Synchrotron and light-scattering observation of the 1q incommensurate phase of quartz under zero stress

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We present evidence for the existence of a $1q$ incommensurate phase at zero stress in quartz, in a temperature interval of about 0.05 K, between the high-temperature β phase and the usual $3q$ incommensurate phase. White-beam synchrotron-radiation topography gives a direct picture of the three possible orthorhombic $1q$ domains. The coexistence of the two phases at the first-order $1q$-$3q$ transition has also been observed. Further information was obtained by light-scattering experiments, giving a peak of the scattered light intensity at the β-$1q$ transition, and a step increase of the intensity at the $1q$-$3q$ transition, and by light-depolarization measurements. These results on the observation of the zero-stress $1q$ phase are discussed in relation with predictions from mean-field theory and from considerations of fluctuation and impurity effects.

I. INTRODUCTION

For about 10 years, it has been known that an incommensurate phase with a triangular $3q$ structure, exists in quartz in a small temperature interval of 1.5 K around 850 K, in between the classical α and β phases.[1,2] In a recent high-resolution neutron study,[3] another incommensurate phase with a $1q$ unidimensional modulation was observed in one sample in an even smaller temperature interval of O (0.01 K) in between the $3q$ incommensurate phase and the high-temperature β phase. In this paper, we present the results of synchrotron radiation and optical experiments that fully confirm the systematic existence of this $1q$ phase.

At the present time many materials with an incommensurate phase have been discovered.[4,5] Sometimes, as a consequence of the symmetry of the high-temperature phase, incommensurate modulations can appear along n equivalent directions. Depending on the coupling between these waves, different incommensurate phase structures can occur. For example, in the case of hexagonal symmetry, different combinations of the three possible modulation waves can produce the following structures: (i) a $1q$ structure with a single modulation as found for example in Nd,[6] (ii) a $2q$ structure, produced by the superposition of two modulation waves, also observed in Nd,[6] (in these two cases, the incommensurate phases have an orthorhombic symmetry, and there is a domain structure, corresponding to the three possible directions of the orthorhombic strain), and (iii) $3q$ structures, produced by the superposition of three waves. Depending on the relative phase of these waves, several structures are possible, as found for example in 2H-$TaSe_2$.[7]

In a Landau theory, the choice between the different structures depends on the balance between different high-order terms in the free-energy expansion and transitions between different structures can exist as a function of temperature, as found in 2H-$TaSe_2$,[8] or under the effect of a symmetry-breaking field, as in Nd.[6]

In quartz, a phase transition from the usual $3q$ incommensurate phase to a $1q$ phase has indeed been observed under the application of an uniaxial compressive stress along the ⟨100⟩ direction of the hexagonal reciprocal lattice.[9] However, most of the previous studies on the incommensurate phase of quartz described in several review papers[10–12] were related mainly to the usual $3q$ phase: The existence of a triangular $3q$ structure has been observed directly in several electron microscopy experiments[12] (even before the understanding of the incommensurate origin of this structure[13]). These observations have also shown that the triangular structure is rotated in the basal plane by an angle ϕ of a few degrees from the $\langle 100 \rangle$ directions of the reciprocal hexagonal lattice. Rotation domains corresponding to the two possible rotation senses of ϕ are also observed. In diffraction experiments, the rotation domains produce a splitting of satellite spots, which has been observed in x-ray,[14] neutron,[3,15] and electron microscopy[16] experiments. The temperature dependences of the angle ϕ and of the modulus of the modulation wave vector q_i measured in an x-ray experiment[14] are in fair agreement with the results of a high-resolution neutron-diffraction experiment[15] given here: At T_{i3}, the higher existence temperature of the $3q$ phase, $\phi=1°$ and $q_i=0.0322a^*$ (where a^* is the unit of the reciprocal lattice); the finite value of ϕ at T_{i3} shows the slightly discontinuous character of this transition. At T_c, the transition temperature from the $3q$ phase to the α phase, $\phi=6.1°$ and $q_i=0.0215a^*$. In recent years, the complex effects of impurities (pinning, global hysteresis, memory effects, regime of discontinuous variations) have been observed by optical[17,18] and synchrotron-radiation[19] experiments. A determination of the phonon-dispersion curves of the β phase[20] has shown that the existence of the incommensurate phase of quartz is explained by a gradient interaction between the soft mode of the α-β transition and an acoustic mode, as suggested in the theoretical work of Aslanyan and Levanyuk.[21]

Concerning the $1q$ phase, it was observed in a neutron experiment[9] under the application of an uniaxial compressive stress along $\langle 100 \rangle$, giving a phase diagram roughly in agreement with a Landau theory analysis.[9,22] More complete results on this phase diagram were obtained by Bachheimer from optical experiments.[23] The stress-induced $1q$ phase has also been observed in synchrotron-radiation,[24] light-scattering,[25] and electron microscopy[26] experiments. Several theoretical works[27–29] have studied the effects of fluctuations on the β-incommensurate transition. However previous experiments were not sensitive enough to allow a test of these theories and of possible deviations from the mean-field theory: The simplest Landau expansion,[9,22] predicts that the domain of existence of the $1q$ phase is proportional to the applied stress and that there is *no* $1q$-$3q$ transition at zero stress.

The aim of this work is to present a more detailed study on different well characterized samples of the zero-stress $1q$ phase, observed in neutron experiments.[3,15] First, we describe the results obtained in a synchrotron-radiation experiment (already reported in a short conference proceeding[30]); then we present the results obtained from optical experiments and finally we discuss these results in relation to previous theoretical works.

