Birefringence study of the irreversible behavior of the incommensurate phase of quartz: effects of chemical impurities
F. Mogeon, G. Dolino

To cite this version:
Birefringence study of the irreversible behavior of the incommensurate phase of quartz: effects of chemical impurities

F. Mogeon and G. Dolino

Université Joseph Fourier, Laboratoire de Spectrométrie Physique (*), B.P. 87, 38402 Saint-Martin-d'Hères Cedex, France

(Received on July 10, 1989, revised on April 17, 1990, accepted on May 22, 1990)

Résumé. — Une étude systématique des propriétés irréversibles de la phase incommensurable du quartz a été faite par des mesures de birefringence sur 9 échantillons (synthétiques ou naturels) de différentes compositions, déterminées par analyse chimique et spectroscopie infrarouge. Les décalages de la température de la transition $\alpha-\beta$, produits par des concentrations importantes d'impuretés ont été mesurés. Les propriétés de la phase incommensurable sont très sensibles à la présence de faibles taux d'impuretés : des hystérésis globales variant de 10 à 220 mK, ont été mesurées et une corrélation avec l'absorption infrarouge due aux liaisons OH a été trouvée. Des effets dépendant du temps tels que des marches d'accrochages et des effets mémoires ont été observés, montrant l'importance des défauts mobiles. Enfin, un régime de variations discontinues des propriétés physiques apparaît pour les petites vitesses de variation de la température. Les résultats de ces expériences ont été comparés à diverses prédictions théoriques, telles que celles de la théorie des Ondes de Densité des Défauts dues à la diffusion des impuretés mobiles.

Abstract. — A systematic study of the variations of the irreversible properties of the incommensurate phase of quartz has been performed by birefringence measurements in 9 samples (either synthetic or natural) of various compositions determined by chemical analysis and infrared spectroscopy. The shift of the $\alpha-\beta$ transition temperature for large impurity concentrations has been verified. The properties of the incommensurate phase are very sensitive to small changes of impurity contents: a global hysteresis going from 10 to 220 mK has been correlated to the OH infrared absorption. Time dependent pinning steps and memory effects have been observed showing the importance of mobile impurities. Finally a regime of discontinuous variation of physical properties appears for slow rate of temperature variations. These results have been discussed in relation to various theoretical models and in particular to the theory of the Defect Density Wave, induced by the diffusion of mobile impurities.

In the last 15 years a large variety of nonlinear behaviors has been found in incommensurate (inc) materials, related to the existence of metastable states induced by defect pinning: most studies have been performed on the complex phenomena related to the non linear electric conductivity produced by the depinning of charge density waves (CDW) [1]. In insulating

(*) URA D0008, associée au CNRS.
materials pinning effects also lead to an irreversible behavior such as the global hysteresis observed with temperature variations [2]: physical properties take different values upon cooling and upon heating due to the pinning of the modulation wave. The studies of Hamano [3], on samples with various impurity concentrations, have clearly shown that these effects are mainly related to the presence of chemical impurities. While at first only static impurities were considered, the existence of the memory effect, discovered in thiourea (SC(NH₂)₂) [4] and in Rb₂ZnCl₄ [5], has been explained by Lederer et al. by the diffusion of mobile impurities [6].

As shown in this paper, the inc phase of quartz presents well defined irreversible features. The properties of this inc phase, which exists around 846 K in a narrow temperature range of 1.5 K in between the well-known α and β phases have been the subject of many studies which have recently been reviewed [7, 8]. A global hysteresis of 0.2 K was first observed in 1985, in an accurate γ-ray diffraction measurement [9]. More recently it has been found that macroscopic properties, such as the optical birefringence, show also various irreversible effects, which have been systematically studied in a natural sample with a large concentration of impurities [10], where we have observed time dependent pinning and memory effects showing the importance of mobile defects in quartz. In addition to these « classical » effects, a new spectacular phenomena has recently been observed [11]: when the rate of temperature variation is slow enough, the variation of physical properties becomes discontinuous, leading to a characteristic staircase behavior.

