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Submitted on 1 Jan 1984

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Incommensurate phase of quartz : I. Elastic neutron scattering

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(Reçu le 25 juillet 1983, révisé le 15 septembre, accepté le 29 septembre 1983)

Résumé. — Nous présentons des mesures de diffusion élastique des neutrons qui montrent que la phase intermédiaire du quartz, existant dans un intervalle de 1,3 K entre les phases α et β, est une phase incommensurable. Autour de nombreuses taches de Bragg, nous avons observé six satellites dans les directions [100] de l'espace réciproque. La modulation est une superposition d'ondes planes sinusoidales car on n'observe pas d'harmoniques d'ordre supérieur au premier. Quand la température décroît, le vecteur d'onde de la modulation diminue depuis 0,033 jusque 0,029 unités du réseau réciproque. En phase β, quelques degrés au-dessus de la température de transition α-incommensurable $T_a = 847,2$ K, on observe de la diffusion diffuse prémonitoire. Une discussion des résultats, en relation avec les théories habituelles des phases incommensurables, montre que la situation dans le quartz est, à maints égards, analogue à celle de NaNO$_2$.

Abstract. — We report on elastic neutron scattering results showing that the intermediate phase of quartz existing in a 1.3 K range between the α and β phases is in fact incommensurate. Six satellites are observed around most Bragg peaks along the three [100] directions of reciprocal space. The modulation corresponds to the superposition of sinusoidal plane waves as no higher order harmonics are observed. With decreasing temperature the modulation vector decreases from 0.033 to 0.029 reciprocal units. Premonitory diffuse scattering is observed in the β phase a few degrees above $T_a = 847.2$ K, the incommensurate transition temperature. The results are discussed in relation with the current theories of incommensurate phases and are in many respects analogous to the situation of NaNO$_2$.

1. Introduction.

The theoretical understanding of phase transition has made dramatic progress in recent years with the introduction of the renormalization group theory [1]. However, the field of structural phase transitions has not been so much influenced by this conceptual developments, as the divergence of critical fluctuations is cut down by the discontinuous first order nature of most crystalline transitions. With improving experimental techniques several such first order transitions have in fact been recognized not to occur in just one step but through one or more intermediate phases presenting incommensurate modulations [2].

In this paper we shall present a new example of such a situation for a very common material : quartz. Silicon dioxide (SiO$_2$) is a compound which exhibits a great variety of phases, either crystalline or amorphous [3]. Quartz is the stable crystalline phase under normal conditions of temperature and pressure. Upon heating to about 847 K, quartz transforms from the low temperature α phase of symmetry group 32 to the more symmetric high temperature β phase of symmetry 622. Since its discovery by Le Chatelier in 1889 [4] this transition has been most extensively investigated. While the older results are described in the book of Sosman [3] the more recent ones can be found in several review papers [5-8]. The change of symmetry at this transition allows the introduction of an order parameter $\eta$ related to the atomic displacements which correspond essentially to a tilting of SiO$_4$ tetrahedra around the threefold axis. $\eta$ is zero in the β phase and can take two equal but opposite values in the α phase, producing a domain structure of the Dauphine twin kind.

In the α phase the temperature variations of most physical properties can be related to the variation of $\eta$ as described by the Landau theory of first order phase transitions [7]. A soft mode has been observed in the early days of laser light spectroscopy by Raman scattering [9].

In β phase a more complex situation arises : several properties such as certain elastic « constants » show important variations above the transition temperature which cannot at all be understood in the framework of usual mean field theory [7]. Furthermore certain
puzzling phenomena have consistently been observed just at the transition in particular an intense light scattering [10], which reveals the existence of heterogeneous structures during the coexistence of the two phases [11, 12]. A heterogeneous structure has indeed been observed directly by electron microscopy and interpreted as microdomains of the Dauphiné twin type [13].

These observations led Aslanyan and Levanyuk [14] to a different hypothesis: they suggested the possibility for the existence of an incommensurate phase resulting from a coupling between elastic strains and the spatial derivatives of the order parameter $\eta$. A first experimental support for this idea emerged when one of us [15] found a slope discontinuity in the temperature variation of the thermal expansion at $T_i \approx T_c + 1.3$ K where $T_c$ is the transition temperature upon cooling. Because of the thermal hysteresis of approximately 1 K this discontinuity is well visible upon cooling only. The presence of this anomaly confirmed by new calorimetric measurements of the heat capacity [16] suggested indeed the existence of an intermediate phase which could correspond to the incommensurate one postulated by Aslanyan and Levanyuk [14].

