Direct neutron observation of a single-q incommensurate phase of quartz at zero stress

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We have used very high-resolution neutron diffraction to prove the existence of a "single-**q**" incommensurate quartz phase at zero stress directly. The transition from the single-**q** to the "triple-**q**" state is first order.

INTRODUCTION

Since its discovery[1] in 1980 and the evidence of its incommensurate (IC) character,[2,3] the intermediate phase of quartz at about 846 K between the well-known α and β phases, in a temperature range of 1.4 K, has been the subject of many studies.[4] A characteristic feature of this incommensurate phase is the existence of three directions for the modulation which are superposed (triple-**q** state). Recently, the influence of uniaxial stress in the basal plane has been studied both theoretically and experimentally by neutron and x-ray scattering.[5,6] The major effect observed under stress σ was the appearance of a single-**q** IC phase between the β and the triple-**q** IC phases. A phase diagram (σ,T) was determined, but the accuracy was not enough to describe unambiguously the behavior at low stress. In particular, it was impossible to check whether the single-**q** IC phase exists at zero stress. This information is important for a theoretical description of the transition.[7] However, several experimental observations suggest the presence of a single-**q** phase. Rayleigh diffusion experiments can be understood by assuming the existence of a single-**q** IC phase over a small temperature range ΔT of about 0.08 K below T_i (Ref. 8) and an accurate determination of the (σ,T) phase diagram at very low stress by optical rotatory power measurements[9] leads to a similar conclusion with a $\Delta T = 0.05$ K. But a direct observation of the existence of a single-**q** IC phase seems necessary to confirm the interpretation of the light scattering experiments and to remove any further ambiguity. In the present paper we report such an observation, performed at the Institut Laue-Langevin (ILL) on two different quartz samples, by high-resolution neutron diffraction.[10]

DESCRIPTION OF THE METHOD

The phenomenological description of the transition[11] shows that a triple-**q** structure induces a rotation of the modulation vector from the crystallographic axis in the basal plane. This $\pm\phi$ rotation was observed experimentally with x rays in reciprocal space,[12] varying from 1° at T_i to 7° at T_c. In direct space, the $\pm\phi$ tilts induce rotation domains which have been observed by electron microscopy.[13] Such a rotation is not expected in the case of a single-**q** structure. Therefore, one can take advantage of this fact to check the existence of a single-**q** structure by a very accurate measurement of the modulation wave vector (orientation and modulus). In order to perform this experiment, we choose the (2,2,0) reflection which has the particularity to have only two very intense satellites in the $(2+\xi,2-\xi,0)$ direction, while the four other satellites are very weak and can be neglected. Figure 1(a) shows the simple arrangement of satellites around the (2,2,0) reflection: Dots correspond to single-**q** satellites and stars to triple-**q** satellites.

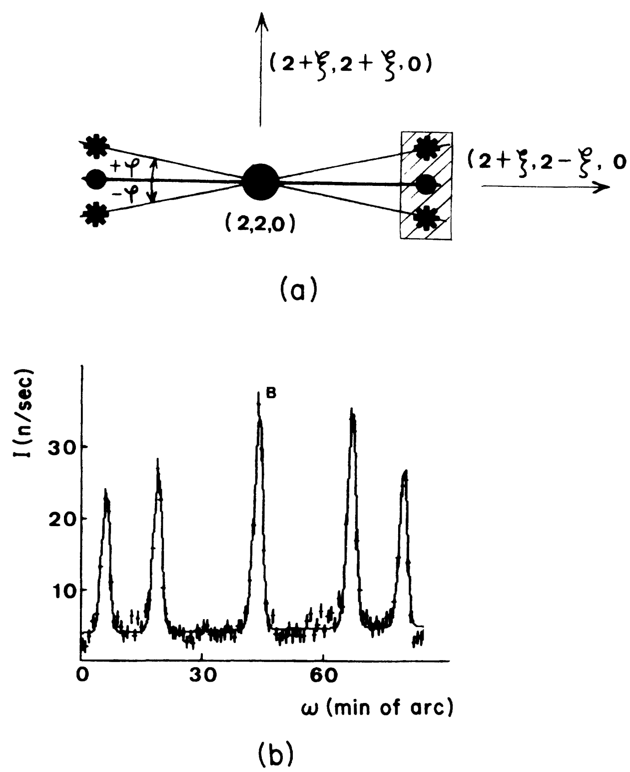

FIG. 1. (a) Schematic representation of reciprocal space around the (2,2,0) lattice point. The smaller dots correspond to the single-**q** phase. The stars represent the triple-**q** state. The hatched area is the region of the scans of Fig. 2. (b) Wide rocking scan across the (2,2,0) reflection in the triple-**q** phase. B is the Bragg peak and the four other peaks correspond to the satellites associated with the $+\phi$ and $-\phi$ rotation domains.

