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Mechanisms at structural phase transitions

H. Böhm*

Institut für Geowissenschaften, Universität Mainz, 55099 Mainz, Germany

Abstract

Structural phase transitions in crystalline solids are accompanied with the change of symmetry. After EHRENFEST [Ehrenfest, P., Phasenumwandlungen im üblichen und erweiterten Sinn, klassifiziert nach den entsprechenden Singularitäten des thermodynamischen Potentials. *Proc. Kon., Amsterdam Acad*., 1933, **36**(Suppl 75b), 153–157] they can be distinguished between first and second order transitions. Two examples for first and second order transitions will be discussed in order two elaborate the characteristic features. The statements are verified by diffraction experiments; the second order transitions will be discussed on the basis of the LANDAU [Landau, L. and Lifshitz, E.M., *Lehrbuch der Theoretischen Physik Band 3, Quantenmechanik*. Akademie Verlag, Berlin, 1986] theory. The first example is the superstructure of $Bi_4Ti_4O_{11}$, and the second example describes the sequence of modulated and non-modulated phases in melilite compounds e.g. $Ca_2CoSi_2O_7$. The sequence of phases in this compound exhibits both first and second order transitions. For both examples it will be shown, to what extent the characteristic criteria of first or second order transitions are valid. It will be pointed out that close to the transition point of second order transitions pronounced deviations are observed. From these features new concepts for the mechanism of the transition can be concluded. Precursors of the low symmetry structure are formed beyond the transition point in the high symmetry phase. For these precursors there is a continuous change from short range order to long range order, which is attained at the transition point. If the precursor domains adopt long range order an intermediate, incommensurately modulated structure may occur between the high symmetric structure and the structure/superstructure of low symmetry.

Keywords: X-ray methods; Phase transitions

1. Introduction

In crystalline solids structural phase transitions occur when a change in temperature or pressure causes a sudden change of symmetry. This symmetry change is associated with a change of the structure. After EHRENFEST[1] such transitions can be distinguished as of first or second order. In first order transitions the changes in entropy and volume are: $\Delta S \neq 0$ and $\Delta V \neq 0$. The basic mechanism is the mechanism of nucleation and growth, which results in a range of coexisting phases in temperature or pressure. The typical feature of such phase transitions is a thermal hysteresis, when characteristic properties are measured on heating or cooling. In second order transitions the changes in entropy and volume are: $\Delta S = 0$ and $\Delta V = 0$. In the conventional interpretation the transition is described as a continuous change of the structure at the transition point accompanied by a sudden change of the symmetry. There is no thermal hysteresis observed. The transformation can be interpreted and described by the phenomenological Landau theory.[2]

In this paper two examples will be discussed in detail to elaborate the characteristic features of first and second order transitions and to focus on new aspects of the mechanisms at second order transitions. The first example is the α–β transition of $Bi_2Ti_4O_{11}$; it exhibits a typical second order phase transition. It has been published by Kahlenberg et al.[3] In the second example members of the melilite family will be discussed. These compounds show a sequence of three phases with first and second order transitions. Contributions to this topic have been published by Seifert et al.,[4] Riester et al.,[5,6] and Kusz et al.[7]

2. Example: $Bi_2Ti_4O_{11}$

The compound exhibits an α–β transition at 233 °C.[3] At the transition the *c* lattice parameter of the β-phase (SG: C2/m) is doubled. Thus, the α-phase (SG: C2/c) exhibits a superstructure of the β-phase along *c*. The intensity of the superstructure reflection is suitable for monitoring the transition (Fig. 1). There is no thermal hysteresis observed between the cooling and the heating cycle. Its intensity is proportional to η^2, the square of the order parameter (see Bruce et al.[8]). The fit with $\eta = \eta_o(T_c - T)^\beta$ in Fig. 1 yields the transition temperature of 233 °C and a value

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* Tel.: +49 61313922848; fax: +49 61313923070.
E-mail address: h.boehm@uni-mainz.de.