In order to test this possibility further, a diffraction experiment was needed. Among the possibilities offered by X-ray or neutron diffraction we opted for the latter technique, mainly because it permits to use furnaces which provide the good temperature control required to perform safe scattering experiments within the very narrow domain of existence of the new phase. Preliminary neutron diffraction results, already published [16], have shown the presence of new satellite peaks within the intermediate phase. In this paper we shall describe more extensive results proving clearly the incommensurate nature of the new quartz phase which lies in between the $\alpha$ and $\beta$ phases.

Previously several neutron scattering studies on quartz had been undertaken mainly dealing with the behaviour of phonon dispersion curves. After the pioneering work of Elcombe concerned with phonon dispersion within the $XZ$ plane at room temperature [17] the problem of the $\alpha$-$\beta$ transformation was investigated by Axe and Shirane [18]. In the $\beta$ phase a low frequency excitation was found and interpreted as a usual overdamped soft mode, the frequency varying with temperature as $\omega_0 \sim (T - T_0)^{1/2}$, with $T_0 \approx T_c - 10$ K. The eigenvectors of this mode were also determined and found to be similar to the atomic displacements at the transition. A few years later Bauer et al. [19] showed that the diffuse scattering occurring at high temperature and discovered by Arnold [20] was of inelastic origin. In a recent paper Boysen et al. [21] published a detailed inelastic neutron study of this low frequency excitation from the centre to the boundary of the Brillouin zone, along the reciprocal [100] direction. These experiments, however, were carried out several degrees above the transition so that the intermediate phase could not be observed.

One should also note the neutron diffraction structure analysis of the $\beta$ phase by Wright and Lehmann [22] who found that a disordered model fitted their data better.

In part 2 of this paper we present our experimental conditions; in part 3.1 our experimental results are introduced while in part 3.2 we describe in detail the satellite patterns observed around a number of Bragg peaks. Temperature variations of the scattering patterns are given in section 3.3 and in part 4 we discuss our results in particular in connection with other incommensurate phases.

In the meantime we have also obtained various other results on the incommensurate quartz phase. Paper II of this series [23] will be concerned with Brillouin scattering experiments and a detailed discussion of these results as related to the model proposed by Aslanyan and Levanyuk [14]. In paper III [24] further neutron scattering results concerning in particular the lock-in transition to the $\alpha$-phase will be presented together with recent electron microscopic observations of the coexistence state.

2. Experimental.

As in our first neutron experiment [16] on quartz we again used the thermal triple-axis spectrometer D10 at the I.L.L. This spectrometer can also be operated in the simple energy integrating diffractometer mode with a detector looking directly at the sample. The monochromator was a vertically focussing (002) pyrolytic graphite crystal set to the wavelength of $\lambda = 2.35 \text{ Å}$. Higher order beam contamination was suppressed by a graphite filter. The graphite analyser was set to the (004) reflection for better resolution and generally set to zero energy transfer. Because of the very good momentum resolution required for this experiment (a few $10^{-3} \text{ Å}^{-1}$) collimations down to 10 min. of arc were used before the analyser. The energy resolution was thus 0.1 THz FWHM or better. A $7 \times 7 \times 7 \text{ mm}^3$ quartz crystal wrapped in a thin aluminium foil was kept at high temperature by a miniature spherical furnace mounted into a four-circle Euler cradle. For better temperature homogeneity two extra heat shields were placed around the sample. The power of the resistive heater was controlled via a thermocouple in direct thermal contact with the sample, resulting in a temperature stability of 0.02 K. The overall thermal gradient across the sample is more difficult to evaluate for this furnace: the range of coexistence of 1 K observed between the $\alpha$ and INC phases (as shown in figures 9 and 10) sets an upper limit to the total temperature inhomogeneity in the sample. On the other hand the strain induced by the cement holding the sample may have contributed to widen the coexistence range in this experiment. Finally the excellent agreement of the present data with more accurate ones obtained with a better furnace (0.1 K/cm gradient) [24] suggests that the temperature gradient was in fact less than a few 0.1 K/cm. With the present experimental
set-up all reciprocal directions could easily be scanned allowing for a quick and safe determination of the symmetry properties of the new satellite patterns observed. This geometry furthermore permits sample rotations around the scattering vector which enabled us to assess that the scattering observed was not due to multiple scattering effects.

