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Nanoquartz vs. macroquartz: a study of the $\alpha \leftrightarrow \beta$ phase transition

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Abstract. The first-order character of the $\alpha \leftrightarrow \beta$ transition in micron-size quartz is shown to be strongly reduced in natural nano-size quartz with no significant variation of the transition temperature. Three different experimental techniques (differential scanning calorimetry, X-ray diffraction and second-harmonic generation) are applied on natural nano-size quartz to evaluate the variation of the character of the transition. The excess entropy of nano-size quartz is described in the framework of Landau theory. The renormalization of the fourth-order term is explained to arise from the elastic 3D-clamping imposed on each grain by the surrounding nanocrystallites. The presence of hydrous species and inhomogeneous internal stress due to the growth process are considered as well in the interpretation. The anomalous increase in the linewidth of diffraction maxima at the transition temperature is related to surface relaxation phenomena.

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1 Introduction

Nanocrystals are at the heart of the development of novel submicron-size devices for a large variety of applications [1,2]. Several of these materials undergo phase transformations in the bulk material. The question arises if these phase transformations also exist in the nanocrystal and if so, to what extent the characteristics of the transition are themselves size dependent. Typical samples are semiconductors [3,4], ionic solids [5], and ferroelectric and ferroelastic materials [6,7] which show significantly different behaviour on a nanometer length scale compared with a micrometer length scale.

Theoretical and experimental work has helped to clarify the question. It appears that modifications relate to two physical effects. Firstly, an increase of the surface to volume ratio leads to an increase in surface related relaxations, which may destabilise thermodynamic phases and significantly modify the order parameter profiles of the nanocrystal [8,9]. The second effect is the implementation of boundary conditions through intergrain contacts as in ceramics or *via* constraints by substrates in thin films [10].

Besides a large body of theoretical work, little is known about the performance of ceramics built from nanocrystals. In contrast to thin films, it is experimentally more difficult to produce powders with uniform and narrow grain size distribution. In nature, such materials do exist, however. A typical example is the mineral agate which, in the case of this study, is a compact intergrowth of nanoparticles (between 50–90 nm, as shown below) of α -quartz (SiO₂). This example of nanomaterial becomes even more significant as all structural parameters of the $\alpha \leftrightarrow \beta$ phase transition are well known [11] (and references therein) and could be used to predict how the nanoceramic material will transform at high temperatures [12].

In the past, several authors reported variations in the character of the α - β transition between macroquartz (micron-size quartz) and submicron-size quartz. In these works, the experiments were performed either in ground quartz (up to 400 hours milling) [13,14], or in natural compact fine quartz varieties, such as: agates and chert [15,16]. Calorimetric and dilatometric studies did indicate that the first-order transition observed in quartz became smoother in fine ground quartz. However, no clear explanation for such an effect was presented. Thus, while some authors did attribute the smoothening of the transition and the decrease of the latent heat to a particle size effect [13], others discussed the actual variation in terms of the ability of fine quartz to release the internal stress created at the transition through the grain boundaries [16].

Recently, it has been predicted [12] that under isotropic 3D elastic clamping conditions, like the conditions present in agates, the fourth-order term in the freeenergy expansion is renormalized by the mechanical inclusion/matrix interaction. The first-order character of the transition is thus destroyed and the transition becomes continuous. It is the purpose of this paper to show to what extent the theoretical predictions are born out by the experimental observations.

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Fig. 1. Peak broadening in nanoquartz, at room temperature, due to small grainsize and internal strain. (a) Bragg peak in nanoquartz (sample mq1). The continuous line indicates the resolution of the instrument. (b) Williamson-Hall plot for three different nanoquartz samples. Notice the smaller grainsize and larger internal strain of nanoquartz compared with quartz. Dotted lines are guides for the eyes.

It should be pointed out that the $\alpha \leftrightarrow \beta$ transition is not direct but develops via an incommensurate phase stable over 1.5 K [17–19]. Nevertheless, the steplike increase of the order parameter of the α -phase at the transition temperature is rather large and it should not be very much affected by the incommensurate phase [12].