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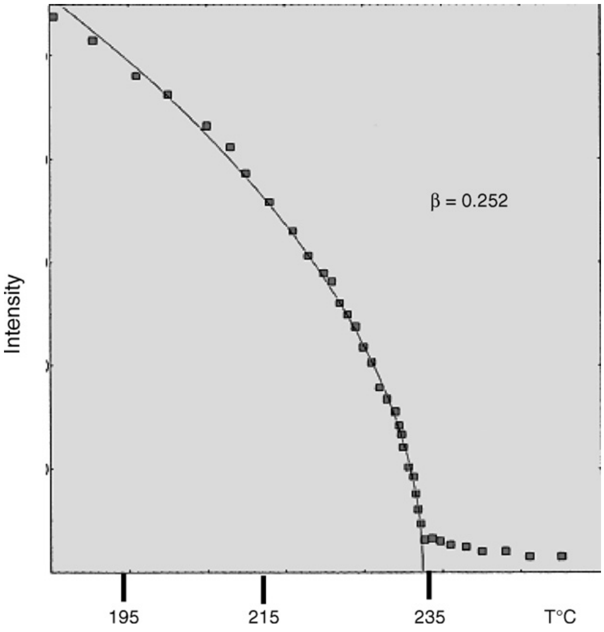

Fig. 1. The integrated intensity of the (0,−2,1) reflection of $Bi_2Ti_4O_{11}$ as a function of temperature. β is the critical exponent.

for the critical exponent $\beta = 0.252$. This is the analysis in the conventional Landau theory; the order parameter varies continuously to zero when the transition point is approached. At the transition a spontaneous strain can be observed by analysing the lattice expansion on cooling. Fig. 3, for example, shows the lattice parameter *b*. At the transition temperature there is an expansion in addition to the negative thermal expansion. From the variation of all three-lattice parameters the principal components of the spontaneous strain tensor can be determined (see Fig. 3). In Kahlenberg et al.[3] it is discussed in detail that at the transition there is an order parameter coupling between η and the spontaneous strain (Figs. 2 and 3).

Fig. 4 exhibits the structure of the α-phase (SG C2/c). The basal planes of the TiO_4-octahedra lie on the c-glide planes, in Fig. 4 depicted as horizontal lines perpendicular to the *b*-axis. The Bi atoms (dark spheres) are below and above the glide planes. When the structures are analysed above and below the transition it becomes obvious, that the Bi atoms trigger the transition. It is the lone electron pair of Bi, which tends to order parallel or anti parallel to the monoclinic *b*-axis. When the ß-phase (SG C2/m) is approached all Bi atoms move towards the *c*-glide plane. At the transition the glide becomes a mirror plane. In the conventional interpretation the transition is described as a continuous movement of the Bi atoms to the position on the glide or mirror planes, respectively. The continuous transition is accompanied by the sudden change in symmetry. In the Section 4 of this paper this statement will be reconsidered.

3. Example: åkermanite compounds

Åkermanite is a mineral, which belongs to the melilite family ($X_2T(1)T(2)_2O_7$) These compounds exhibits a big variety in the chemical composition. The X-cation comprises Na, Ca, Sr, Ba,