We shall now specify the crystal axis systems used throughout this paper (also defined in [21]) : the unit cell of hexagonal \( \beta \)-quartz is defined by two vectors \( \mathbf{a} \) and \( \mathbf{b} \) intercepting an angle of 120° and \( \mathbf{c} \), perpendicular to the \( \mathbf{a} \), \( \mathbf{b} \) plane (\( a = b = 4.913 \) Å, \( c = 5.405 \) Å at room temperature). Thence the reciprocal unit cell is defined by \( \mathbf{a}^* \), \( \mathbf{b}^* \) (the \( \mathbf{a}^* \), \( \mathbf{b}^* \) angle is 60°) and \( \mathbf{c}^* \).

Sometimes an orthogonal axis system is used with the optical axis \( \mathbf{Oz} \) along \( c \) (and thus \( \mathbf{e}^* \)), the electrical axis \( \mathbf{Ox} \) along \( \mathbf{a} \) and \( \mathbf{Oy} \) along \( \mathbf{b}^* \) (see Fig. 5). In the following we shall use the hexagonal reciprocal axis system with positions given by 3 Miller indices.

Before we come to the presentation of the neutron results obtained with the full resolution of the spectrometer we shall present some measurements on the thermal behaviour of quartz and on the variation across the transitions of the Bragg intensities obtained at lower resolution without the analyser. This will allow us to introduce and precisely classify the different phases and non equilibrium states found as the \( \alpha \)-\( \beta \) transition is crossed both ways in relation with the behaviour of the heat capacity variation.

3. Results.

3.1 General. — Figure 1 presents the variation of \( C_p \) in the temperature range around \( T_c \) obtained by differential scanning calorimetry (DSC) [16]. Upon heating we observe a smooth increase of \( C_p \) in the \( \alpha \)-phase, produced by the decrease of the order parameter \( \eta \). The nucleation of the high temperature phase occurs at a temperature \( T_h \), corresponding to the beginning of the DSC peak of the first order transition accompanied by an enthalpy change of \( \Delta H_h = 1.3 \) cal/g. As long as this peak lasts the sample is in an inhomogeneous state with the \( \alpha \)-phase and the high temperature phase coexisting. At higher temperatures the pure \( \beta \)-phase is reached. Upon cooling a marked increase of \( C_p \) is observed at \( T_i \) indicating the presence of a second-order phase transition to the new intermediate phase which we shall call INC (and not \( \alpha_1 \) as proposed inadequately in [16]). This INC phase survives for about 1.4 K and as shown earlier it is a reversible, at least partially stable phase.

At \( T_s \) a \( C_p \) peak is again observed indicating the start of the coexistence state of the INC and \( \alpha \)-phases which lasts until \( T_c \) below which the homogeneous \( \alpha \)-phase is reached. Upon cooling the enthalpy change \( \Delta H_h \) is about 1 cal/g, the difference with \( \Delta H_h \) corresponding to the anomalous increase of \( C_p \) in the INC phase upon heating. It should be added here that the temperature ranges of the coexistence states upon heating and cooling depend on the experimental conditions (sample size, thermal contact to holder, homogeneity of temperature distribution and temperature variation rate). Thus the nucleation temperatures \( T_h \) and \( T_c \) of the first order transition are not thermodynamic quantities and may change from one sample to another. On the other hand the transition at \( T_i \) appears to be of second order so that \( T_i \) is a true thermodynamic property which depends on thermodynamic variables only.

In general \( T_h \) occurs very close to \( T_i \) so that it is difficult to ascertain the existence of the INC phase when heating from the \( \alpha \) phase. In certain samples, however, we observed a value of \( T_h \) a few tenth of K below \( T_i \) so that the INC phase could clearly be observed upon heating too. In the following we shall give most temperatures relative to \( T_i = 847.2 \) K.

Bragg peak intensities as a function of temperature have been studied earlier by R. A. Young [25] using X-rays and by Wright and Lehmann [22] using neutrons. Structurally these intensity changes can be related in first approximation to a decrease of the SiO\(_4\) tilt angle \( \phi \) from a value of 17 degrees at room temperature to 6 degrees at the \( \alpha \)-\( \beta \) transition [6-8]. Figure 2 gives the temperature variation of the (022) Bragg peak intensity as measured in this study using D10 in the diffractometer mode of operation.

The overall behaviour of the Bragg intensity curve is not unlike the \( C_p \) curve of figure 1. Upon heating from the \( \alpha \) phase one first observes a smooth intensity increase followed by a strongly overshooting part corresponding to the coexistence state. Upon cooling the intensity starts to increase around \( T_h \) and a strong overshoot is also observed during the coexistence state. Here the range of coexistence is wider in temperature than in the DSC experiments. This is due to the fact that for the neutron experiments a massive sample had to be used which necessarily induces thermal...
inhomogeneities when the temperature is changed continuously through the transition (typical rate : 0.02 K/min.).