2 Experimental procedure

The first-order transition observed in quartz (at 847 K from β -quartz (P6₂22) to α -quartz (P3₂21) [20,21]) is expected to become continuous under isotropic 3D clamping. Three different techniques have been applied to evaluate the change on the character of the transition: X-ray diffraction (XRD), differential scanning calorimetry (DSC) and optical second-harmonic generation (SHG).

2.1 The agate samples

From the structural point of view, several submicron crystalline silica minerals exist in nature, such as: microcrystalline quartz and moganite, and microcrystalline opal with a disordered cristobalite/trydimite structure. These forms are classified depending on their growth and microstructure [22,23]. Agates are a variety of microcrystalline quartz (chalcedony). The agates selected for this work are of the wall-lining type. They form within gas cavities of volcanic host rocks when microcrystalline quartz nucleates on the walls and grows inwards forming fibers. The bands (at the micron scale) are a consequence of the growth process and the varying defect concentration (mostly hydrous species) [24]. Agates have often been reported to contain moganite, a novel silica polymorph [25,26]. Nevertheless, none of the specimens studied in this work did contain moganite as tested by X-ray diffraction methods.

For each of the techniques, a different specimen obtained from the same agate was used. All the experiments were carried out on untreated specimens which were colourless and translucent. The agate used for this work is from Ardownie, Scotland. For the X-ray diffraction measurements two more agates from Iran and Mexico were also used.

2.2 X-ray diffraction

X-ray diffraction experiments were performed on a slab of agate of $10 \times 3 \text{ mm}^2$, and $500 \ \mu\text{m}$ thick in order to decrease the thermal gradient inside the sample (the thermocouple is in contact with the bottom surface while the beam is focused on the top surface). Powdered silicon (NBS) was spread on top of the sample for calibration purposes. The diffractometer used has been described previously [27]. It uses Cu K α_1 radiation and employs a 120° position-sensitive detector. The measurements were carried out under vacuum ($<5 \times 10^{-4}$ mbar), from room temperature up to 1173 K. A diffractogram was collected every 20 K with a counting time between 2–3 hours.

Data were analyzed using the Fullprof software [28]. Due to the poor crystalinity of the samples under study, a full Rietveld refinement could not be undertaken. Thus only a profile matching type analysis was carried out in order to extract the cell parameters as a function of temperature. The peak broadening in agate samples due to small grainsize and internal strain is shown in Figure 1a. Hereafter, we will refer to the agate samples as nanoquartz. The micron-size quartz used as reference will be termed quartz, and it was a powder from a single-crystal of a quartz sample from Brazil. For the profile matching analysis only peaks up to 80° in 2 θ were used, as the intensity was very weak at higher diffracting angles. Moreover, given the large intensity difference between the second Bragg peak ($2\theta \approx 26^{\circ}$) and the rest, it was difficult to achieve good convergence during refinement. Therefore, the first two peaks were also removed from the refinement. Approximately, 35 diffraction maxima were used to refine the lattice parameters and a scale factor. During the experiments a significant increase in the linewidth of the peaks was noticed close to the transition point. In order to account for such broadening an isotropic strain factor was included in the refinements. No extra peaks, apart from the ones corresponding to α -quartz were observed at room temperature.

2.3 Differential scanning calorimetry

Calorimetric measurements were made with an automated Perkin Elmer DSC 7 differential scanning calorimeter [29]. All scans were made with a flow of dried nitrogen gas with the calorimeter block being thermostated at 293 K. For temperature and heat capacity calibration a standard quartz disc (cut from a single-crystal) of 5 mm diameter by 0.7 mm thick, and weighing 24.4 mg was used. The reference quartz samples used for the three different type of experiments (XRD, DSC and SHG) had the same origin. The transition temperature and heat capacity of quartz were taken from the literature (Tabs. I, II and VI [30]). The nanoquartz sample was a disc of 6 mm diameter by 1 mm thick and weighing 46.4 mg. The weighting of the sample and the Au-pans was repeated five times and was accurate within ± 0.2 mg. Heat capacity was determined following the scanning method described in [31]. Heat capacity experiments consist of three alternating measurements: a baseline run (empty Au-pan), a calibration run (standard quartz in our case), and the unknown sample (nanoquartz). The baseline scan is then subtracted from both the standard and specimen scans. For this work, only a small temperature interval around the transition (847 K) was studied. The 773–903 K temperature range was covered by six 30 K intervals with 10 K overlap. The first run was done in the following way. The two Au empty pans, without a lid, were loaded in the calorimeter, heated to the starting temperature and held constant for several minutes to allow thermal equilibrium. The starting baseline was recorded for 2 min. Then the temperature interval was scanned at 10 K/min, and lastly, the final baseline was measured for 2 min. Next, the calorimeter was cooled down to room temperature and measurements over the same temperature interval were made on the standard quartz and the nanoquartz. As the same specimen pans were used for all three scans, no correction for pan mass was required. The precision is estimated to be between 2-3%. Following [31], the thermal lag during the experiment was estimated to be about 1 K in the case of the nanoquartz (probably due to the mass difference between the reference quartz and the nanoquartz); however no temperature correction was carried out in our data.