II. SYNCHROTRON-RADIATION EXPERIMENTS

A. Experimental setup

The synchrotron-radiation experiments were performed at the LURE topography station using the white-beam Laue method.[31] This technique was introduced by Gouhara and co-workers[2,14] for the study of the incommensurate phase with observations of the incommensurate phase of quartz, using a powerful x-ray generator. It has been used with synchrotron radiation to observe the incommensurate phases of quartz[24] and of $AlPO_4$.[32] A major interest of this method is that one can make observations in reciprocal space as well as in direct space: With a narrow beam, one gets a high-resolution diffraction pattern of the sample, while with a large beam one gets topographic pictures of the sample, using either usual lattice reflections or satellite peaks. The experimental setup shown in Fig. 1 was similar to the one already described[19] for a study of the discontinuous variation of the modulation wave vector and used the same furnace and temperature control with a 1-mK resolution. To prevent the superposition of satellite pictures, we use an incident beam limited by a horizontal slit of 6×0.2 mm^2. To increase the resolution, the photographic film (Kodak AX) was put at a large distance from the sample (1.5–2 m). The results reported here were obtained around the (111) reflection with an incidence angle of 8° of the synchrotron beam relative to the $\langle 100 \rangle$ sample normal (Y cut); this corresponds to a radiation wavelength $\lambda\sim0.07$ nm. In some cases, simultaneous optical measurements were performed on the quartz samples to locate the transition temperatures.[18] The positions of satellite reflections in the reciprocal space are shown in Fig. 2(a) for the three possible orthorhombic domains (q_1,q_2,q_3) of the $1q$ phase and for the two possible rotation domains ($+\phi$ and $-\phi$) of the $3q$ phase. The corresponding diffraction patterns given by a computer simulation, for the experimental conditions given above, are shown in Fig. 2(b). The two samples investigated here have been used in a previous synchrotron-radiation experiment;[19] both were (100) plates of $10\times10\times1.5$ mm^3 cut from synthetic crystals which have been the subject of detailed optical studies.[18] $S5$ is a standard quality sample with 1.5 ppm of Al and around 10^3 dislocations/cm^2, while $S3$ is a very pure sample with less than 0.1 ppm of Al and a few dislocations/cm^2.

B. Experimental observations on a standard quality sample $S5$

A typical diffraction pattern obtained around the (111) lattice reflection in the $3q$ phase at $T_{i3}-0.04$ K is shown in Fig. 3(a); it is similar to that given in our previous paper.[19] The central black rectangle is the picture of the cross section (6×1.5 mm^2) of the sample by the beam.

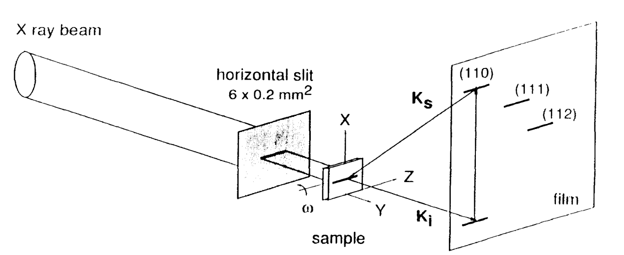

FIG. 1. Experimental setup for the white-beam Laue method using synchrotron radiation at LURE (see text).

The grey rectangles are satellite reflections corresponding closely to the pattern of Fig. 2(b). Due to the small intensity of incommensurate satellites close to T_{i3}, the temperature is kept constant for 25 mn, to get a good photographic contrast. A splitting of the satellites produced by the existence of $\pm\phi$ rotation domains is observed. However, it is not possible to resolve any structure inside the satellite pictures, indicating that the rotation domains have sizes smaller than the experimental resolution of 0.2 mm. Only ten satellites reflections are present, instead of 12, as the $+\phi$ and $-\phi$ satellites at $+q_1$ and at $-q_1$ are too close to be resolved. A good agreement with the simulation is obtained for $q_i = 0.0320a^*$ and $\phi = \pm 1°$. (Relative variations of $\pm 0.0001\ a^*$ for q_i and of $\pm 0.1°$ for ϕ can be measured, however the uncertainty on the absolute value of q_i, which depends on the accurate measurements of all the geometrical parameters, is larger by one order of magnitude. We recall that in more accurate neutron measurements using a two-crystal diffractometer,[15] Mogeon has found $q_i = 0.0322a^*$ at T_{i3}).

Fig. 3(b) shows the diffraction pattern obtained after a heating of 0.07 K, so that the sample is in the $1q$ phase at $T_{i3} + 0.03$ K. Now only six satellites are observed: The computer simulation shows that, within the experimental incertitude of $\pm 0.0001a^*$, there is no change of $q_i = 0.0320a^*$ but that $\phi = 0°$, as expected for $1q$ satellites. The observation of six satellites in the $1q$ phase, shows that the three orthorhombic domains (q_1, q_2, q_3) are present in the sample. Some structures are observed in the satellites pictures, showing that some $1q$ domains have sizes of the order of 1 mm. But the contrast is not good enough to get a clear representation of the shapes of the orthorhombic domains. Other observations have shown that the $1q$ phase is present in a 0.06-K temperature interval between β and $3q$ phases.