These strong intensity variations are related to extinction phenomena : because of the rather long neutron wavelength used for the sake of resolution, and given the sample size as well as the good crystal quality, the Bragg intensities recorded here are obviously strongly reduced by extinction. The coexistence of phases with different specific volumes induces elastic strains within the sample which in turn produce an important reduction of the extinction and lead to the observed intensity overshoots [26, 27]. The slow intensity enhancement at the onset of the INC phase might well be due to an extinction reduction caused by the very large thermal expansion of this new phase [15].

Let us describe in some more detail the changes in shape and intensity observed for the (022) Bragg peak at the transition : the intensity profile of a Q-scan along the b* direction for two temperatures (α phase) is given in figure 3a. In heating from the α to the β phase one notices a considerable intensity decrease and a peak shift of 0.007 b* due to thermal expansion. These measurements performed without the energy analyser yield the total scattered intensity including the neutrons scattered inelastically by thermal phonons.

The intensity of this Thermal Diffuse Scattering (TDS) at the bottom of the (022) peak is clearly observed on the magnified scale of figure 3b. The β phase TDS is about double of the α phase one. This difference cannot be attributed to the acoustical phonons as they are known to be steeper in the β phase (with the exception of the transverse TA mode associated with the \( C_{44} \) elastic constant which becomes slightly softer in the β phase [23]). Consequently there must be another contribution to the TDS observed in the β phase, probably from the overdamped soft optical mode observed by Axe and Shirane [18]. In the α phase this mode is underdamped and has a frequency of about 1 THz [9] so that it does not contribute significantly to the TDS intensity.

We now turn to the more detailed results obtained within the INC phase and above \( T_1 \) using the full resolution of the spectrometer.

### 3.2 Satellite Structure.

We shall now describe the neutron scattering results obtained within the pure INC phase at \( T_1 - 0.8 \) K using the best collimations as specified in chapter 2. First we describe the satellite pattern as observed around the (022) reciprocal lattice point which was investigated in great detail. The result of a Q-scan along the (000) reciprocal direction is given in figure 4 : Around the (022) Bragg peak two narrow satellite peaks are observed at \( \pm 0.030 \) b* on top of a broad background distribution. A map of the intensity distribution within the (001) plane is given in figure 5 : six satellites in the three equivalent [100] directions are clearly observed.
Fig. 4. — Q-scan in the triple-axis-mode for zero energy transfer in the $a^*$ direction around the (022) reciprocal lattice point performed within the INC phase at $T_i - 0.8$ K. Two satellite peaks at $(\pm 0.030, 2, 2)$ are clearly resolved. (The Bragg peak intensity is partly shown on a reduced scale.) The crosses are experimental points, the vertical size corresponding to the error bars. The solid line is the result of a Gaussian fit (4 G). The fourth Gaussian (dashed line) corresponds to an inelastic background. Detailed fit results are given in table I.

By the hatched ellipsoids corresponding to the peak sections at half maximum it can be clearly seen that all satellites are in fact broader than the central Bragg peak, the width of which corresponds to the experimental momentum resolution. The Q-scan intensity profiles were fitted to a sum of 4 G, 1 for the Bragg peak, 2 for the satellites, the fourth one being required to account for the broad background distribution. The fit parameters are given in table I. The presence of the satellite peaks evidences the existence of incommensurate modulation waves with the same wavevectors $q_0 \approx 0.03 a^*$ along the three [100] directions. The next step was to look whether we could observe higher order combinations of these modulation vectors. The usual theories of incommensurate phases include two limiting cases for the shape of the modulations: close to $T_i$, it is a sinusoidal plane wave of wave vector $q_0$. Near $T_c$, in the so-called « multisoliton regime », the modulation tends to deform into a rectangular profile, leading to the existence of higher order harmonics at wave vectors $2q_0$, $3q_0$, ... When several equivalent modulation directions are allowed, they can either be locally superposed or spatially separated: these two cases have indeed been observed in TaSe$_2$ [28]. The neutron scattering experiment giving a sample average it is difficult to tell whether the order 6 symmetry is a local property or an average one. In this experiment we have looked very carefully for the presence of higher order satellites both of the type $2q_0$, $3q_0$ and $q_0 \pm q_0$ due to a multi-$q$ type structure as observed for instance in TaSe$_2$ [28]. As already evidenced by the spectra of figure 4 no extra intensity is observed at the $2q_0$ and $3q_0$ reciprocal positions. To search for the possibility of multi-$q$ combinations we have performed further Q-scans across the $(-0.03, 2, 2)$ satellite and along [100], [010], and [110] directions as indicated on figure 5 by the