2.4 Second-harmonic generation

The transition from α -quartz to β -quartz is accompanied by large changes in the magnitudes of the second-harmonic coefficients. These describe the conversion of a fundamental light wave to a frequency-doubled light wave in an acentric crystal in the form of a third-rank tensor with similar symmetry restrictions as the scheme of piezoelectric modulii, d_{iik} :

$$P_i^{\rm NL}(2\omega) = \epsilon_o d_{ijk}^{2\omega} E_j(\omega) E_k(\omega) \tag{1}$$

where $P_i^{\rm NL}(2\omega)$ is the second-order non-linear polarization in the crystal and $E_i(\omega)$ the electric components of the fundamental light. The use of SHG in the study of phase transitions is described in an early review by Vogt [32]. The only coefficient expected in quartz is d_{11} which is nonzero in α -quartz and zero above $T_{\rm c}$. This belongs to the same representation as the order parameter for the $\alpha\text{-}\beta$ transition. The intensity of the optical second-harmonic generation in quartz and nanoquartz can therefore be used to elucidate the temperature-dependence of the order parameter below the transition as has been previously demonstrated [33]. The intensity of optical frequencydoubled light is usually several orders of magnitude less than that of the fundamental wave. For this reason, a high-intensity high-power laser light source is needed if optical SHG signals are to be detected from illuminated crystals. We used a Q-switched Nd-YAG laser with a high peak power and low jitter as the fundamental light source, with a 20 ns pulse width and 200 mJ pulse energy. This equates to a peak pulse power of around 10 MW, in a beam of 6 mm diameter (approx. 3.5×10^7 Wcm⁻²). This is a very respectable power density, but one that is further amplified in this instrument by focusing the beam down to a diameter of a few 100 μ m. The light passing through the sample was filtered, to remove the fundamental wave, using a high-power interference beam splitter. A narrow band-pass (532 nm) filter was then used to exclude background light, and frequency doubled light (532 nm) was measured using a low-background photomultiplier. In addition to the light measured at the sample, the fundamental beam was split before falling on the sample. Part passed through a second standard quartz sample, filtered in the same way as that at the sample and passed to a photomultiplier from which a measure of the incident intensity was made. Further filters are placed along the optic axis of the instrument to exclude light from the laser flashlamp, the furnace, and interference of frequency doubled light created at the sample with frequency doubled light created at the quartz reference. For each pulse the peak intensity at the sample and the reference were measured. Typically around 20 pulses were measured for each temperature, giving a mean and standard deviation for each datum.

A randomly oriented irregular cleavage shard of a single crystal of quartz was used to measure the temperaturedependence of the frequency-doubled intensity of light through the phase transition. This was compared with the



Fig. 2. Cell parameters: (a) *a*-axis and (b) *c*-axis as a function of temperature in mq1 (\Box), mq2 (\circ), and (\bullet) quartz [11]. Error bars were estimated by refining the data several times.

behaviour observed for a fragment of nanoquartz. Measurements were made with a collimated and focussed beam in transmission geometry, and data were collected at 5 K intervals up to 930 K for the nanoquartz and at 10 K intervals up to 973 K for the quartz sample. Temperatures at the sample were determined using an independent thermocouple which was placed in direct contact with the sample. It is estimated that the uncertainty in the temperature measurement is ± 1 K. Data were normalized against the signal obtained for a single-crystal of quartz (of different dimensions) held at room temperature.

