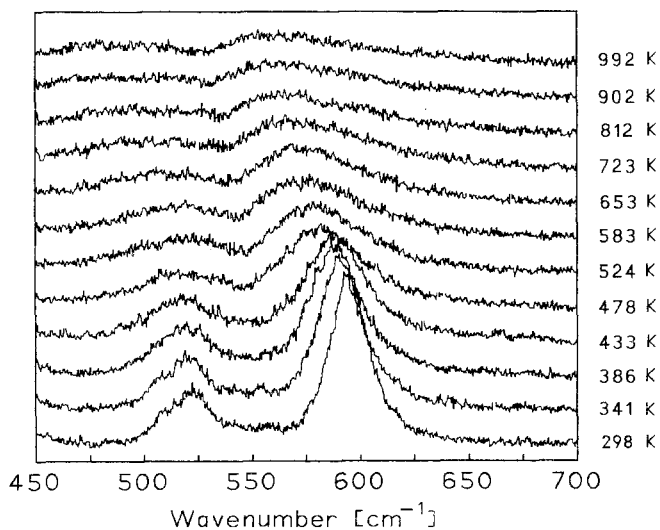


Fig. 3. A_g -Raman spectrum between 450 cm^{-1} and 700 cm^{-1} at different temperatures. (Note the coarser intensity scale than in Fig. 2 so that the signal near 450 cm^{-1} becomes very weak)

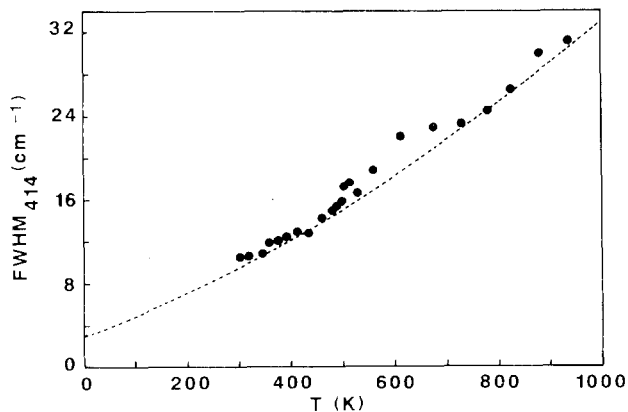


Fig. 4. Temperature evolution of the spectral line width (FWHM) of the 414 cm^{-1} mode. A weak increase of the line width appears between 500 K and 800 K

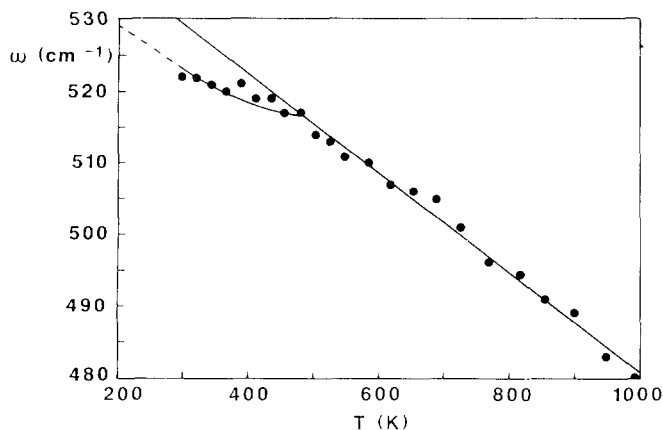


Fig. 5. Frequency of the 522 cm^{-1} mode as a function of temperature

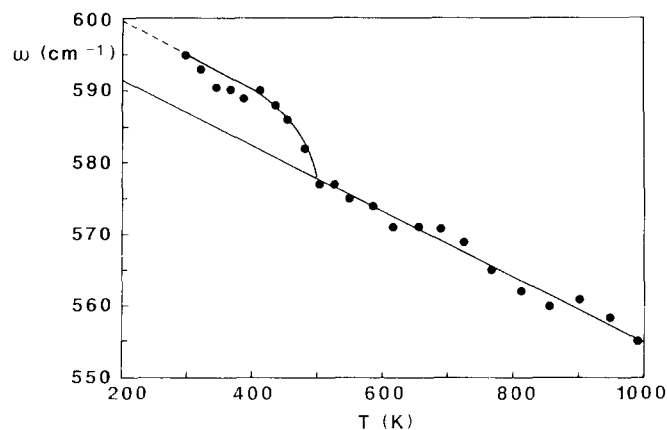


Fig. 6. Frequency of the 595 cm^{-1} mode as a function of temperature

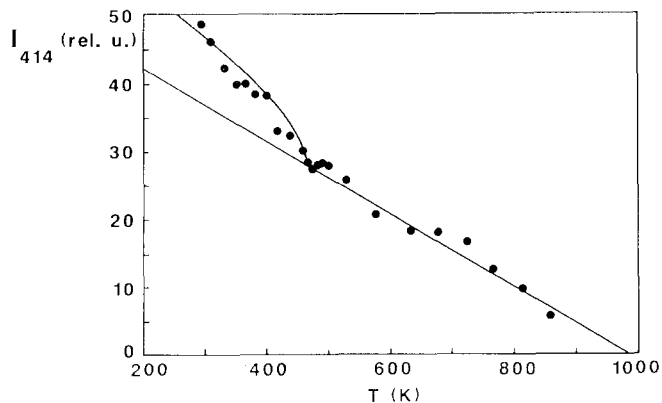


Fig. 7. Evolution of the peak intensity of the 414 cm^{-1} A_g mode with temperature