Table I. — Gaussian fit parameters corresponding to the Q-scan of figure 4 ($T_i - 0.8$ K) and figure 8 ($T_i + 1.5$ K). $I$ is the peak intensity in neutrons per minute, $W$ is the full width at half maximum, $q_0$ the reciprocal distance from satellite to Bragg-peak, both in units of $10^{-3} a^*$. The two satellites being practically identical, mean values are given.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>(022) Bragg</th>
<th>Satellite</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_i - 0.8$ K</td>
<td>360000</td>
<td>35.000</td>
<td>150</td>
</tr>
<tr>
<td>$T_i + 1.5$ K</td>
<td>25</td>
<td>6.6</td>
<td>23</td>
</tr>
</tbody>
</table>
Table II. — Peak width (Gaussian, FWHM) for scans along the three (100) directions corresponding to the scans presented in figure 5 at \( T_i - 0.8 \) K (INC phase).

<table>
<thead>
<tr>
<th>Peak width (( 10^{-3} a^* ))</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(( \xi 2 2 ))</td>
<td>( \xi 2 - \xi 2 )</td>
<td>( 0 2 + \xi 2 )</td>
<td></td>
</tr>
<tr>
<td>Satellite</td>
<td>9.8</td>
<td>9.2</td>
<td>15.1</td>
</tr>
<tr>
<td>Bragg</td>
<td>6.8</td>
<td>7.1</td>
<td>13.8</td>
</tr>
</tbody>
</table>

lines labelled a, b and c. None of these scans revealed any higher order component. The results of the fits to the first order satellites are detailed in table II: along all scan directions the satellites are systematically broader than the Bragg peak by about 0.003 \( a^* \).

With our four-circle setting we could also reach all other Bragg-peak/satellite positions within the range of momentum transfer (4.5 \( \text{Å}^{-1} \)). Thus we were able to observe the presence of similar satellite patterns around most Bragg peaks, the reciprocal distance from the Bragg spots to the satellites for a given temperature corresponding always to the same modulation \( q_o \).

Around general reciprocal points we thus observe six satellites of in general different intensities. The only exceptions are the satellite patterns around Bragg spots of the type \( (h00) \) for which the satellites of the type \( (h \pm 0.03 0 0) \) are systematically extinct. If indeed the displacements corresponding to the INC transition belong, as supposed by Aslanyan and Levanyuk, to the representation \( \Sigma_3 \) then for \( (h00) \) positions the structure factor vanishes [29]. This is indeed what the experiment shows and for \( h = 1, 2, 3 \) we thus observe a 4 satellite pattern around the Bragg peak. In the case of \( h = 3 \) figure 6 gives an example of such a particular satellite pattern. For \( h = 1, 2 \) the same patterns are observed although at lower intensity.

3.3 Temperature variations. — We shall start with a description of the pretransitional diffuse scattering observed in the \( \beta \) phase and then give the temperature behaviour of the satellite patterns through the INC phase.

Repeating the same \( Q \)-scans around \( (022) \) as before but at \( T_i + 1.5 \) K (\( \beta \) phase) we obtain the results given in figure 7. For the scan along \( a^* \) two broad humps at \( \pm 0.035 2 2 \) are observed. A scan along the \( (2 \xi 2 - \xi 2) \), directions yields no humps but a broad distribution about the Bragg peak position. Energy scans of this diffuse scattering for \( Q = (0.034 2 2) \) have shown that this scattering is of inelastic origin. We observe neutron groups centred around zero energy transfer presenting an energy width FWHM of about 0.4 THz. This width is in agreement with what was reported in the \( \beta \) phase [18, 21] at slightly higher \( q \) values and interpreted as the overdamped soft mode.

The complete study of the \( Q \) dependence of this diffuse scattering shows that it also presents an order 6 symmetry (Fig. 8) as the satellite patterns within the INC phase. Here the fitting procedure is more delicate because of the huge intensity difference between the Bragg peak and the diffuse humps. Finally the best procedure was to start removing the Bragg peak and fit the humps only. With the obtained results the Bragg peak was added at the end to yield a final fit with a certain amount of correlation between the various parameters. The final values of the parameters are given in table I. It is thus established that approaching the incommensurate transition temperature \( T_i \) from the \( \beta \) phase premonitory diffuse scattering is observed at the positions of the INC satellites. This scattering is of inelastic origin and is probably related to the overdamped soft mode observed earlier. Further inelastic neutron scattering experiments are forseen to clarify this point.