3 Results

3.1 XRD

Figure 1b is a Williamson-Hall plot [34,35], which is used to assess the peak broadening arising from small grainsize and/or internal strain. In the graph the full width at half maximum (FWHM) as a function of the diffraction angle, θ , is shown for the three nanoquartz samples (labeled as mq1 (Scotland), mq2 (Iran) and mq3 (Mexico)) and quartz. The peaks typically used were: (010), (011), (110), (012), (200), (201), (112), (211), (113), (014), (221), (132) and (124). The FWHM was obtained by fitting individual peaks to a normalized Pseudo-Voigt type function. In a Williamson-Hall plot, the FWHM $\cos\theta$ versus $\sin\theta$ is represented, and is commonly expressed as:

FWHM
$$\cos \theta = \lambda / L + \epsilon \sin \theta$$
. (2)

The point where the linear extrapolation of the data intercepts the ordinate axis is equal to λ/L (from Scherrer's equation [36]), with λ the wavelength of the radiation used and L(nm) the estimated diameter of the grains in the polycrystal. Additionally, the slope gives an estimate of the internal strain, which in our case arises from the mechanical constraint imposed on each grain by the surrounding matrix. The strain is likely to depend on the growth of the polycrystal, and thus to vary from one sample to another.

In Figure 1b, quartz does not show any internal strain (as expected), and the nominal grainsize derived from the figure is only indicative of the instrumental resolution. In the three nanoquartz samples the slope indicates an internal heterogeneous strain of about $\Delta d/d = 3 \times 10^{-3}$. After correcting for instrumental resolution, and using Figure 1b, the grainsize was estimated to be about 90 nm in samples mq1 and mq2, and 50 nm in sample mq3. These grainsizes are in very good agreement with values given previously in the literature (60–90 nm) [22]. Thus, given the grainsize (<100 nm) we believe that the term nanoquartz is more appropriate than microquartz, for these samples.

The evolution of the cell parameters in mq1 and mq2 samples as a function of temperature is shown in Figure 2. For comparison, the cell parameters of quartz [11] have been included. The first-order step of quartz disappears in nanoquartz. Although heating and cooling runs were performed in mq2, data collected during cooling were of poor quality indicating sample deterioration. Therefore no reliable cell parameters could be extracted from this run. Sample deterioration was evident from the "milky" appearance shown by the sample when back to room temperature. The cell parameters of nanoquartz above the transition are similar to those of quartz.

The FWHM of mq1 and mq2 was found to depend on temperature. Close to the transition temperature the FWHM of the diffraction peaks increased, and decreased again above the transition (Fig. 3). The variation in the FWHM was analyzed in two different ways. Firstly, the FWHM as a function of temperature was calculated by fitting individual peaks. For this purpose, two of the strongest peaks were used: (112) and (211), at about 50 and 60° in 2θ , respectively. Secondly, during the refinement of the diffractograms, the FWHM of all peaks was simultaneously refined by using the expression: FWHM(2θ)= $\epsilon \tan \theta$, where ϵ is the isotropic internal strain (the Lorentzian contribution to the line broadening,



Fig. 3. FWHM of peak (112) (about 50° in 2θ) for mq2: heating (•) and cooling (•). The dotted line indicates the transition temperature in quartz. Error bar indicates the estimated standard deviation.

see [28]). As shown in Figure 4, the strain obtained in these two ways shows similar results. In order to compare the FWHM of peak (211) with the strain (ϵ) in Figure 4, the contribution to the total FWHM coming from the particle size had first to be removed. The variation of the strain with temperature can also be observed in a Williamson-Hall plot (Fig. 5). The increase of FWHM at the transition was observed in both samples, mq1 and mq2, whereas no such effect is observed in quartz. From the evolution of the FWHM as a function of temperature the transition in nanoquartz appears to be spread over a large temperature interval, about 100 K, when heating the sample. However, the transition is sharper when cooling the sample, see Figure 3. Although in Figure 3 the FWHM is smaller above the transition than below, this is probably due to the fact that measurements were not performed at temperatures high enough to determine properly the baseline. Figure 5 clearly shows that the strain above and below the transition is the same.