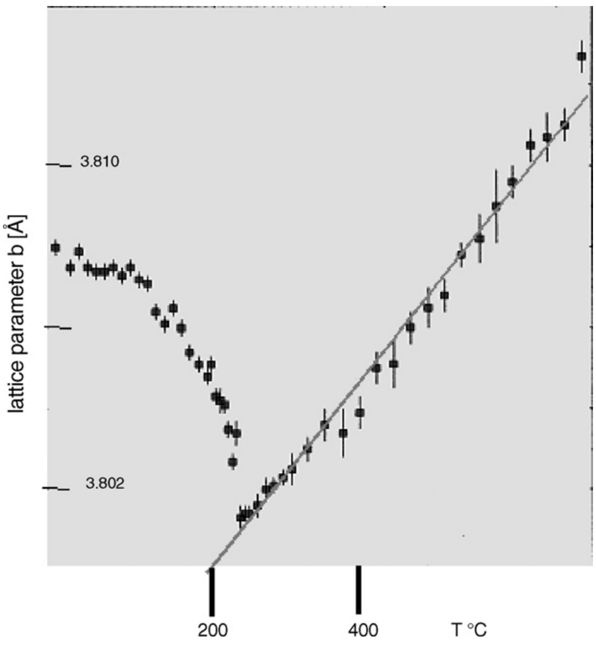

Fig. 2. The variation of the lattice parameter *b* of $Bi_2Ti_4O_{11}$ with temperature.

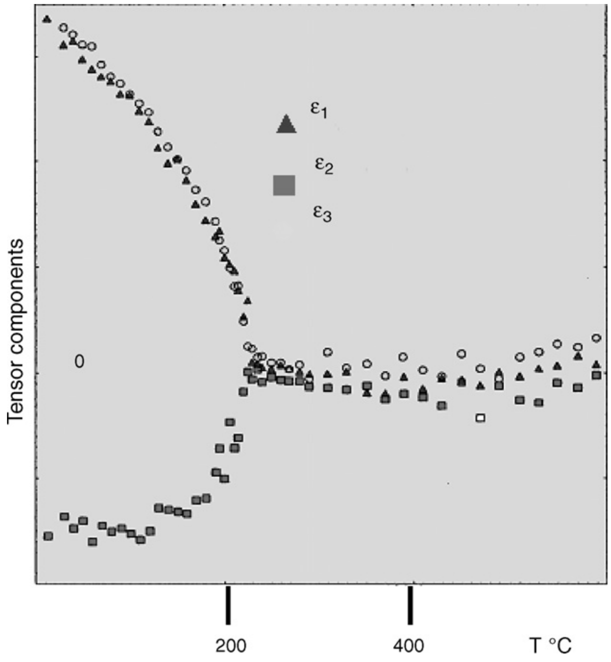

Fig. 3. The principal components of the tensor of the spontaneous strain.

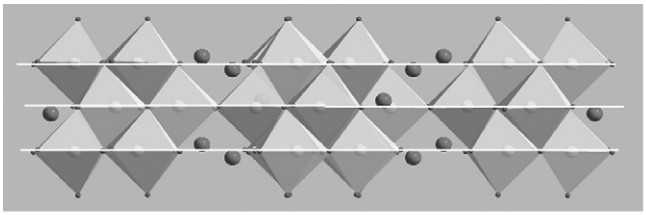

Fig. 4. The structure of the α-phase of $Bi_2Ti_4O_{11}$ (projection on the (*b*, *c*) plane). The basal planes of the TiO_4-octahedra lie on the *c*-glide planes (here horizontal lines) and the Bi atoms (dark spheres) are below and above the glide planes.

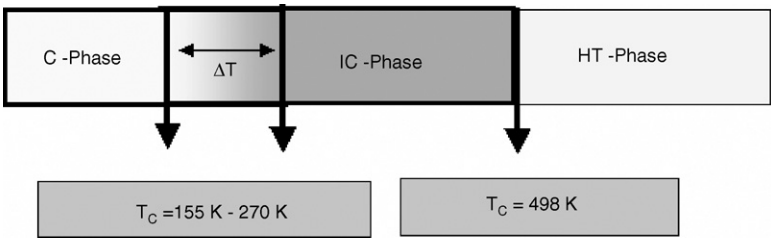

Fig. 5. The sequence of phases and transition temperatures of $Ca_2CoSi_2O_7$.