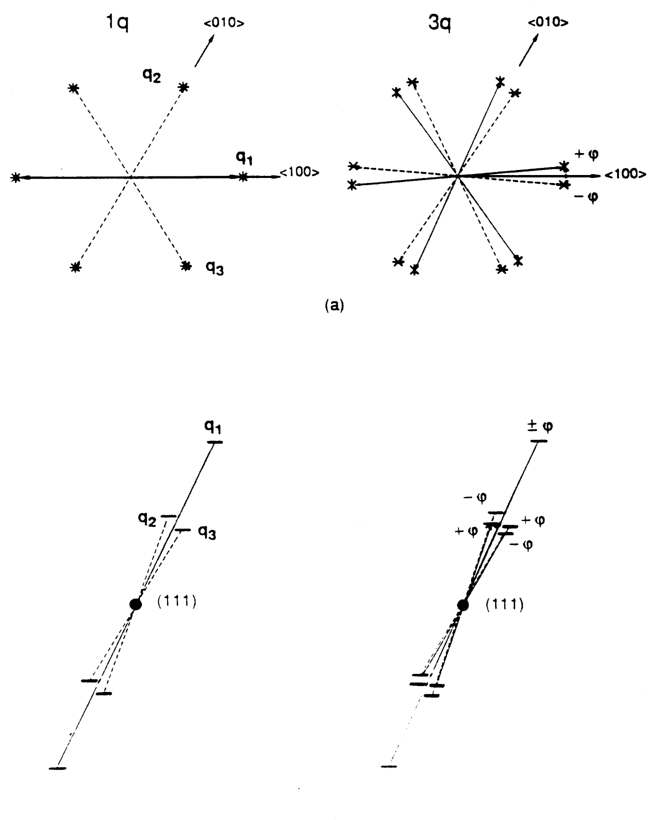

FIG. 2. Positions of satellite reflections in the $1q$ and $3q$ incommensurate phases of quartz: (a) in the hexagonal reciprocal space, (b) on the photographic plate around the (111) reflection, for experimental conditions corresponding to those of Fig. 1, with an incidence angle $\omega = 8°$. In the $1q$ phase, the full arrows correspond to the single orthorhombic domain q_1. The two other possible domains q_2 and q_3, with modulation wave vectors rotated by 60 and $-60°$, respectively, are indicated by dashed arrows. In the $3q$ phase, the full arrows correspond to the six satellites of a $+\phi$ domain, while the dashed arrows correspond to the $-\phi$ rotation domain.

C. Experimental observations on a very pure sample $S3$

In Fig. 4, we present more detailed results obtained upon cooling on the very pure sample $S3$, using the same experimental setup. However the Z axis of the sample was vertical so that the whole diffraction pattern is rotated. The topographic pictures were obtained at the four different temperatures given on the phase diagram in the top inset of Fig. 4.

Figure 4(a) is obtained in the β phase at $T_{i1} + 0.02$ K

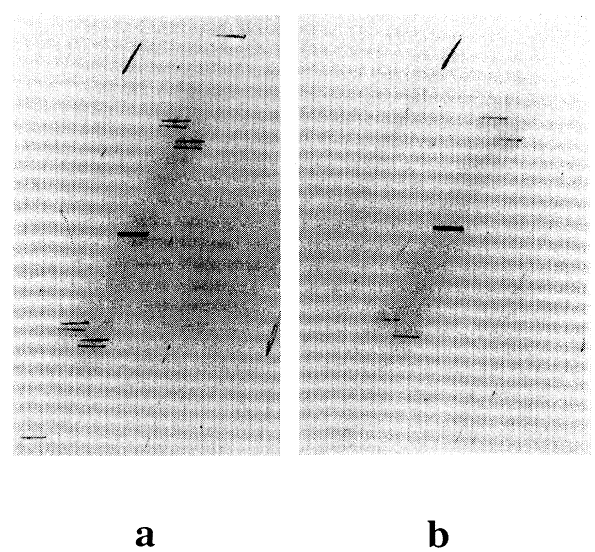

FIG. 3. Synchrotron-radiation pictures of the $3q$ and $1q$ phases in a synthetic quartz sample $S5$, of standard good quality, obtained with the experimental setup of Fig. 1. (Parasitic spots or streaks are due to the aluminum windows of the furnace). (a) In the $3q$ phase, at $T_{i3} - 0.04$ K; the sample has a fine structure of rotation domains (with unresolved sizes less than 0.2 mm), producing a global splitting of satellite lines. (b) In the $1q$ phase, at $T_{i3} + 0.03$ K; in this sample, domains with the three orthorhombic strains (q_1, q_2, q_3) are present, although q_1 domains are less intense than q_2 and q_3 domains; some domain sizes are around 1 mm.

(where T_{i1} is the transition temperature between the β phase and the $1q$ incommensurate phase). One observes only the (111) lattice reflection, with a shape corresponding to the projection along the diffracted beam of the section of the sample by the incident beam. Diffuse anisotropic streaks are also observed, at six equivalent positions corresponding to $q_i=(0.032,0,0)$. These streaks are due to the quasielastic scattering produced by the soft mode of the β-incommensurate transition, which has been studied in a recent inelastic neutron-scattering experiment.[20]