We shall now follow the scattered neutron spectra from the \( \beta \) phase down through the INC phase and into the \( \alpha \) phase. Figure 9 displays the intensity variations of Bragg \( (022) \) and related satellite peaks (peak intensities form Gaussian fits). In figure 10 are given the corresponding values of the incommensurate...
Fig. 7. — *Q*-scan around the (022) reciprocal lattice point at \( T + 1.5 \text{ K} \) (\( \beta \) phase). *a*) Scan along the \( a \) direction (i.e. \((2 \xi, 2 - \xi, 2)\)). *b*) Scan along the \( a^* \) direction (i.e. \((\xi, 2, 2)\)).

Fig. 8. — Intensity map in the (001) plane as deduced from *Q*-scans around the (022) reciprocal point at \( T; + 1.5 \text{ K} \) (\( \beta \) phase). Broad humps at the INC satellite positions are visible.

Fig. 9. — Temperature variation of the peak intensities (from Gaussian fits) of Bragg and satellite reflections : + (022) Bragg peak, \( \times (-0.03, 2, 2) \) satellite (magnified 50 times), * these points correspond to the temperatures \( T_i + 1.5 \text{ K} \) and \( T_i - 0.8 \text{ K} \) chosen respectively for figures 4 and 5 and figures 7 and 8. The lines are guides to the eye; a full line corresponds to a homogeneous phase (either pure \( \alpha \), \( \beta \) or INC) whereas dashed lines indicate coexistence states between the \( \alpha \) and INC phases.

Above \( T_i \), where broad humps are observed at the satellite positions the temperature variations are smooth. The onset of the INC phase is characterized by the rapid growth of narrow satellites. Actually the most striking feature at \( T_i \) is the rapid decrease of the satellite width \( W_s \). The intensity variations accelerate at \( T_i \) while \( q_0 \) decreases steadily. Within 1 K below \( T_i \), the temperature interval of the homogeneous INC phase, the satellite peaks remain narrow with a constant width of \( W_S = 0.01 \ a^* \), while \( q_0 \) decreases from about 0.033 \( a^* \) at \( T_i \) to 0.029 \( a^* \) at \( T_c \). The strong increase of the Bragg-peak intensity can probably be understood in terms of an extinction reduction due to the important thermal expansion of the INC phase [15]. At \( T_e = T_i - 1 \text{ K} \) the nucleation of the \( \alpha \) phase initiates the coexistence region resulting in marked anomalies in the intensity behaviours of both Bragg and satellite peaks as well as in the increasing widths of the satellites.
During the present experiments the width of the coexistence region extended over a little more than 1 K. This temperature interval is not intrinsic but rather given by temperature gradients throughout the sample or strains caused by the cement used to hold the sample. In figures 9 and 10 the temperature variations of the parameters are indicated by dashed curves within the coexistence region: \( q_0 \) decreases while \( W_s \) increases so that close to \( T_c \) the satellites merge into the Bragg peak. At temperature \( T_c \) only the narrow \( \alpha \) phase Bragg peak remains visible. Upon heating the \( \alpha \) phase persists until \( T_h \), a temperature very close to \( T_c \) so that the observation of the INC phase is difficult. Further temperature cycles were performed with very similar results on the surroundings of other Bragg spots such as (300), (301) and (103). A more detailed study of the coexistence state and of the \( q_0 \) behaviour performed on a larger sample with a special furnace allowing for a simultaneous measurement of the thermal expansion is reported in paper III [24] and discussed together with recent electron microscopy observations of the mixed state.

The continuous temperature behaviour of \( q_0 \) did not show any hysteresis to within the temperature resolution of the present experiment. This seems to establish the incommensurate nature of the modulation rather than the existence of a high-order superstructure.

Figure 11 synthesizes the present results quite well: we display \( Q \)-scans across the (103) Bragg peak in the \( \alpha^{*} \) direction for three different temperatures corresponding to the pure \( \beta \) phase (a), the homogeneous INC phase (b) and the coexistence state (c). The (103) Bragg intensity being rather weak a good satellite separation is obtained here. At \( T = T_i + 0.2 \) K diffuse inelastic humps at the future satellite positions are observed (Fig. 11a). Within the INC phase at \( T_i - 0.7 \) K two well resolved satellites appear (Fig. 11b) and move towards the central Bragg peak as the temperature is lowered. In figure 11c we see a scan performed in the coexistence state at \( T_i - 1.7 \) K where the satellites are hardly separated from the Bragg peak, the intensity of which is already overshooting as a result of extinction reduction due to the phase mixing.
4. Discussion.