just to mention a few. The T(1) can be Be, Mg, Al, Co and others. The most prominent T(2) representatives are Si, Al and Ge. Some Ca compounds, like $Ca_2CoSi_2O_7$ (Co-åkermanite) exhibit a sequence of three tetragonal phases as pointed out by Seifert et al.,[4] which will be discussed in more detail. A high temperature phase (HT) transforms into a phase with an incommensurately modulated structure (IC). At lower temperatures the IC phase shows a transition into a commensurate superstructure (C). In Fig. 5 the schematic of the phases and transition temperatures is shown. The transformations of the phases can best be seen in the diffraction pattern. In Fig. 6 the room temperature image of the tetragonal ($h\,k\,0$) layer is shown. Beside the reflections of the tetragonal unit cell (main reflections) weaker reflections within this cell are observed which are located on incommensurate positions (satellite reflections). The indexing of the reciprocal lattice is possible with a (3 + 2)-dimensional basis (a^*,b^*,c^*,q_1,q_2). (a^*,b^*,c^*) describe the main reflections and (q_1,q_2) the satellite reflections, respectively. The main reflections are correlated with the average structure, the satellites with the modulated structure. For further details see Riester et al.[5,6] On approaching the HT phase the intensity of the satellite reflections continuously tends to zero (Fig. 7). Extrapolation of the curve to zero would yield a transition temperature of about 498 K. However the intensity never attains the value of zero. This feature will be elaborated in the next chapter. Since there is no hysteresis between the heating and the cooling cycle, the transition can be considered as of second order.

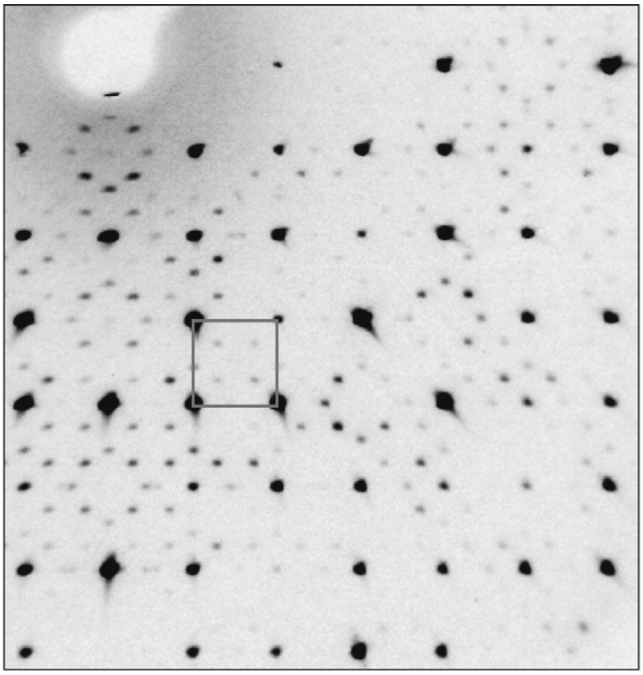

Fig. 6. The precession image at room temperature of the tetragonal ($h\,k\,0$) layer of $Ca_2CoSi_2O_7$.

When the temperature is varied in the range of the IC phase the magnitude of the q-vector changes. This is shown in Fig. 8. The sequences on cooling and on heating exhibit a pronounced hysteresis, revealing a first order transition. On cooling the transition occurs at 155 K, whereas on heating it happens at 270 K. Between these temperatures there is a range of co-existing IC- and C-phases, in which the new phase is formed by nucleation and growth.