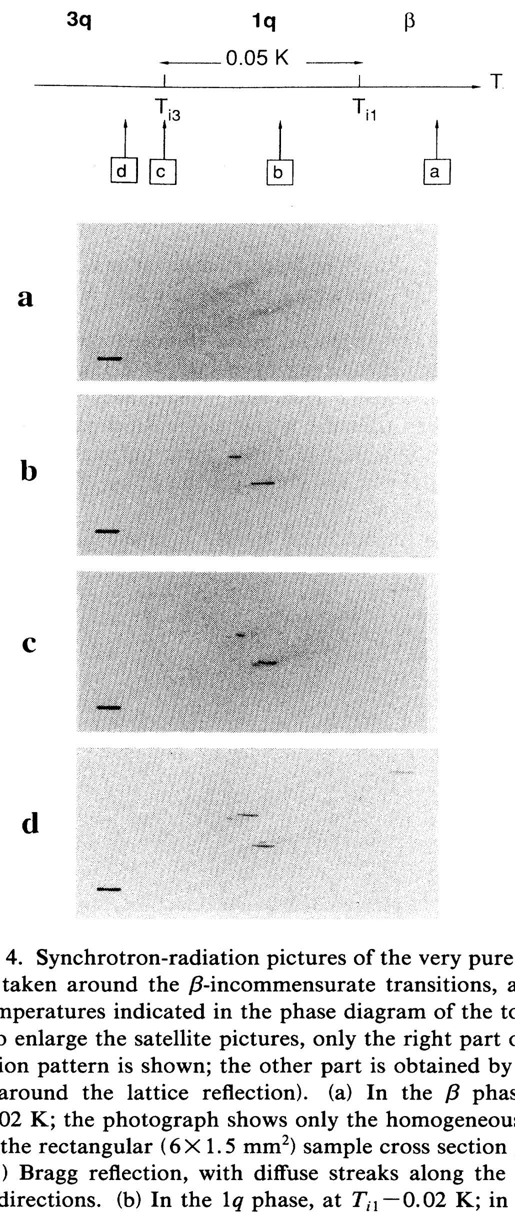

FIG. 4. Synchrotron-radiation pictures of the very pure sample $S3$ taken around the β-incommensurate transitions, at the four temperatures indicated in the phase diagram of the top inset. (To enlarge the satellite pictures, only the right part of the diffraction pattern is shown; the other part is obtained by symmetry around the lattice reflection). (a) In the β phase, at $T_{i1}+0.02$ K; the photograph shows only the homogeneous picture of the rectangular (6×1.5 mm^2) sample cross section given by (111) Bragg reflection, with diffuse streaks along the three $\langle\zeta 00\rangle$ directions. (b) In the $1q$ phase, at $T_{i1}-0.02$ K; in addition to the Bragg reflection, the photograph shows $1q$ satellites corresponding to two orthorhombic domains (q_2 and q_3) with $q_i=0.0320a^*$ and $\phi=0$. (c) At $T_{i3}=T_{i1}-0.05$ K, the transition temperature between the $1q$ and $3q$ phases; the photograph shows the coexistence between the $1q$ phase [with the same orthorhombic domains structure as in (b)] and the $3q$ phase (with a rotation domain structure). (d) In the $3q$ phase, at $T_{i3}-0.01$ K; rotation domains are present corresponding to $\phi=\pm 1°$; each domain produces six satellites corresponding to $\pm q_i=0.0320a^*$.

Figure 4(b) shows a picture obtained in the incommensurate $1q$ phase at $T_{i1}-0.02$ K. In addition to the (111) lattice picture one observes four satellite pictures corresponding to $\pm q_2$ and $\pm q_3$ positions, while there is no satellite at $\pm q_1$: In this sample, there are only two orthorhombic domains corresponding to q_2 and q_3 modulation waves. The q_1 domain (where q_1 is perpendicular to the sample surface) is absent and only a residual diffuse streak is observed. This may be the results of surface stresses produced by cutting and polishing the sample. Comparison of the photographic picture with computer simulation gives $q_i=0.0320a^*$ and $\phi=0°$. The absence of rotation is a specific feature of the incommensurate $1q$ phase, which was used to characterize the $1q$ phase in the previous neutron-diffraction experiment.[3] In addition to a high-resolution measurements of satellite positions, the present synchrotron-radiation experiment gives a direct picture of the shapes of $1q$ domains: In this good quality $S3$ sample, the $1q$ domains have simple rectangular shapes with the size of several mm. Topographies obtained with a vertical translation of the incident beam, show that these shapes extend for several mm along the vertical Z direction. No change of the domain shapes was observed as long as the sample remains in the $1q$ incommensurate phase.

Figure 4(c), obtained by a further cooling to $T_{i1}-0.05$ K corresponds to the T_{i3} transition temperature between the $1q$ and the $3q$ phases and shows the coexistence of the two phases: On the right side of the satellite pictures one observes the same $1q$ domains as in Fig. 4(b), while on the left side one observes the characteristic pattern of the $3q$ satellites with the presence of well resolved rotation domains. The largest part corresponds to a $+\phi$ domain (with six similar pictures given by the six equivalent satellites), the smaller one to $-\phi$ (also with six equivalent pictures). The corresponding computer simulation gives $q_i=0.0320a^*$ and $\phi=1°$. The observation of the discontinuous rotation of 1° of ϕ is a direct proof of the small first-order nature of the $1q$-$3q$ transition.

Finally Fig. 4(d), obtained at $T_{i3}-0.01$ K, shows that the whole sample is in the $3q$ phase, and gives a full picture of the rotation domains also with mm size, typical of good quality samples. These results give a high-resolution determination of the wave vector parameters in $1q$ and $3q$ phases. The coexistence of $1q$ and $3q$ diffraction patterns confirms the first-order nature of the transition. This coexistence was observed only on one picture, and was stable during at least 25 mn. A temperature change of 0.01 K is enough to go into an homogeneous phase; in this case the horizontal temperature gradient was smaller than 0.01 K on 5 mm.

These observations on two samples fully confirm, but with a better resolution, the existence of the $1q$ phase observed in a previous neutron experiment. The $1q$ temperature interval observed here (0.05–0.06 K) is larger than that of 0.025 K of the neutron experiment, probably due to a smaller value of the thermal gradient on these smaller sample. Furthermore, this experiment gives direct pictures of the shape of the orthorhombic domains of the $1q$ phase and of the rotation domains of the $3q$ phase.

III. LIGHT-SCATTERING EXPERIMENTS

The incommensurate phase of quartz has been the subject of several light-scattering studies, which show the variations of Raman,[33,34] Brillouin,[35] and Rayleigh[36] scattering around the α-incommensurate-β transition temperatures. In the β phase above T_{i1}, several features are observed in the low-frequency spectrum: a broad quasielastic peak due to the fluctuations of the order parameter (with a full width of 500 GHz), narrow Brillouin peaks from the acoustic modes (between 15 and 30 GHz), and an elastic peak due to defects (with instrumental resolution). In the incommensurate phase, the intensity of the broad quasielastic peak increases and new sharp structures appear around 250 GHz, which have been attributed[37] to the effect of the folding of acoustic modes by the modulation at $q_i \sim 0.03a^*$; the frequency of the longitudinal acoustic mode in the Brillouin spectrum decreases; the intensity of the elastic peak increases and a dynamic central peak appears around T_i.[36] Previous studies of the temperature variation of the central peak have shown the presence of two peaks around the β-incommensurate transition.[36,38] Abe *et al.*[25] have observed that the separation of these two peaks increases linearly as a function of a compressive stress applied along the Y axis, giving a phase diagram similar to that obtained in the neutron experiment.[9] (For the optical experiment, we use orthogonal axis with OY and OZ parallel, respectively, to the $\langle 100 \rangle$ and $\langle 001 \rangle$ axis of the reciprocal lattice). One can then associate the two peaks to T_{i1} and T_{i3}. In this section we present zero-stress measurements of these two peaks on several samples.