In this paper we present the first systematic study of these irreversible properties in several samples with different impurity concentrations. One can already notice that quartz is a favorable case to study impurity effects: due to its technological importance for frequency control, many studies have been performed on its defects [12, 13]. Furthermore one can easily obtain samples with different impurities: quartz is a well defined natural mineral [14] which can however incorporate many different impurity concentrations. While in natural samples metallic impurities are generally found with concentrations going from 10⁻⁵ to 10⁻⁴ [14], one can now get synthetic samples with impurity concentrations smaller than 10⁻⁶ [12].

1. Sample characterization and experimental conditions.

We first recall some information on the impurities of quartz:

— The major metallic impurity is Al³⁺, which is found in substitution of Si⁴⁺ [12]. Charge neutrality is obtained by the presence of a neighbouring interstitial ion, usually Na⁺ or Li⁺.

— In fact, in synthetic samples, the major impurity is often related to the presence of water, either as molecular H₂O or dissociated to give SiOH or AlOH [12, 15]. These defects produce various infrared (IR) absorption lines between 3 200 and 3 600 cm⁻¹. Since the work of Dodd and Fraser [16], the quality of quartz samples is often characterized by the IR absorption at 3 500 cm⁻¹.

Our study was performed on 9 samples:

— 5 synthetic samples with various concentrations of Al, labeled S1 to S5 in the order of increasing global hysteresis.
— 1 synthetic sample (S(Ge)) doped with 570 ppm of Ge.

(The high purity sample S3 was grown by GEC (UK) [17], while all the other synthetic samples were grown by SICN (France), with properties described in [18]).

— 3 natural samples N⁺, N⁺ and N(Al) (N(Al) which contains 180 ppm of Al was studied in our previous paper [10]).
The results of chemical analysis of some of these samples are given in table I. We also give the value of the IR absorption $\alpha_{3500} (\alpha_{3500} = (1/\ell) \log_{10} (I_{3500}/I_{3800})$ where $I_{3500}$ and $I_{3800}$ are the intensity transmitted at 3500 and 3800 cm$^{-1}$. A better IR characterization is obtained by the full IR spectra [19, 20]. Figure 1 gives 3 typical spectra measured at room temperature with a Perkin Elmer $\lambda$9 apparatus:

For our best samples S1, S2 and S3 one obtains the spectrum of figure 1a (measured on S3) with little OH absorption: the broad lines at 3200, 3300 and 3400 cm$^{-1}$ come from various overtones of the fundamental SiO vibrations around 1200 cm$^{-1}$ [19]. There is only a small indication of the narrow $s_4$ line at 3585 cm$^{-1}$. The absorption coefficients $\alpha_{3500}$ given in table I are rather small, going from 0.022 to 0.029 cm$^{-1}$ which is probably quite close to the intrinsic absorption. (We have found no value in the literature for the intrinsic absorption of pure quartz).

Table I. — Caracterization of the 9 samples used in the present study. Chemical analysis were performed by atomic spectroscopy for synthetic samples and by neutron activation for N(Al). (All concentrations given in atomic ppm relative to Si). $\alpha_{3500}$ is the IR absorption at 3500 cm$^{-1}$ and $\delta T_q$ is the value of the global hysteresis at constant $q$ at $T_0 + 0.2$ K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth speed mm/face/day</th>
<th>Impurity (in ppm)</th>
<th>$\alpha_{3500}$ (cm$^{-1}$)</th>
<th>$\delta T_q$ (mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
<td>Ge</td>
<td>Li</td>
</tr>
<tr>
<td>S1</td>
<td>0.21</td>
<td>5</td>
<td>$&lt; 0.5$</td>
<td>1.5</td>
</tr>
<tr>
<td>S2</td>
<td>0.01</td>
<td>&lt; 0.005</td>
<td>0.01</td>
<td>$&lt; 0.005$</td>
</tr>
<tr>
<td>S3</td>
<td>0.3</td>
<td>1.5</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>S4</td>
<td>0.5</td>
<td>1.5</td>
<td>0</td>
<td>2.7</td>
</tr>
<tr>
<td>S5</td>
<td>0.6</td>
<td>19</td>
<td>670</td>
<td>5</td>
</tr>
<tr>
<td>S(Ge)</td>
<td></td>
<td>180</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>N'</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N''</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(Al)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1b shows a spectrum typical of medium quality quartz (obtained on S5 but S4 and S(Ge) show similar spectra). The broad band between 3000 and 3600 cm$^{-1}$ is more intense, giving a larger absorption at 3500 cm$^{-1}$ and the 3585 cm$^{-1}$ line is now quite apparent.