We shall start by comparing the new quartz INC phase to the number of incommensurate phases discovered in recent years for various kinds of materials. In insulating materials the physical origin of the occurrence of INC phases complex but from the point of view of the mechanism involved one usually classifies the materials into two classes. For the class I incommensurate systems, symmetry properties imply the existence of a Lifshitz invariant \( \frac{\partial^2 \eta_2}{\partial x_1 \partial x_2} - \frac{\partial^2 \eta_1}{\partial x_1 \partial x_2} \) when the order parameter \( \eta \) is at least of dimension 2. This for example is the case for biphenyl [31] or K\(_2\)SeO\(_4\) and its isomorphs [32]. The class II systems do not have Lifshitz invariants because the order parameter is of dimension one. An INC phase may still occur if for some reason a soft mode presents a minimum somewhere in the Brillouin zone. This can be expected for example if a Lifshitz type invariant can be constructed by coupling the order-parameter to another degree of freedom \( \xi \) as first suggested by Levanyuk and Sannikov [32] to explain the INC phases of NaN\(_2\O\) [33] and Thiourea [34]. This type of coupling is forbidden at \( q = 0 \) and is linear in \( q \); hence it may lead to a minimum in a dispersion curve at some finite \( q \neq 0 \). Aslanyan and Levanyuk [14] have shown that a similar invariant exists in quartz and isostructural systems with the extra degree of freedom \( \xi \) being a strain \( u_{xy} \). This strain is already linear in \( q \) so that the coupling will be in \( q^2 \). The expected effect on the \( C_{66} \) elastic constant should be visible at small \( q \) and indeed the Brillouin measurements described in paper II confirm this point.

Most known transitions from the normal high temperature phase to an INC phase are second order, and quartz definitely conforms this rule: there is no sign of hysteresis at \( T_e \).

For the lock-in transition, however, the situation is more complex: while experimentally lock-in transitions are generally first order, the simplest theories based on a decoupling of the amplitude and phase fluctuations give a second order transition for the multi-soliton regime with a continuous logarithmic decrease of \( q_0 \) as the lock-in transition is approached.

\[
q_0 \sim \left| \log (T - T_e) \right|^{-\frac{1}{2}}.
\]

More elaborate theories, however, may lead to first order transitions [35, 36]. In general, however, class II INC systems are expected to exhibit rather narrow incommensurate temperature intervals so that the multisoliton regime has no time to develop and the lock-in transition is discontinuous [37]. This corresponds well to the case of NaN\(_2\O\) where \( T_1 - T_e \) is of only 1.5 K, no higher harmonics are observed and the lock-in transition is first order [33]. The situation in thiourea is more complex, the incommensurate temperature interval being much wider, both higher order satellites and intermediate lockings to \( q = \frac{1}{2} \) and \( \frac{1}{3} \) are observed [34]. Hence quartz is rather similar to NaN\(_2\O\) (\( T_1 - T_e = 1.3 \) K, no higher order satellites nor intermediate lockings).

It has been proposed [38] that the INC phase of NaN\(_2\O\) also results from a coupling away from \( q = 0 \) of the order parameter with an acoustic branch which will produce a minimum in the resulting dispersion curve near the zone centre. Without discussing the physical origin of such a minimum the NaN\(_2\O\) INC phase has recently been described with the following free-energy expression [39]:

\[
F = \frac{A}{2} \eta^2 + \frac{B}{4} \eta^4 + \frac{C}{6} \eta^6 + a \text{grad}^2 \eta + b \text{grad}^4 \eta + c \eta^2 \text{grad}^2 \eta
\]

with \( a < 0 \) in order to produce a minimum in the dispersion relation at \( q \neq 0 \). The development is taken to the sixth order in \( \eta \) to obtain a first order transition with \( B < 0 \) in the absence of the INC phase. The last term is required to describe a temperature dependent modulation vector. If an electric field is applied to NaN\(_2\O\) the INC phase disappears and there is a direct transition from the paraelectric to the ferroelectric phase. A similar formalism might be applicable to quartz too, but it seems difficult to describe the observed \( C_p \) behaviour (Fig. 1) by such a mean field treatment. It will be necessary to take into account the here observed diffuse premonitory scattering in the \( \beta \) phase as well as the intense diffuse scattering persisting in the INC phase. Only when further experiments will have allowed to elucidate the mechanism at the origin of this scattering will one be able to develop a convenient formalism. Of course the study of the effect of the field conjugate to the order parameter in the instance of quartz would be very instructive too. Such a field could be simulated by simultaneously applying an electric field \( E_x \) and a stress \( \sigma_{xx} \) which will result in an energy term of the form \( d_{xx} E_x \sigma_{xx} \) proportional to the order parameter [7]. A similar result could be obtained by using uniaxial stress in the \( YZ \) plane which can produce a contribution \( S_{\gamma \eta}, \sigma_{\gamma \eta}, \sigma_{x \eta} \) also proportional to \( \eta \) [7]. This latter coupling is probably most easily observed if we judge by the analogous effect on Dauphiné twinning [40].