Fig. 9 exhibits the HT phase (tetragonal, SG P-42_1m). The octahedra of Co and Si form a layer structure, Ca occupies sites of eight-fold coordination between the layers. The ionic radius of Ca is too small for eight-fold coordination. Therefore the oxygen cage surrounding the Ca atom becomes distorted when the temperature is lowered to form Ca sites of coordination lower than 8 (Riester et al.[6]), preferably such of coordination 6. Structure investigations of Riester et al.[6] of the C-structure (Fig. 10). revealed that four Ca sites of six-fold coordination together form a cluster (encircled areas in Fig. 10). Such clusters tend to order in the IC- and C phases, forming octagons. Octagons of six-fold coordinated Ca-clusters are the characteristic structural feature of the IC- and C-phases. Octagonal motives are also shown in the TEM images of the iso-structural $Ca_2ZnGe_2O_7$ by Van Heurk et

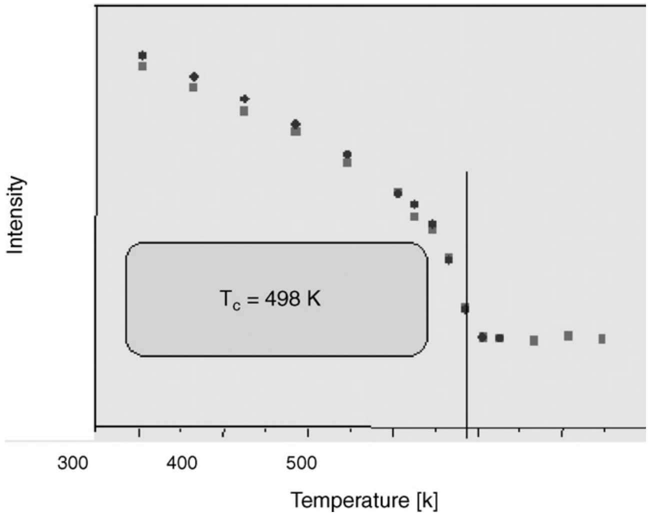

Fig. 7. The variation of a satellite intensity with temperature. The different symbols refer to measurements taken on heating and cooling.

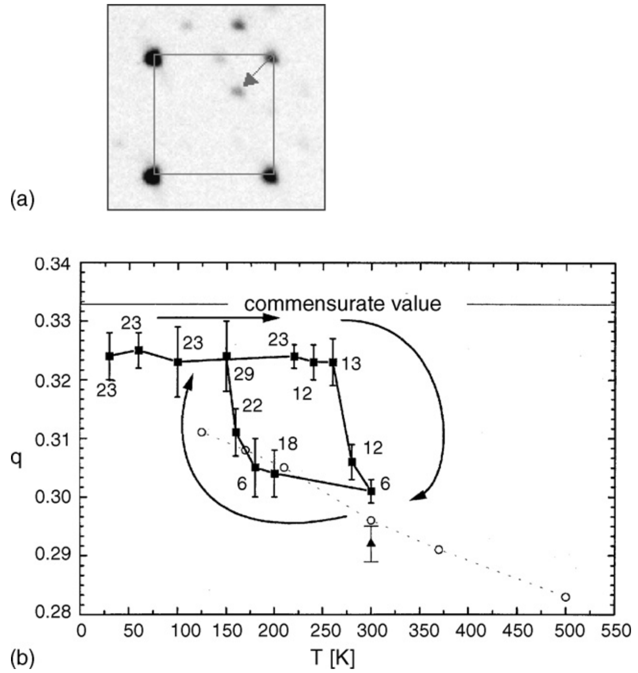

Fig. 8. The position of the q-vector in the tetragonal unit cell of main reflections. (a). The magnitude of the *q*-vector (*q*-value) as a function of temperature (b). The sequence of measurements is indicated by arrows, the numbers refer to the equilibration times in hours.