Figure 1c shows a spectrum typical of natural quartz (obtained on N(Al)) where several narrow lines are observed superposed on a broad background.

As shown in our previous paper [10], very detailed informations on the irreversible behavior of quartz can be obtained by birefringence measurements performed with the de Sénarmont method using a computer controlled set-up. In fact we only measure the variations of the optical phase retardation $\Delta = 2 \pi \Delta n \ell / \lambda$ where $\Delta n$ is the birefringence, $\ell$ the sample length normalized to 10 mm at room temperature and $\lambda = 633$ nm the wavelength of the He-Ne laser. (The origin of $\Delta$ was arbitrarily chosen in the $\beta$ phase.) We used the same high stability furnace than in our previous study [10], with slow rate of temperature variations, often from 0.2 to 0.05 K/h.
2. Experimental results.

2.1 α-β TRANSITION. — We first present some results showing the shifts of the α-β transition temperature in samples with a large concentration of impurities. For a long time it has been considered that the temperature of the α-β transition was a well determined physical constant [21]. However since the systematic study of Keith and Tuttle [22], it is known that the α-β transition temperature is changed by the presence of impurities: they found that the coupled incorporation of Al and Li decreases the transition temperature, while that of Ge increases the transition temperature. As shown in figure 2, we found similar results in our samples. The typical shape of the birefringence hysteresis cycle of the α-β transition has already been described [10]: upon heating there is a large discontinuity at $T_h$ due to the 1st order transition from the low temperature α phase; in general the inc phase is observed for a few tenths of a degree before the transition to the β phase, at $T_i$. This transition at $T_i$ appears continuous and occurs at the same temperature upon heating and upon cooling. (However several recent experiments [23, 24] have shown that another inc phase with a single modulation wave exists in a small temperature range of a few hundreds of K around $T_i$). With further cooling there is a first order transition at $T_c$ from the inc phase to the α phase. The inc phase corresponds to the part between $T_i$ and $T_c$ where the curve $\Delta(T)$ displays a strongly non linear variation. The $T_i$ values obtained on our 9 samples are
Fig. 2. — Measurements of the birefringence variations (Δ) for 3 quartz samples, showing the shifts of the transition temperatures produced by various chemical impurities:

S3 - The transition temperatures of this pure synthetic sample are used as reference temperatures.

N(Al) - $T_i$ is shifted downward by 1.40 K for this natural sample containing 180 ppm of Al.

S(Ge) - $T_i$ is shifted upward by 1.27 K for this synthetic sample containing 670 ppm of Ge.

Given in table II in the order of increasing $T_i$, for natural and synthetic samples respectively. (We have not tried to determine absolute temperature, and we have fixed $T_i = 849.70$ K for sample S4). In table II we also give the values $T_h - T_c$ of the hysteresis of the first order α-β transition and the values $T_i - T_c$ corresponding to the existence ranges of the inc phase.