A. Experimental setup

We measured light scattering at right angle from a 0.5-W argon laser beam in the $X(ZZ)Y$ configuration; the scattered light is analyzed with a high-resolution grating monochromator of 2-m focal length. The samples of $10\times10\times10$ mm^3 were heated in the high stability furnace used in the synchrotron-radiation experiment. (The same setup has also been used for a study of the low-frequency scattering in the incommensurate phase[37].) Measurements were performed on five samples: Samples $S'3$ and $S'5$ were cut in the same synthetic crystals as the synchrotron samples; $A2$ and $A3$ were cut in japanese synthetic crystals of standard quality (with about 5 ppm of Al); N(Al), cut in a natural crystal with 180 ppm of Al, has been used in previous optical measurements.[39] The infrared absorptions α_{3500} of the four synthetic samples at 3500 cm^{-1} (linearly related to the concentration of OH bond[18]) are given in Table I.

B. Experimental results

Typical Brillouin spectra obtained on sample $S'3$ at room temperature (a) and in the β phase at $T_{i1}+0.1$ K (b), are shown in Fig. 5: At room temperature, one observes the two longitudinal peaks (around ± 30 GHz) with low-frequency shoulders, due to the transverse-acoustic modes. The central peak (with instrumental width) is mainly due to parasitic scattering from the furnace and from sample surfaces, as bulk defect scattering is very weak in this good quality sample. Above T_{i1}, the main change is the increase of the elastic peak (due to a greater sensitivity to bulk defects) and the apparition of a dynamical central peak between the Brillouin lines.[36]

TABLE I. Transition temperatures of four synthetic quartz samples determined from light-scattering experiments. $T_{i1}-T_{i3}$ and $T_{i3}-T_c$ are the temperature intervals of existence, on cooling, of the $1q$ phase and of the $3q$ phase, respectively; T_h-T_c is the hysteresis width of the first-order transition between the α phase and the $3q$ incommensurate phase; α_{3500} is the OH infrared absorption at 3500 cm^{-1}.

	$T_{i1}-T_{i3}$ (K) ($1q$)	$T_{i3}-T_c$ (K) ($3q$)	T_h-T_c(K)	α_{3500} (cm^{-1})
$S'3$	0.056	1.39	1.28	0.029
$A2$	0.054	1.33	1.13	0.037
$A3$	0.053	1.25	1.04	0.049
$S'5$	0.060	1.27	0.74	0.054

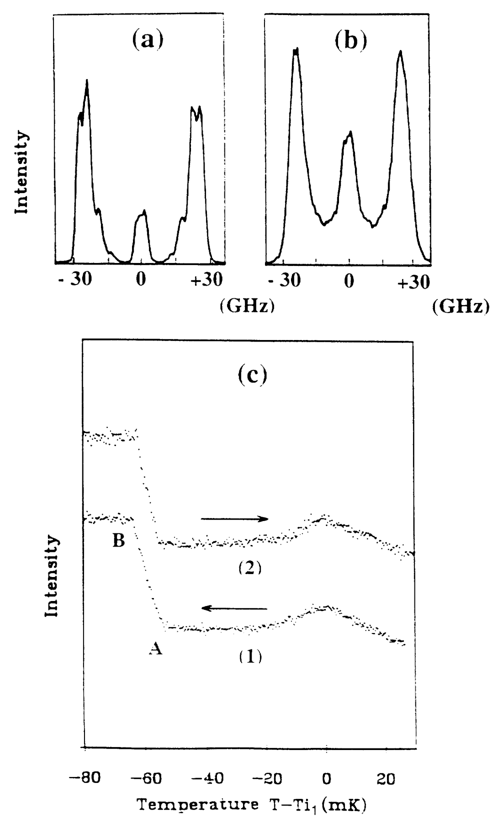

FIG. 5. Measurements of the quasielastic light-scattering intensity in the very pure quartz sample $S'3$, around the β-incommensurate transitions. (a) Brillouin spectrum at room temperature. (b) Brillouin spectrum in the β phase, at $T_{i1}+0.1$ K. (c) Temperature variation of the quasielastic scattering upon cooling (curve 1) and heating (curve 2). The peak maxima correspond to T_{i1}, while the step discontinuities correspond to T_{i3}.

The temperature variation of the quasielastic scattering (integrated within ±15 GHz) around the β-incommensurate transitions is given in Fig. 5(c) upon cooling (curve 1) and upon heating (curve 2). (The measurements were performed with rates of temperature variation between 100–300 mK/h, without any influence on the results). On cooling from the β phase, there is first a peak of the scattered light intensity, and then at a temperature lower by 0.05 K, there is a jump of this scattered intensity. The same variation is obtained on heating (curve 2). By comparison with synchrotron results, and with the previous light-scattering measurements under uniaxial stress,[25] we can confirm the identification of the temperature of the higher-temperature peak with T_{i1}, and the temperature of the step with T_{i3}. This experiment confirms the existence of the 1q phase in a temperature interval of 0.05 K, between the β phase and the usual 3q incommensurate phase. The β-1q transition at T_{i1} appears rather continuous, while the step at T_{i3} is in agreement with the existence of a first-order 1q-3q transition. The linear variation of the scattered intensity from A to B suggests that a narrow 1q-3q interface crosses the laser beam with a constant velocity. Indeed we have observed a broadening of this linear variation region when we increase the scattering volume along the laser beam from 0.6 to 2.5 mm (with a beam diameter of 0.1 mm). The slope of AB corresponds to an horizontal temperature gradient of about 0.01 K/mm. Similar results were obtained on the four synthetic quartz samples, as shown for example by curve (a) of Fig. 6 for sample $S'5$. However this sample is inhomogeneous and a distorted curve (b) is obtained after a lateral translation of the laser beam by 2 mm. [The results obtained on another sample N(Al) (plotted in Fig. 5 of Ref. 40) were rather different as only