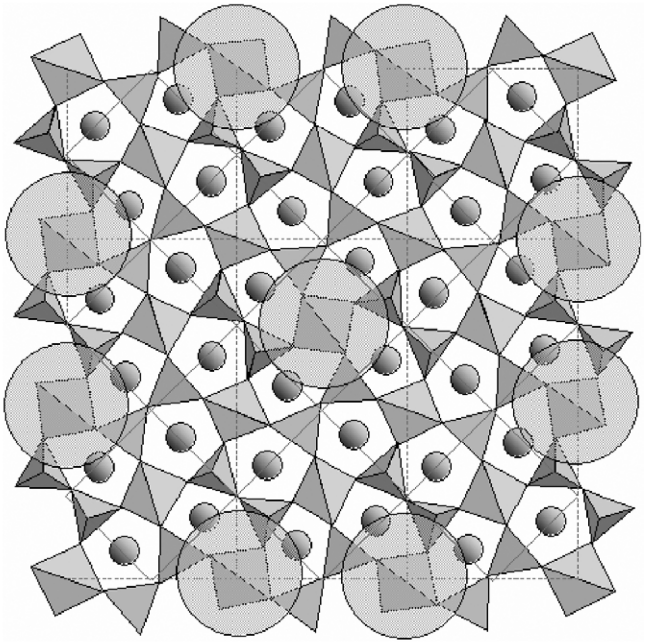

Fig. 10. The 3 × 3 superstructure of the C phase of $Ca_2CoSi_2O_7$. Clusters of six-fold coordinated Ca-sites are accentuated by circles.

al.[9] Riester et al.[6] interpret them as the partially ordered clusters of six-fold coordinated Ca atoms.

For the IC phase it is conjectured by Riester et al.[6] that octagons of six-fold coordinated Ca-clusters superimpose in an arbitrary, partially ordered pattern (Fig. 11) (as it is hinted by the TEM image of Heurk et al.[9]) causing the incommensurate character of the structure. In the C-phase structure refinements prove, that the superposition is completely ordered, forming centred octagonal rings (see Fig. 10 and Fig. 12). This results in a 3 × 3 superstructure. The transformation from the IC- to the C-phase (and vice versa) is only possible, when a nucleus is growing in the parent phase.

4. Discussion

In the previous chapters phases are discussed which show typical 2. Order phase transitions, where the continuous variation of the order parameter can be discussed in the conventional Landau theory. However, one aspect is ignored in such a discus-

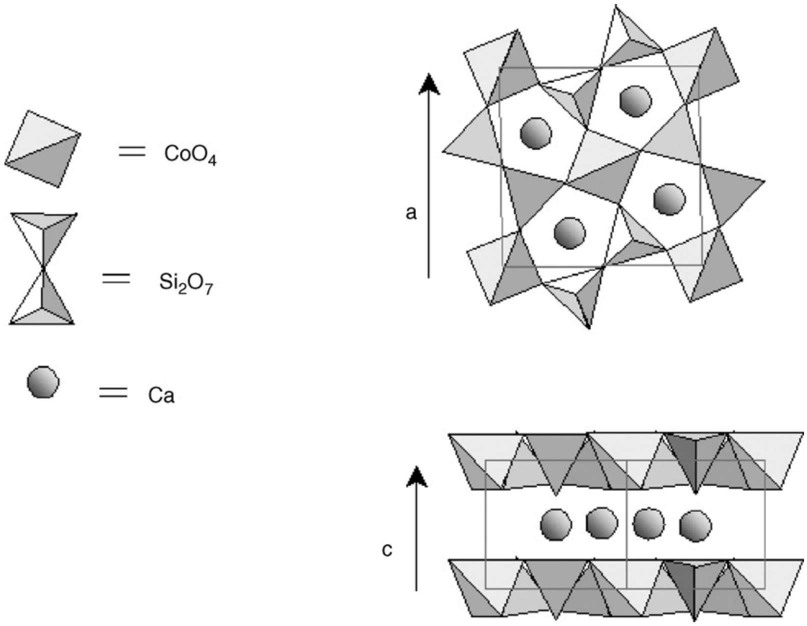

Fig. 9. The tetragonal HT phase of $Ca_2CoSi_2O_7$.