3.2 DSC

The data for the specific heat of nanoquartz are shown in Figure 6. The dotted line in Figure 6 is the specific heat baseline which follows the polynomial form given in [11]. It was derived by fitting experimental data between 900 to 1400 K and extrapolated to lower temperatures. Notice the significant difference between the specific heat of



Fig. 4. Strain as a function of temperature (heating) in sample mq1 obtained in two different ways: by fitting the FWHM of peak (211) using a normalized Pseudo-Voigt type function (\bullet) , and from the refinement of the whole diffractogram (\diamond) .



Fig. 5. Willianson-Hall plot for sample mq1 as a function of temperature: (•) room temperature, (\Box) 833 K, (•) 873 K and (•) 1193 K. Notice the increase of slope indicating the increase of strain. (\triangle) is standard quartz. The dotted lines are guides for the eyes.

quartz and nanoquartz. The large latent heat associated to the first-order transition in quartz vanishes. The transition temperature however is equal to that of quartz, 847 K, within the accuracy of our experiment. Although it is not relevant for this work, it is worth pointing out the tail observed above the transition in the quartz data taken from the literature when compared to the data obtained in this work. As showed in [37], the anomaly related to the



Fig. 6. Experimental data of specific heat between 773 and 900 K: (•) quartz [30], (•) quartz as obtained in this work, and (\triangle) nanoquartz. The dotted line is the baseline taken from [11].



Fig. 7. Excess entropy for: (\circ) quartz [30], (\bullet) quartz as obtained in this work, and (\triangle) nanoquartz. Continuous and dotted lines are the best fit to the 2-4-6 Landau potential described in the text.

incommensurate- β transition (around 848 K) does depend strongly in the thermal history of the sample. Thus, the heat treatment of the sample can lead to a rounding of the Cp peak, and appear as a tail above the α -incommensurate transition, as in [30]. The fact that we do not see such a tail could be due either to a longer heat treatment during the experiments (difficult to estimate), or to a larger heating rate during the measurements (10 K/min).

In order to compare data from nanoquartz with those from quartz the excess entropy was calculated by integration of the excess specific heat data [38]. Results are shown in Figure 7.



Fig. 8. Excess second-harmonic intensity as a function of temperature: (\circ) quartz [33], (\bullet) quartz as obtained in this work and (\triangle) nanoquartz.

3.3 SHG

The second-harmonic intensity obtained in nanoquartz as a function of temperature is shown in Figure 8. The small residual intensity observed above the transition, most likely due to surface effects, has already been subtracted. Data obtained in quartz are in agreement with those reported previously (Tab. I [33]). The absolute intensity of the SHG signal is a function of polar order, sample thickness, opacity and orientation, with temperaturedependent phase mismatch also playing a part. To a first approximation the data can be cross-compared taking account of the overall thickness of the nanoquartz sample with that of the quartz fragment (which was approximately twice as thick). The SHG data show the same qualitative trends as the calorimetric results, with a significant tail above the transition point. The intensity of the tail seems to vary from one experiment to another (XRD, DSC and SHG), which is probably related to different defect-contents (as explained below). In all three experiments the tail is spread up to 900–920 K.

4 Discussion

Under isotropic 3D clamping conditions in nano-size polycrystals, following [12], in the case of the linear-quadratic coupling between strain and order parameter in quartz, the first-order character of the transition is destroyed and the transition is expected to become continuous. Using the known elastic constants and coupling parameters, the renormalization of the fourth-order Landau term in quartz (b = -1931 J/mol [11]) leads in this approximation to b = 851 J/mol. Nevertheless, one should keep in mind that defect configurations and surface relaxation phenomena which couple to the order parameter might also have a significant contribution at the transition and weaken the effects of the clamping. Experimentally, as shown in Figures 2, 7 and 8, there is a clear evidence of the drastic change in the behaviour of the $\alpha \leftrightarrow \beta$ transition in nanoquartz, compared to what is observed in quartz. In all three independent experiments, the discontinuity observed at the transition in quartz disappears, and a continuous transition is found at its place. This observation is in agreement with previous works on small-grain quartz, natural [15] and artificially ground [13,14], where a decrease of the thermal response in DTA experiments had been reported. In these works however, the effect was only associated with the nano- size of the grains, without taking into account strain effects.