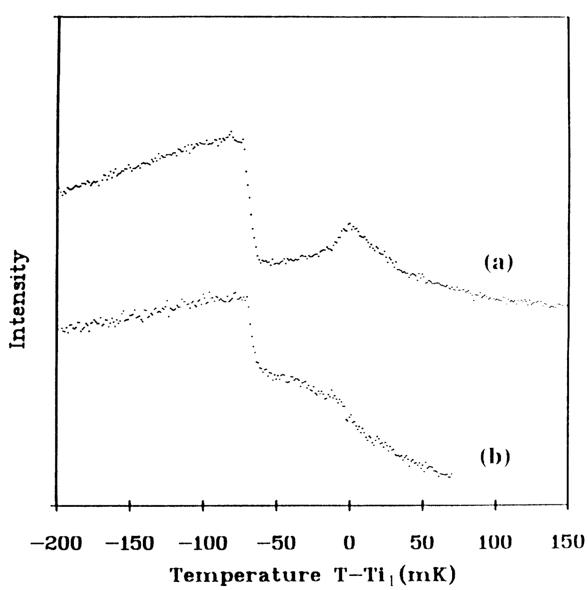

FIG. 6. Temperature variation of the quasielastic light scattering in a standard quality sample $S'5$ around the β-incommensurate transitions. (a) At a good quality position of the sample. (b) At a bad quality position, after a 2 mm translation of the laser beam.

a single large peak was observed at the β-incommensurate transition—so that in this case the presence of a 1q phase could not be confirmed].

The results obtained during these measurements for the different transition temperature intervals are given in Table I. (The maximum difference with previous measurements,[18] is about 0.2 K, except for samples $S'5$ where previously $T_h - T_c = 1.20$ K was found; this variation can be due to a modification of the temperature gradients in the furnace, or to sample inhomogeneities). In the four good quality synthetic samples, similar light-scattering curves are obtained, showing the existence of a 1q phase in a temperature interval of 0.05 K between the β phase and the usual 3q incommensurate phase.

C. Discussion of optical experiments

The scattered light intensity measured in the present experiment is due to several contributions: There is an elastic intensity due to crystal defects, which changes with temperature, following probably the variation of elastic constants; another contribution comes from the dynamical central peak[36] due to scattering by fluctuations, which is expected to be maximum at the second-order β-1q transition at T_{i1}, where the frequency of the incommensurate soft mode goes to zero.[20] Finally, a new source of elastic scattering can be produced by incommensurate phase defects, such as domain walls or "deperiodization" lines.[41] Indeed 1q domains with different orthorhombic strains, produce a slight modification of refractive indices which can be a new source of light scattering. Rotation domains in the 3q phase are expected to have the same indices, but some perturbations can appear at domain walls, which, due to photoelastic effects, can be increased by temperature gradient or residual stresses. However, domain scattering is very sample dependent; in the very good $S'3$ sample, domains in 1q and 3q phases are of mm size, and will produce little light scattering, while in $S'5$ larger effects can be expected from smaller domains. Finally under usual temperature conditions there is always a temperature gradient in the sample, which produces a variation of the modulation wave vector creating deperiodization lines. Depending also on the sample quality, these lines can be randomly dispersed or associated, forming grain boundaries as observed by synchrotron topography.[19] Recently, some of us,[40] have observed a memory effect in the light-scattering intensity of the impure natural sample N(Al), which indicates that some defects, of the incommensurate phase, are at the origin of some light scattering. Finally, we recall the existence of the strong opalescence observed at T_c, due to some unknown interaction between the incommensurate structure and the α phase.[42] Other optical techniques have been used to study the β-incommensurate transitions. Although very sensitive to the change of the incommensurate modulation in the 3q phase, birefringence is not very useful to study the β-incommensurate transition, as the curve of birefringence as a function of temperature shows only a smooth curvature in this region.[18] Some small anomalies are sometimes observed around T_{i1} or T_{i3}, but they are not reproducible. However under uniaxial stress the 1q phase can be observed by birefringence measurements,[23] and is characterized by a linear temperature variation of the birefringence, which is quite different from the nonlinear variation of the 3q phase. More sensitive measurements of the depolarization of light propagating along the optical Z axis[23,43] have been performed on the four synthetic crystals (the measured intensity is related to the small transverse component of the elliptical polarization produced by induced strain birefringence). Results are plotted in Fig. 7. In samples $S3$ and $S5$, two peaks are clearly observed on the depolarization curves, and correspond to the transitions from the β to 1q phases and from the 1q to the 3q phases as verified by simultaneous x-ray synchrotron-radiation measurements. They confirm the existence of the 1q phase on a temperature interval of about 0.05 K. But this technique is very sensitive to defects as only an erratic behavior is observed in samples $A2$ and $A3$, probably as a consequence of the temperature variation of residual strains inside the samples. So although the light depolarization technique allows in principle the observation of the β-1q and of the 1q-3q transitions, its high sensitivity to defects makes it not very suitable for systematic studies of these transitions.

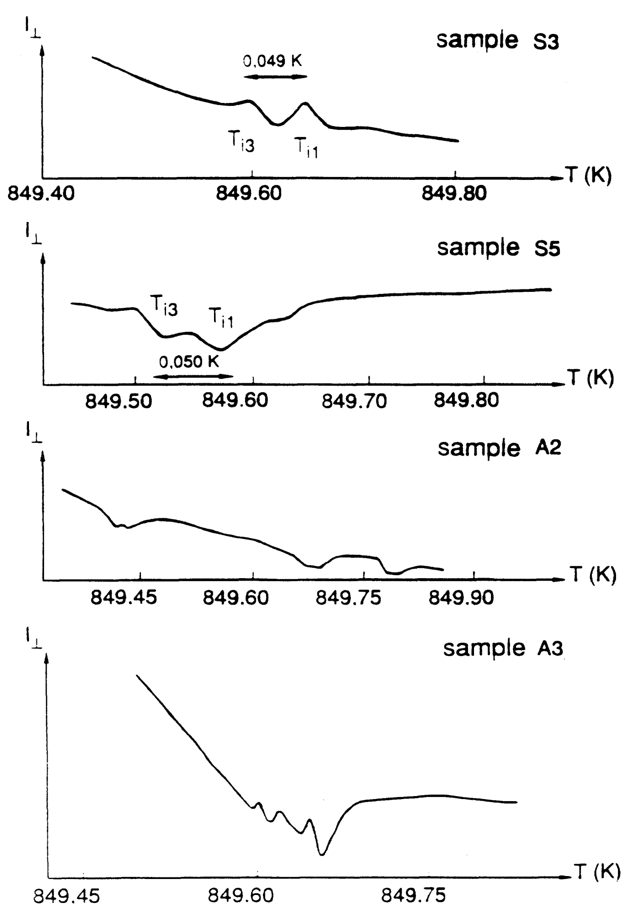

FIG. 7. Measurements of the depolarization of the light propagating along the optical axis for the four synthetic samples. For $S3$ and $S5$, two peaks associated to the transition temperatures are clearly observed, while for $A2$ and $A3$, only an erratic behavior is observed.