EXPERIMENTAL SETUP

The small values of the modulus of the modulation vector ($\mathbf{q}\sim0.033a^*$) and of the angle ($\phi\sim1°$) around T_i impose a very high-resolution diffraction experiment; the small expected temperature range of existence of the single-**q** structure of a few 10^{-2} K imposes a very good temperature stability and homogeneity. To get both we used a neutron ($-n,+n$) double crystal arrangement in which the width of the Bragg peak depends only on the degree of crystalline perfection[14] and we worked at large Bragg angle ($\theta_B\sim80°$) in order to increase the $\Delta k/k$ resolution. The experiment was performed at the Institut Laue-Langevin on the S21 facility.[15] The first quartz crystal was placed in a standard ILL furnace at a temperature of 940 K where the dilatation coefficient of quartz is zero, and the matching of the lattice parameter with the second (sample) crystal at 846 K is rather good. Thus, small temperature fluctuations of the first crystal do not perturb the measurement and the diffraction peak is not broadened too much by the lattice parameter mismatch. The second (sample) crystal was placed in a specially designed furnace similar to that used in a previous γ-ray diffraction experiment and which allows very good temperature stability and homogeneity, as shown previously.[16] In the first experiment, the samples were natural crystals of 25-mm edge cube and, in the second one, $25\times25\times5$ mm^3 plates, all of good optical quality. However, in both cases, the measured width of the Bragg peaks was about 120″, significantly larger than the expected value for perfect crystals ($\sim3''$). Scans were performed at constant temperature after stabilization of the simultaneously recorded birefringence. Figure 1(b) shows the experimental diffraction pattern in the triple-**q** incommensurate phase.

RESULTS

The diffraction pattern associated with the hatched part of the reciprocal space of Fig. 1(a), for different decreasing temperature around T_i, is shown in Fig. 2. In Fig. 2(a) at $T=855.422$ K, the crystal is in the β phase. Only a broad diffuse peak is recorded. In Fig. 2(b) at $T=855.416$ K, a narrower peak appears on top of the first broad peak; it corresponds to the single-**q** satellite. Furthermore, two side peaks are visible; they correspond to the triple-**q** satellites. In Fig. 2(c) at $T=855.404$ K, the single-**q** peak decreases while the triple-**q** peaks increase. We clearly observe the coexistence of the single-**q** and triple-**q** incommensurate structures. At last, in Fig. 2(d) at $T=855.398$ K, the triple-**q** peaks become predominant while the single-**q** peak has almost completely disappeared. At lower temperatures, the triple-**q** peaks continue growing and their separation increases with the variation of tilt angle ϕ. For increasing temperature the same phenomena are observed.

From this measurement we cannot make any conclusions about a possible thermal hysteresis. However, we can assert that it would be smaller than 0.006 K. The observed temperature range of the single-**q** structure is about 0.025 K. It is smaller than that expected from the optical measurements. This is probably related to a thermal gradient in the sample. Indeed, due to the size of the neutron beam, both horizontal and vertical thermal gradients perturb the measurement while, in the case of optics, because of the tiny beam cross section only the thermal gradient along the horizontal light beam is taken into account.

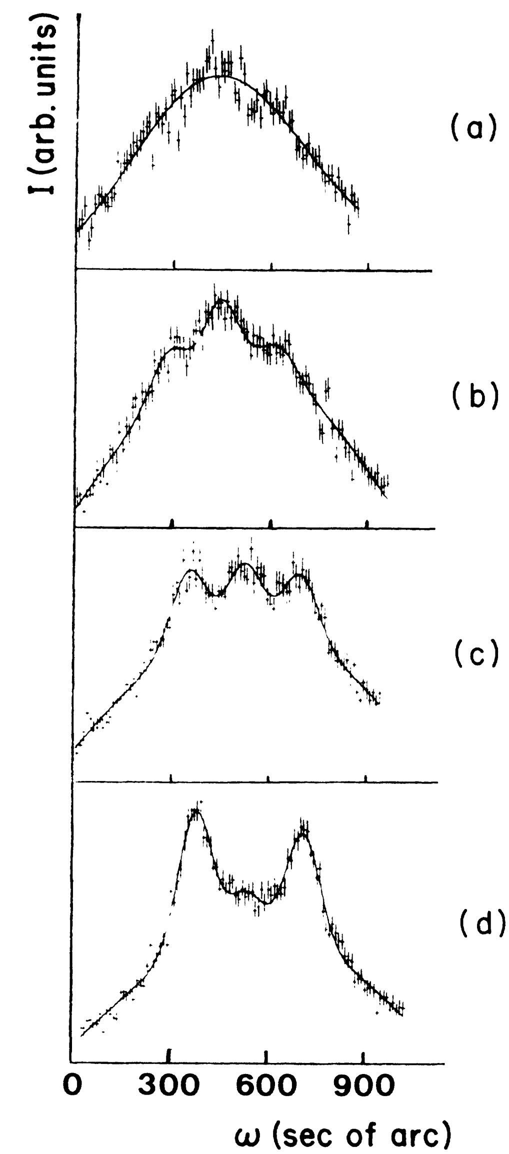

FIG. 2. Rocking scans at different temperatures (see text) around the β IC transition showing the evolution from (a) the β phase to (b)–(d) the different stages of the coexistence between the single-**q** and the triple-**q** incommensurate phases.

In conclusion, from this experiment we can assert two important results: (1) The existence of a 1-**q** incommensurate structure at zero stress is unambiguously proved. (2) The first-order character of the single-**q**$\rightarrow$ triple-**q** incommensurate phase transition has been directly observed for the first time. This confirms, without ambiguity, the interpretation of the optical measurements and permits the use of them for a better determination of the phase diagram.[8,9] It is now interesting to determine the origin of this single-**q** phase. It could be due simply to residual stresses in the sample. However, the observation of this phase in several different samples suggests a possible intrinsic origin. Such a result would be important from a theoretical point of view to check the validity of a recent renormalization-group calculation which predicts an instability of the transition point.[17]

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