The clear change in the character of the transition can be first evaluated in the framework of the Landau theory. In previous works, the excess entropy observed at the first-order transition of quartz has been described by a 2-4-6 Landau potential with a = 9.8 J/(mol K), b = -1931 J/mol and c = 10190 J/mol, $T_c = 840$ K and $T_{\rm tr} = 847$ K [11]. The continuous line in Figure 7 is the expected temperature evolution of such a Landau potential.

If we assume that the variation in the excess entropy of nanoquartz is due to the renormalization of the fourthorder term of the Landau potential as a consequence of the elastic clamping, then, a similar expression should also be valid for nanoquartz with b > 0. In nanoquartz however, excess entropy is also observed above the transition point. As explained below, the tail is believed to originate from strain fields created by the defects (mostly hydrous species) present in natural nanoquartz. Thus, the excess free energy expression may include, apart of the 2-4-6 Landau potential, a term of the form -hQ in order to take into account the coupling between the order parameter (Q) and the conjugated field, h, created by the lattice impurities [38]. This expression leads to a temperature dependence for Q (above T_c) characterised by what is commonly known as a *defect tail*. In a general case, the field h may be divided into two terms: one uniform which depends on the host matrix, and a second term associated to the spatial distribution of the defects. In the most simple approximation, the field generated by the defects can be assumed to be uniform with no spatial distribution [39]. The reason for including such a coupling term is purely empirical. We are aware that the physical meaning of h is difficult to identify, given the symmetry properties of the order parameter. We can only say that defect fields seem to have appropriate components which can be cast into a simple field description as shown in Figure 7.

Using the above explained mathematical expression, the experimental excess entropy for nanoquartz was adjusted keeping $a, c, T_{\rm tr}$ and T_c fixed (with the values obtained in quartz), and only b and h parameters were left to vary in a least square fit procedure. Figure 7 shows the result of the best fit, with b = -700(50) J/mol and h = 30 J/mol. The small value of $h, h \approx 3a$, indicates that the nominal field component is relatively weak compared with the entropy term. Although b was found to be negative in nanoquartz, implying that the transition is not of second-order, the absolute value is three times smaller than the value obtained for quartz. Thus, the firstorder character of the transition is strongly reduced in nanoquartz. The use of a constant field to describe the defect tail is probably far from reality, and a better description would be achieved with an inhomogeneous and temperature dependent field, h(r). However, such an analysis is beyond the scope of this paper.

The question arises now whether the observed effect is related either to the elastic clamping effect of the nanosize grains, to the lattice defects or to a combination of all these factors. Besides, and due to the relatively small grainsize, surface relaxations might as well play a significant role. Next, we discuss our experimental results taking into account all these factors.

The samples under study are compact nano-size grain polycrystals with a large anisotropic and inhomogeneous internal strain originating both from the growing process and possible defect configurations. When heating the sample, the grains are not free to expand giving rise to the increase in linewidth shown in Figures 3, 4 and 5. The fact that the internal strain at room temperature is larger in mq2 than in mq1 (see Fig. 1b) might explain why the lattice expansion above the transition is smaller in mq2 sample. Above the transition, as a consequence of the structural rearrangements, the grains are able to relax and hence the excess strain observed at the transition disappears. Lattice parameters are known to expand when decreasing the diameter of the nano-size grains [40]. The nanoquartz samples studied here do not show any significant lattice expansion at room temperature when compared with quartz, however.