In conclusion, at least for good samples, the variation of the quasielastic light scattering gives a clear determination of the existence of the 1q phase with the advantage of measurements in small internal volumes of about $1\times0.1\times0.1$ mm^3, which allows a spatial study of the sample. For the four synthetic samples measured in this experiment, one observes the 1q phase in a temperature interval of 0.05 K. With the previous observation of similar light-scattering features in Japan (although on 0.1 K),[24,36] there is now a good evidence for the systematic existence of the zero-stress 1q phase observed by neutron scattering.[3]

IV. DISCUSSION

In this part, we first recall the results of the mean-field theory of the incommensurate phase of quartz, then we present the modifications suggested by several studies of fluctuation effects, and finally we discuss some possible effects of chemical impurities. As developed in review papers,[10,11] the α-β transition of quartz can be well described by the Landau theory: In the α phase, the order parameter η, of dimension $n=1$, is associated at the macroscopic level to the piezoelectric constant d_{xxx} and at the microscopic level to the rotation angle of SiO_4 tetrahedra; $\eta=0$ in the β phase, $\eta=6°$ at the first-order α-β transition, increasing to 16° at room temperature. Aslanyan and Levanyuk[21] have predicted the existence of an intermediate incommensurate phase, between the classical α and β phases, from the existence in the Landau free energy of a gradient coupling term $[(u_{xx}-u_{yy})(\partial\eta/\partial x)-2u_{xy}(\partial\eta/\partial y)]$, between the strains u_{ij} and the gradient of the order parameter η. The choice between a 3q or a 1q structure for the incommensurate phase, depends on the competition between various higher-order terms.[9,22,44] One can find some combinations of the high-order coefficients, which induce a 3q phase, as observed experimentally. In this simple approach, where only the coefficient of η^2 is temperature dependent, there is no possibility of a zero-stress transition from the 3q phase to the 1q phase. However, a simple extension[9,22] of this model shows that the application of a uniaxial stress σ_{yy} favors the 1q phase, due to a linear coupling between the stress and the orthorhombic strain of the 1q phase. The β-1q and 1q-3q phase boundaries are straight lines in the T-σ_{yy} plane, which cross on the T axis at $\sigma_{yy}=0$. Clearly this point is rather singular as three phases (β, 1q, and 3q) coexist. One can expect that the degeneracy of this point can be lifted by various perturbations. The present results show indeed that at zero stress there is no crossing of β-1q and 1q-3q transition lines, but that (at least in good quality samples) the 1q phase is systematically present in a temperature interval of 0.05 K between T_{i1} and T_{i3}. In a Landau theory, the existence of a 1q phase between the β phase and the 3q phase at $\sigma_{yy}=0$, can only be obtained by introducing new (and rather arbitrary) nonlinear terms.

Several attempts have been made to explain the existence of a 1q-3q transition by considering the intrinsic effects of fluctuations: Assuming that the transition is continuous, Mukamel and Walker[27] predicted a critical variation of the rotation angle ϕ of the modulation wave vector of the 3q phase given by $\phi=(T_i-T)^{\nu}$, where ν is the exponent of the inverse correlation length.

In a following paper,[28] Biham *et al.* performed a renormalization analysis of an Hamiltonian describing the phase transition of quartz (with an order parameter of dimension $n=6$ for the 3q phase). They found no fixed point, which indicates a first-order transition at the β-3q transition—in better agreement with the experimental results for $\phi(T)$, but they did not consider the possibility of an intermediate 1q phase.

The possibility of β-1q-3q transitions has recently been considered by Borckmans, Dewel, and Walgraef[29] who performed a perturbation analysis of fluctuation effects. They found that for some values of the parameters of the initial Hamiltonian, a 1q phase appears (at zero stress) between the β and the 3q phases, and that all the transitions (1q-3q but also β-1q) are first order. The predicted phase diagram is now closer to the present experimental results, although the measured β-1q transition is rather continuous; but a very small first-order discontinuity cannot be excluded. However, it appears that in their perturbation treatment, Borckmans, Dewel, and Walgraef consider the effects of the third-order term $(\eta_{q_1}\eta_{q_2}\eta_{q_3})$ on the fluctuations only for the transition to the 3q phase and not for the transition to the 1q phase, introducing an artificial dissymmetry in their calculation.

Another approach has been worked out by Parlinski, Kwiecinski, and Urbanski[45] using computer simulations for a simplified model with hexagonal symmetry (not exactly applicable to quartz because all incommensurate phases occur with $\phi=0$). Incommensurate 3q and 1q phases are found in the phase diagram and detailed pictures of the various incommensurate phases and of their transitions are obtained, but the 3q phase is found at a higher temperature than the 1q phase.

At the present time, it appears that the results obtained from the consideration of fluctuation effects are rather limited. Furthermore, treatment of the effect of symmetry-breaking stress have not been attempted.

We now consider the effect of defects on the incommensurate phase of quartz. A first possibility is related to the effect of internal stresses: Uniaxial components in the X-Y plane can lift the degeneracy of the β-1q-3q phase transitions and lead to a stress-induced 1q phase. However such stresses would probably be different in various samples and this is not in agreement with the reproducible value of 0.05 K found in the present experiment. Furthermore, the dissymmetric pattern of the 1q domain structures observed in synchrotron-radiation experiments in $S3$ is probably due to such internal stresses; these stresses seem just large enough to influence the orientation and the shape of 1q domains, but not to change significantly the phase diagram.