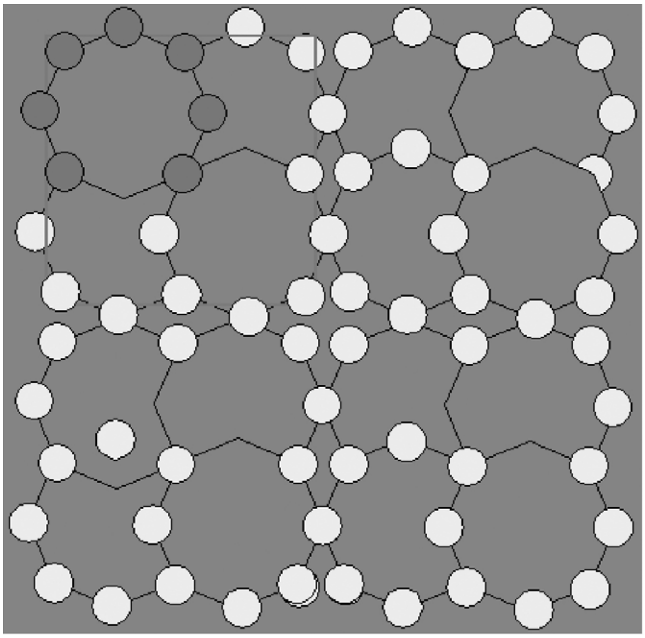

Fig. 11. An arbitrary superposition of octagonal rings of six-fold coordinated Ca-clusters in the IC-phase of $Ca_2CoSi_2O_7$.

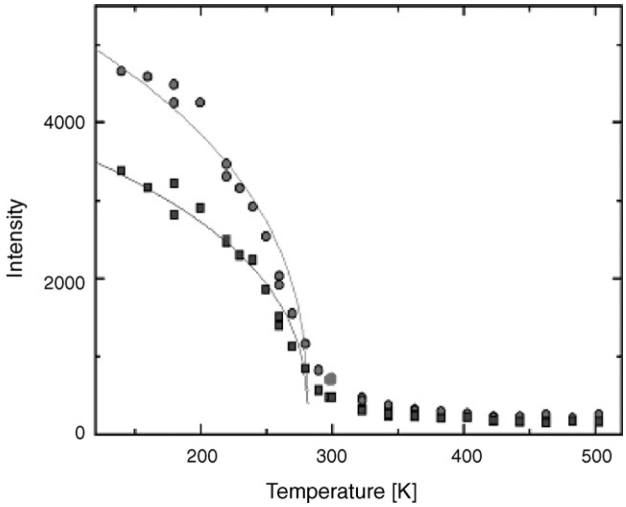

Fig. 13. The intensity variation of two satellite reflections with temperature of the åkermanite solid solution $Ca_{0.84}Sr_{0.16}MgSi_2O_7$.

sion. The quantity, representing the order parameter does not completely vanish at the transition point (see Fig. 1 and Fig. 7). Kusz et al. studied the phase transition of the åkermanite solid solution $Ca_{0.84}Sr_{0.16}MgSi_2O_7$. In Fig. 13 the intensity variation of two satellite reflections with temperature is shown. A similar continuous decrease as in Fig. 7 for $Ca_2CoSi_2O_7$ is observed, again there is no complete vanishment at the transition point. If this curve is fitted with $\eta = \eta_o(T_c - T)^{\beta}$ a transition temperature of 4 °C is determined. In addition the FWHM for the same reflections and for two main reflections was measured. It is shown in Fig. 14. However, since the intensity is not vanishing above the transition, the FWHM can also be determined above T_c. In the range of the HT-phase the FWHM value increases continuously in contrast to the constant value of the two main reflections. The value of FWHM is a measure of the degree of order in a crystal. Sharp reflections, like the main reflections are indicative for long range order. The satellite reflections attain the same FWHM as the main reflections at −23 °C. At this temperature the IC-phase has reached long range order. Above this temperature the motives of the IC-phase still exists with a decreasing degree of order also within the HT-phase. This must be concluded for both examples, for the åkermanites and for $Bi_2Ti_4O_{11}$. In akermanites clusters of octagonal rings partially order also way above the transition; the size of such clusters increases when the transition temperature is approached. This is very well in agreement with the observation of Seifert et al.[4] and Mervin et al.[10] who showed that distortions of the $T(1)O_4$ and $T(2)O_7$ groups are also observed in the HT phase, in contrast to the idealized structure of Fig. 9. Thus, the HT structure of Fig. 9 is an idealized, but not realistic picture of the structure. The question remains,