As shown in figure 2, only the two samples with large impurity concentrations show large shifts of transition temperatures: furthermore the hysteresis $T_h - T_c$ shows a remarkable variation from 1.5 K for N(Al) to 0.87 K for S(Ge) while for the other 7 samples this hysteresis remains around 1.16 ± 0.06 K. N(Al) is then the only sample where on heating the transition occurs directly from the α phase to the β phase, while in all the other samples the inc phase is observed above $T_h$ in a range of about 0.2 K. One can note that our values of $T_i - T_c$ are around 1.4 K, rather smaller than the value of 1.8 K given by Gouhara and Kato.
Table II. — Variation of the transition temperatures $T_i$ for the 9 samples studied (in the order of increasing $T_i$, first for natural samples and then for synthetic samples). $T_i$ is the transition temperature between the inc phase and the $\beta$ phase, $T_h - T_c$ is the hysteresis of the first order transition ($\alpha$-inc) and $T_i - T_c$ is the width of the inc phase.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_i$ (K)</th>
<th>$T_h - T_c$ (K)</th>
<th>$T_i - T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(Al)</td>
<td>848.17</td>
<td>1.50</td>
<td>1.45</td>
</tr>
<tr>
<td>N'</td>
<td>849.57</td>
<td>1.22</td>
<td>1.37</td>
</tr>
<tr>
<td>N''</td>
<td>849.60</td>
<td>1.20</td>
<td>1.40</td>
</tr>
<tr>
<td>S3</td>
<td>849.57</td>
<td>1.14</td>
<td>1.40</td>
</tr>
<tr>
<td>S5</td>
<td>849.57</td>
<td>1.20</td>
<td>1.41</td>
</tr>
<tr>
<td>S2</td>
<td>849.63</td>
<td>1.16</td>
<td>1.36</td>
</tr>
<tr>
<td>S4</td>
<td>849.70</td>
<td>1.18</td>
<td>1.40</td>
</tr>
<tr>
<td>S1</td>
<td>849.90</td>
<td>1.10</td>
<td>1.50</td>
</tr>
<tr>
<td>S(Ge)</td>
<td>850.84</td>
<td>0.87</td>
<td>1.24</td>
</tr>
</tbody>
</table>

[25]. Finally we present a comparison of the shifts of the transition temperatures shown in figure 2 with previous works:

— For the system Si$_{x}$Ge$_{1-x}$O$_2$, Miller et al. [26] have found an increase of the $\alpha$-$\beta$ transition temperature of 100 K for $x = 0.1$, a value compatible with our results and those of Passaret and Regreny [27], for smaller values of $x$.

For the influence of Al, Ghiorso et al. [28] found a decrease of 2 K of the transition temperature for a sample with 400 ppm of Al. Smykatz-Kloss [29] gives a decrease of 5 K for a sample with 700 ppm of Li. Supposing that these two results correspond to the couple Al$^{3+}$Li$^+$, found in the defined compound AlLiSiO$_4$ [30], these values are in rough agreement with our result for N(Al).

The variations of the $\alpha$-$\beta$ transition temperature produced by small impurity concentrations present in modern synthetic samples are rather difficult to observe, due to the existence of a 1st order transition hysteresis of 1.2 K. However, as shown below, the global hysteresis of the inc phase of quartz is very sensitive to the presence of such small impurity concentrations.

2.2 GLOBAL HYSTERESIS. — The global hysteresis of quartz — i.e. a different variation of physical properties upon heating and upon cooling — was first observed during a measurement of the temperature variation of the modulation wavevector $q$ by $\gamma$-ray diffraction [9]. Similar global hysteresis can be accurately studied by measurements of the variations of the birefringence [10], as shown by the curves of figure 3 obtained on sample S5: upon cooling one observes the increase of $\Delta$ in the inc phase from $T_i$ to $T_c$ where the first order transition to the $\alpha$ phase occurs. If the cooling is stopped a little above $T_c$ and if one starts heating again, one observes first a plateau A, with a small slope, followed by a part B where the birefringence shows a larger decrease. We have already shown by a simultaneous measurement of birefringence and $\gamma$-ray diffraction [10] that the plateau A corresponds to a region where the modulation wave vector $q$ keeps a constant value, while in region B, $q$ is increasing. The heating and cooling curves of figure 3 converge around $T_i$. The global hysteresis $\delta T_q$ of sample S5, measured along plateaus of constant $q$ obtained during small heating and cooling cycles as ABCD, is plotted in figure 4. The hysteresis decreases on going
Fig. 3. — Birefringence measurement of the global hysteresis cycle of sample S5 in the inc phase. The cycle ABCD shows a typical hysteresis cycle obtained during a small temperature cycle.