Discussion

The first order phonon spectra of titanite in the two phases $A2/a$ and $P2_1/a$ are described by the optically active representations

$$[\text{optic}^{A2/a} = 9A_g + 12B_g + 11A_u + 13B_u$$

$$[\text{acoustic}^{A2/a} = 1A_u + 2B_u$$

$$[\text{optic}^{P2_1/a} = 24A_g + 24B_g + 23A_u + 22B_u$$

$$[\text{acoustic}^{P2_1/a} = 1A_u + 2B_u.$$

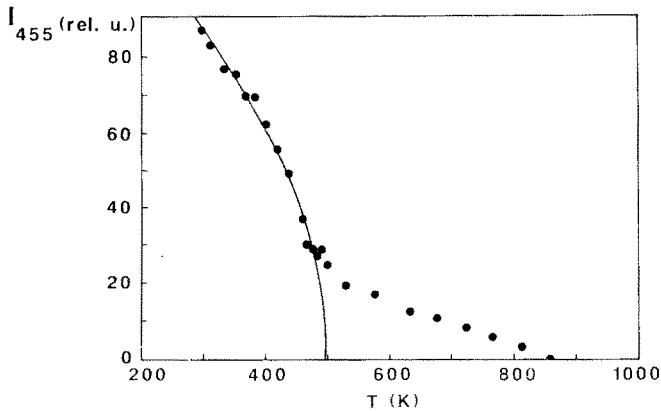


Fig. 8. Evolution of the peak intensity of the $455\text{ cm}^{-1} A_g$ mode with temperature

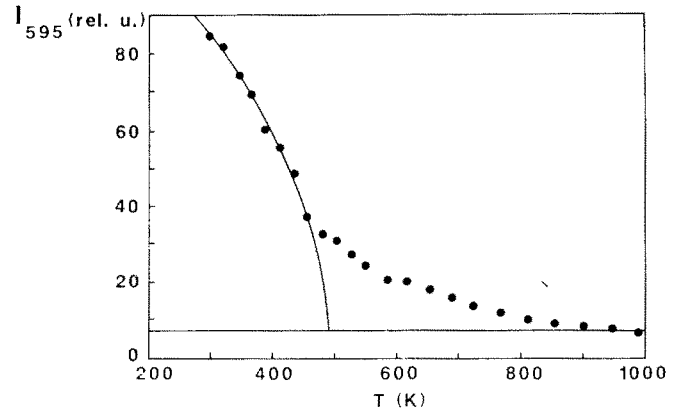


Fig. 10. Evolution of the peak intensity of the $595\text{ cm}^{-1} A_g$ mode with temperature

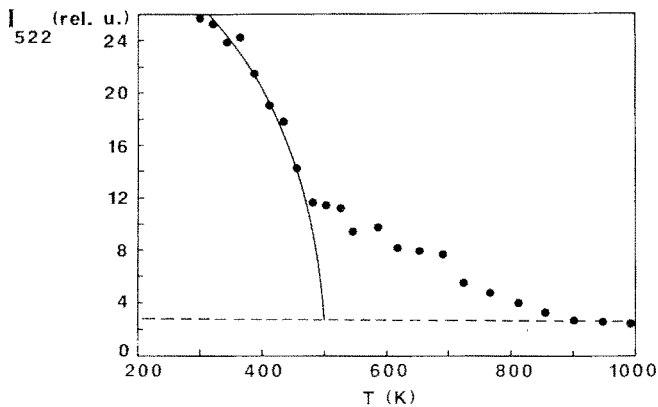


Fig. 9. Evolution of the peak intensity of the $522\text{ cm}^{-1} A_g$ mode with temperature

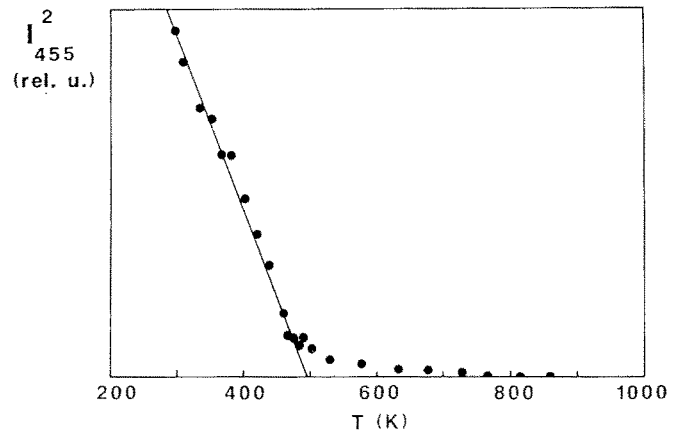


Fig. 11. Squared peak intensity of the $455\text{ cm}^{-1} A_g$ mode as a function of temperature