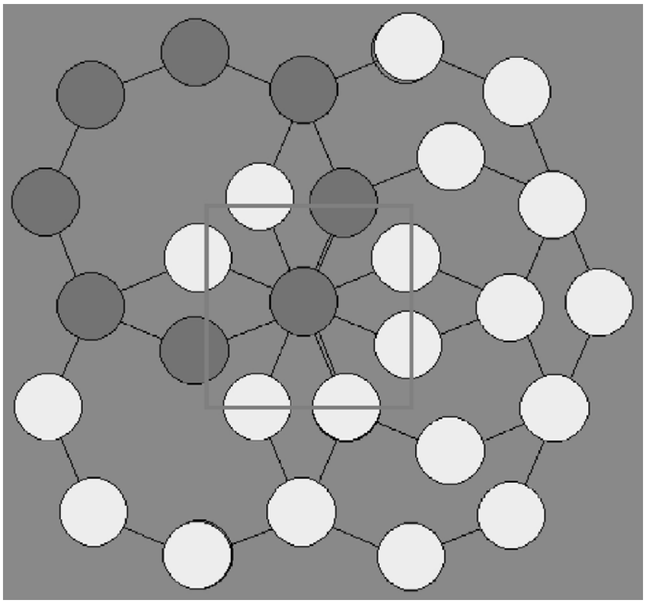

Fig. 12. The 3 × 3 superstructure formed by octagonal centred rings of six-fold coordinated Ca-clusters.

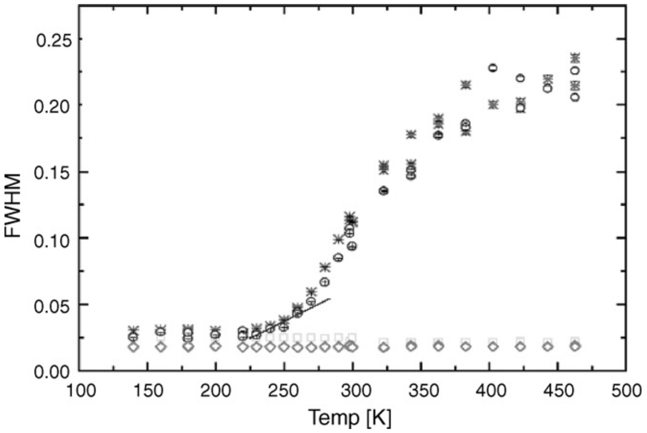

Fig. 14. The variation of the FWHM of two satellite reflections and of two main reflections (lower curves) with temperature of the åkermanite solid solution $Ca_{0.84}Sr_{0.16}MgSi_2O_7$.

what is T_c. Is this the temperature where the order parameter attains the value of zero (4 °C) or the temperature, where the new phase has attained long range order (−23 °C). The first one is only a hypothetical extrapolated value, the latter one at least has physical significance.

In the same way we must conclude that for $Bi_2Ti_4O_{11}$ the lone electron pair of the Bi atoms triggers ordered clusters with increasing degree of order also in the ß-phase until long range order is attained at the transition temperature. In fact, Nistor et al.[11] have observed antiferroelectric ordering of the lone pair of Bi and macroscopic antiphase boundaries at the phase transition by electron microscopy. There is no continuous shift of the Bi atoms off the mirror plane at the transition as it may be conjectured from the conventional Landau theory. Thus we may conclude that a continuous phase transition is characterized by a continuous increase of structural order, rather than by a continuous shift of atomic positions.

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