The variation of the linewidth as a function of temperature has to be analyzed considering two contributions: the surface relaxation inside each of the grains, and the anisotropic strain imposed on each grain by the inhomogeneous surrounding matrix. Lattice relaxation on the surface of the grains is known to give rise to asymmetric diffraction peaks and increase of the linewidth as a function of temperature [41]. Although no clear asymmetry was found in our diffraction peaks, a clear increase of the linewidth is observed, see Figures 3 and 4. The asymmetry of the peaks could possibly be hidden by the spread of the lattice parameters enhanced by the internal inhomogeneous strain. The fact that the increase in linewidth is spread over 100 K when heating the sample but it is sharper when cooling down (see Fig. 3) is likely to be a consequence of the inhomogeneous strain between grains. It can be explained as follows. When increasing the temperature, grains expand anisotropically increasing the strain between grains and thus the linewidth of the diffraction peaks. This effect will be superimposed to the surface relaxation existing on each single grain. Grains will then transform into the β phase and relax after structural rearrangements. When then the sample is cooled down, the strain between grains is no longer relevant and only the linewidth increase associated with the surface relaxation is observed.

We discuss now the origin of the tails observed above the transition temperature. The tails present in the three independent experiments (see Figs. 2, 7 and 8) are most probable due to inhomogeneous strain fields created by lattice imperfections. The most important defects found in natural nano-size quartz are hydrous species, typically with a weight content around 0.6-2% wt. Three different types of hydrous species have been characterized in natural nanoquartz [23]: molecular water, OH-groups located on the grain boundaries and OH-groups incorporated in the structure. Molecular water leaves the structure at about 373 K, and its effects are not relevant for the present case. The two other types of species however will only start leaving the structure around 773 K [22]; and temperatures as high as 1073 K are necessary to drive off all the hydrous species [13]. Therefore, the defect tail observed in all three experiments is most probable related to the latter two forms of hydrous species. Preliminary results on heat-treated nanoquartz (to be published elsewhere) seem to suggest that dehydration is accompanied by a decrease of the defect tail without a significant change of the excess entropy. Another effect which could also be relevant, and related to the lattice imperfections, is the presence of micron-size bands in this type of natural quartz. The bands are known to be oscillations of defect concentrations [24]. Thus the inhomogeneity of these bands might as well contribute to the defect tail.

Nevertheless, the tail above the transition point could also be attributed to the spread of the transition temperature as a consequence of the inhomogeneous strain on each grain or inside the grain. The transition temperature between α and β quartz is known to increase as a function of applied pressure with a slope of ca. 5 MPa/K at room pressure [42]. Given that longitudinal elastic constants in quartz are about 100 GPa [11], and that the internal strain in nanoquartz (see Fig. 1) is about 3×10^{-3} , one expects the transition temperature to rise by ca. 60 K. Such an argument had already been pointed out by Keith and Tuttle (1952) [43] in relation to their work on chert and novaculite (another variety of microcrystalline quartz). They found that while there was no heat effect on the slabs of sample, there was a measurable heat effect when samples were ground to a grainsize comparable to the individual grains. Therefore, it is possible that the internal stress plays a fundamental role concerning the character of the transition.

The inhomogeneity of the order parameter thus arises from inhomogeneous strain fields which are created by defect configurations and/or by the growth process of the nanoquartz *per se*. In order to achieve a better understanding of the origin of the tail, a complete characterization of the defect configurations present in natural nanoquartz is first needed. With that purpose, annealing experiments are under progress.

5 Conclusions

The first-order discontinuity observed in quartz at 847 K is shown to be very much reduced in nano-size quartz. The analysis of the excess entropy of nanoquartz in the framework of Landau theory reveals that when using the

same 2-4-6 Landau potential as in the case of quartz, the fourth-order term is significantly renormalized being the new fourth-order term coefficient b = -700(50) J/mol, compared with b = -1931 J/mol found in quartz.

The renormalization of the fourth-order term is in agreement with the elastic clamping expected in compact nano-size quartz. The importance of the clamping effect in this natural nanoquartz is also evident from the increase of the XRD peak linewidth at the transition point. Elastic clamping effects are strongly linked to surface relaxations effects, which are relevant in nano-size materials. The interplay between clamping effects and surface relaxation phenomena is thus an essential part of the transformation behaviour, and merits further investigation. The weak defect field found in nanoquartz suggests that the effects of lattice imperfections play a minor role in the transition mechanism. The defect tail present in the studied natural nanoquartz samples originates either from defect configurations and/or inhomogeneous internal strain.

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