Another possibility comes from the presence of chemical impurities: It is well known that such defects produce a large change in the behavior of crystals at phase transitions,[46] often similar to that of fluctuations. For an $n=6$ order parameter such effects may be rather large, but to our knowledge, no detailed theoretical examinations of this question have been reported. Although quartz is often considered as a pure material, some impurities are always present:[18] In general, natural samples contains some Al impurities with concentrations of a few 10^{-5}, while in standard good synthetic samples, the Al concentration is around 10^{-6}, and can even be lower than 10^{-7} for very pure materials, such as $S3$. However, due to the hydrothermal growth process some traces of water are always present, as detected by the infrared OH absorption. The present results on four synthetic samples, show that the β-1q-3q temperature phase diagram is not very sensitive to small change in the concentrations of these impurities; on the other hand the domain structures (rotations domains in the 3q phase, orthorhombic domains in the 1q phase) seem to be more sensitive to the presence of such impurities (or may be to the presence of dislocations). Such sensitivity is also found in the irreversible temperature behavior of the 3q phase (global hysteresis, memory effects. . .).[18] The larger impurity concentrations found in natural samples can modify the β-incommensurate phase diagram, but these small effects may be masked by the difference of impurity concentrations in different growth sectors.[47]

In this paper we have observed the systematic presence of the 1q phase, in a small temperature interval of 0.05 K, between the β phase and the 3q phase, for four good quality synthetic samples; the presence of 1q phase appears as an intrinsic feature of the zero-stress phase diagram of quartz, although at the present time, no theoretical model is able to predict the observed behavior.

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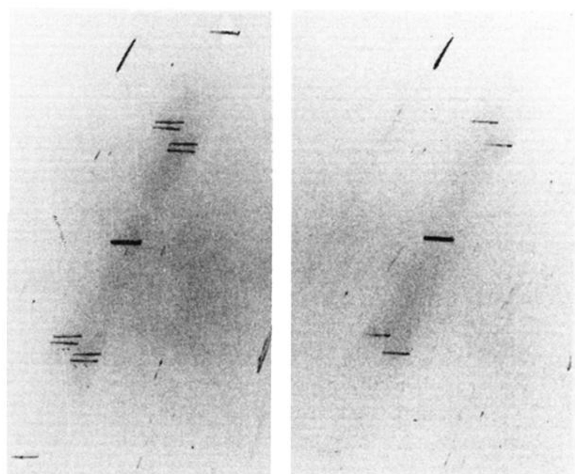

a **b**

FIG. 3. Synchrotron-radiation pictures of the $3q$ and $1q$ phases in a synthetic quartz sample $S5$, of standard good quality, obtained with the experimental setup of Fig. 1. (Parasitic spots or streaks are due to the aluminum windows of the furnace). (a) In the $3q$ phase, at $T_{i3}-0.04$ K; the sample has a fine structure of rotation domains (with unresolved sizes less than 0.2 mm), producing a global splitting of satellite lines. (b) In the $1q$ phase, at $T_{i3}+0.03$ K; in this sample, domains with the three orthorhombic strains (q_1,q_2,q_3) are present, although q_1 domains are less intense than q_2 and q_3 domains; some domain sizes are around 1 mm.

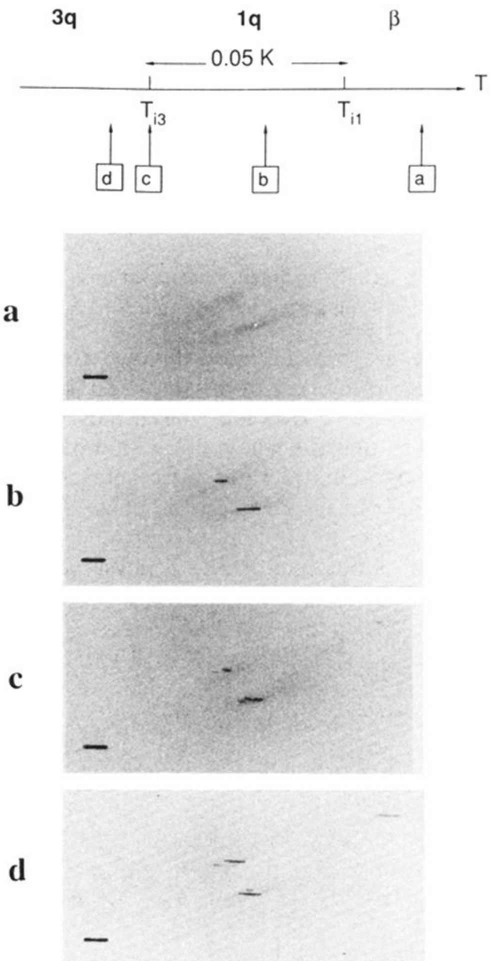

FIG. 4. Synchrotron-radiation pictures of the very pure sample $S3$ taken around the β-incommensurate transitions, at the four temperatures indicated in the phase diagram of the top inset. (To enlarge the satellite pictures, only the right part of the diffraction pattern is shown; the other part is obtained by symmetry around the lattice reflection). (a) In the β phase, at $T_{i1}+0.02$ K; the photograph shows only the homogeneous picture of the rectangular (6×1.5 mm^2) sample cross section given by (111) Bragg reflection, with diffuse streaks along the three $\langle\zeta 00\rangle$ directions. (b) In the $1q$ phase, at $T_{i1}-0.02$ K; in addition to the Bragg reflection, the photograph shows $1q$ satellites corresponding to two orthorhombic domains (q_2 and q_3) with $q_i=0.0320a^*$ and $\phi=0$. (c) At $T_{i3}=T_{i1}-0.05$ K, the transition temperature between the $1q$ and $3q$ phases; the photograph shows the coexistence between the $1q$ phase [with the same orthorhombic domains structure as in (b)] and the $3q$ phase (with a rotation domain structure). (d) In the $3q$ phase, at $T_{i3}-0.01$ K; rotation domains are present corresponding to $\phi=\pm1°$; each domain produces six satellites corresponding to $\pm q_i=0.0320a^*$.