We expect 21 ramanactive modes in $A2/a$ and 48 ramanactive modes in $P2_1/a$. One of the phonons which lose their ramanactivity during the symmetry increase is the 455 cm^{-1} mode and we will discuss this mode now in some detail. Its scattering intensity (Fig. 8) decreases with increasing temperature. The low-temperature values extrapolate to zero at 497 K , although strong scattering is still observed at temperatures up to 860 K . It is from this result that we follow the earlier work of Bismayer et al. (1992) and define an empirical $T_c = 497\text{ K}$. The quantitative relationship between the intensity and the thermodynamic order parameter Q follows directly from the concept of hard mode Raman spectroscopy (Bismayer 1990, Salje 1992).

$$\Delta I \propto AQ^2 + BQ^4$$

where A and B are coefficients independent of temperature. For modes which are symmetry forbidden in the high-symmetry phase and do not transform as the order parameter, we find $A=0$. The empirical order parameter exponent can then be estimated using

$$\Delta I \propto Q^4 \propto (T_c - T)^{4\beta}$$

In order to test the assumption $\beta \approx 1/8$, we plot $(\Delta I)^2 \propto (T_c - T)^{8\beta}$ and find an approximately linear corre-

lation at $T < 497\text{ K}$ (Fig. 11). The direct analysis of the raw data with $T_c = 497\text{ K}$ leads to $\beta = 0.12 \pm 0.03$ in good agreement with earlier findings of Bismayer et al. (1992).

We come now back to the notion that titanite is an unusual antiferroelectric material because its spontaneous strain was reported to be very small (Ghose et al. 1991). This observation is significant in view of the short range character of the quadrupolar coupling which decays with the 5th power of the distance rather than the third power as in systems with strong coupling between the order parameter and the strain. Antiferroelectric phase transitions without such coupling should not show mean field behaviour (Marais et al. 1991) and, in particular, Landau theory should not be applicable. Our present results show that the phonon renormalisation at room temperature is ca. 8 cm^{-1} for both the modes at 525 cm^{-1} and 595 cm^{-1} . These values are typical for structural phase transitions (Bismayer 1990; Salje 1992). The coupling between the order parameter and these optical phonons is not weak, therefore, and any anomaly must be related to large mode Grüneisen parameters. Unfortunately, the lattice parameters published by Ghose et al. (1991) are not exact enough to warrant the calculation of these mode Grüneisen parameters and further structural work is necessary to clarify this point.

At $T > 497$ K, the excess intensities of the Raman signals decrease gradually with increasing temperature. Simultaneously, additional very weak lines which do not exist either below 497 K or above 860 K appear in the intermediate temperature range (Fig. 2, near 400 cm^{-1}). The fact that these lines are not compatible with either of the two symmetries $P2_1/a$ or $A2/a$ indicates that the intermediate structural state is different from both the low and high temperature structures. This observation agrees, at least qualitatively, with the result of transmission electron microscopy by Van Heurck et al. (1991). These authors report high densities of anti-phase boundaries (APB) under comparable temperature conditions. These APBs separate slabs of $P2_1/a$ material from each other. The APBs are not compatible with the $A2/a$ symmetry. We may now assume that structural relaxations which occur near APBs and, in particular, near junctions between different branches of APBs which are strong enough to modify the phonon spectra. This effect is similar to the phonon renormalization due to the macroscopic strain, as usually seen in ferroelastics with the main difference being that the structural relaxations are locally confined.

These relaxations and the local structural deformation with respect to the $A2/a$ phase can again be described by an order parameter Q' which scales the intensities I of the Raman signals in the intermediate regime on a microscopic scale. We find experimentally that I is a linear function of T near 860 K with

$$I \propto (860 - T).$$

At temperatures below 500 K, I increases non-linearly with decreasing temperature. Although we do not know the symmetry properties of Q' , we might assume that in lowest order $I \propto Q'^2$. This leads to the following scenario:

If Q' is a truly thermodynamic quantity and if the quadratic scaling is correct then the intermediate state is a true phase in the thermodynamic sense with a second order phase transition to $A2/a$ at T_c' . The APB arrangements are the same as in polytypic phase transitions (Salje et al. 1987; Winkler et al. 1990; Houchmanzadeh et al. 1992; Cheng et al. 1990). The nonlinearity of Q'^2 near 500 K relates then to the coupling between Q and Q' . In this model there is a critical temperature $T_c' \approx 860$ K above which the crystal has $A2/a$ symmetry. Further work to clarify the structural relevance of the intermediate state are under way.

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