The dynamical aspects of the commensurate to incommensurate transition of quartz are likely to be quite different from those of NaN\(_2\O\). Whereas the latter material exhibits an order-disorder transition produced by a 180° flipping of NO\(_2\) dipoles resulting in a relaxational type behaviour [39] the quartz situation is much less clear. A disordered structure has been reported for the high temperature \( \beta \) phase [22]. On the other hand Axe and Shirane [18] have interpreted their \( \beta \) phase neutron groups as due to an overdamped soft mode. In the \( \alpha \) phase a well defined and underdamped soft mode is consistently observed. The inelastic scattering centred at zero
energy transfer that we have observed along the [100] direction at small $q$ ($|q| < 0.05 a^*$) probably corresponds to the very low lying branch reported by Boysen et al. [21] which can be attributed to the interaction of a transverse acoustic and the soft mode of the transition. Further studies are necessary to confirm this point as well as to clarify the displacive or order-disorder character(s) of the transformation.

Relative to other insulating materials with INC phases quartz has the particular rotation symmetry of order six ($\beta$ phase). This allows at least in principle the existence of three modulation waves at $120^\circ$ and the presence of a third order term in the free energy:

$$\eta_{\alpha}, \eta_{\beta}, \eta_{\gamma}, \text{ with } \sum_{i=1}^{3} q_i = 0.$$  

Similar terms are found in the description of charge density wave materials such as 2 H-TaSe$_2$ and for adsorbed atoms on graphite.

A third order term has also consequences for the lock-in transition, the simple theory would lead to a second-order transition for a single $q$ modulation and to a possible first-order one in the case of three modulation waves [35]. But the consideration of the physical effects of this term needs further study [41].

Comparing the observed neutron satellite pattern which clearly exhibits a 6-fold symmetry to the electron microscopy pictures one would rather conclude to a triple $q$ state. While from the diffraction experiment one cannot distinguish between a true local 3 $q$ state or a 6-fold diffraction pattern which is in fact a superposition of 3 types of single $q$ regions (domains) the microscopy pictures show triangular patterns, although not always equilateral, which would tend to prove the existence of a true 3-$q$ state. One could indeed argue that the non ideal symmetry of the observed triangular objects is due to the rather large thermal gradients. An experimental check could be to apply a uniaxial stress in the XY plane which by breaking the elastic isotropy would induce a 1-$q$ state.

Indeed some observations by optical microscopy of the interface morphology under uniaxial stresses have shown the presence of parallel lines perpendicular to a [100] direction which might be related to a single-$q$ phase although the scale of 10 micrometers for the optical observation is quite different from the $\sim$ 125 Å of the incommensurate wave [42].

5. Conclusion.

The results described in this paper conclusively demonstrate the existence of an intermediate incommensurably modulated phase in quartz between the $\alpha$ and $\beta$ phases in agreement with the prediction of Aslanyan and Levanyuk [14]. The magnitude of the incommensurate modulation vector continuously decreases with temperature, a behaviour characteristic of many other incommensurate systems. Thus a new family of materials joins the already large number of incommensurate systems. There are several compounds which are analogous to quartz presenting the same phase diagrams with reconstructive phases (quartz, tridymite, crystobalite) and displacive $\alpha$-$\beta$ type phase transitions. Probably the most studied example is AlPO$_4$ [43] which is very closely related to quartz. Electron microscopy observations [13, 24] have shown, at the interface of the $\alpha$ and $\beta$ phases a structural pattern very similar to the one observed in quartz. It is thus very probable that AlPO$_4$ also has an incommensurate phase. It has also been reported that the tridymite phase of quartz also presents an incommensurate phase [44]. An incommensurate phase has also been reported in the 1-D superionic-conductor $\beta$-Eucryptite (LiAlSO$_4$) which has a crystal structure of the $\beta$-quartz type [45]. This INC phase is related to the modulation in the Li positions but tilting of the SiO$_4$ tetrahedra [46] analogous to the one occurring at the quartz $\alpha$-$\beta$ transition has been reported.

Altogether quartz seems to be the good prototype material to study an incommensurate-type behaviour of the entire family because very large single crystals of very good quality are available. We have recently obtained new results using Raman light scattering techniques which we will report on elsewhere [47].

Acknowledgments.

We acknowledge fruitful discussions with M. Vallade and technical assistance of R. Chagnon.

References