Fig. 4. — Variation of the global hystérésis $\delta T_q$, measured at constant wavector $q$, inside the inc phase for the 3 synthetic quartz samples S1, S3 and S5.
from $T_c$ to $T_i$, but it seems that $\delta T_q$ keeps a finite value around $T_i$. Such measurements are however difficult to perform not only because one has to measure very small quantities but because the end of the constant $q$ plateau is not as sharp near $T_i$ as it is near $T_c$. In figure 4 we have also plotted the results obtained for 2 other synthetic samples: for S3 the hysteresis which was around 40 mK near $T_c$ is reduced to 20 mK in the middle of the inc phase. Sample S1 showed the smaller hysteresis (10 mK) measured in this experience also decreasing toward $T_i$.

The values of the hysteresis $\delta T_q$ measured at $T_c + 0.2$ K for the 9 samples investigated are given in table I. There is no apparent correlation between $\delta T_q$ and transition temperatures. The results on the very pure sample S3 seems at first surprising, as a global hysteresis similar to that of other samples is observed. But then one must remember that there is one element for which a chemical analysis is difficult, which is hydrogen. However the presence of OH bonds is easily detected by IR spectroscopy and indeed the spectrum of S3 plotted in figure 1a is similar to those of S1 and S2 showing that these samples have similar concentrations of OH. A more quantitative relation is obtained by the plot in figure 5 of $\delta T_q$ as a function of $\alpha_{3500}$ the absorption at 3 500 cm$^{-1}$. With the exception of S(Ge), the other samples show a rather good correlation of the global hysteresis with $\alpha_{3500}$. It is also rather remarkable that natural and synthetic samples follow the same relation. It seems that no hysteresis ($\delta T_q = 0$) would be obtained for a sample with $\alpha_{3500} = 0.018$ cm$^{-1}$, which may be the limiting value of absorption for a quartz sample without OH bonds. We have also tested the possibility of a correlation with the absorption of the $s_4$ line at 3 585 cm$^{-1}$ but the results were not as good as for $\alpha_{3500}$.

![Figure 5](image-url)

Fig. 5. — Plot of $\delta T_q$, the global hysteresis at constant $q$, measured at $T_c + 0.2$ K as a function of $\alpha_{3500}$ the IR absorption coefficient at 3 500 cm$^{-1}$, showing a linear correlation for all samples with the exception of S(Ge).

If the correlation observed here in 8 samples between the IR absorption $\alpha_{3500}$ and the global hysteresis is confirmed by future studies, this would be a rather important result, as there are few cases where a relation has been established between irreversible effects in inc
phases and a particular chemical impurity. In anyway the present results clearly show that the global hysteresis of quartz is an extrinsic effect due mainly to the presence of chemical impurities. It is only in very pure samples without residual OH bonds that one can expect to observe an eventual intrinsic hysteresis which then would be smaller than 10 mK.

Before passing to time dependent effects, we will comment the peculiar behavior observed in sample S3 near $T_c$ shown in figure 2: about 50 mK above $T_c$ a change of the slope of the curve $\Delta(T)$ is observed on cooling. This particular behavior which was observed only in the pure sample S3 may correspond to a new inc phase with a different structure, already observed in the electron microscopy experiment of Snoeck et al. [31]. We may also recall that various unexplained light scattering phenomena [32, 33] have been observed near $T_c$, which may also be related to the inhomogeneous structure observed in the X-ray experiment of Gouhara and Kato [34].

2.3 TIME DEPENDENT PINNING AND MEMORY EFFECT. — New effects appear when the temperature variation is stopped for a time $t_s$ at a temperature $T_s$ (in the lower half of the inc phase). At constant temperature, the birefringence remains stable, even for our longest waiting time of 60 hours. When the temperature variation starts again in the same sense, the modulation wavevector $q$ remains constant in a temperature interval $\delta T_s = T_s - T_f$, producing a pinning step, shown in figure 6, for sample S3. After a waiting time $t_s = 12$ h. The width $\delta T_s$ of the pinning step increases with the waiting time $t_s$ as shown by the insert of figure 6. It appears that as soon as the temperature variation is stopped, a step appears and that the variation of the width $\delta T_s$ of this step can be represented by an exponential law $\delta T_s (\text{mK}) = 10.7 + 7.3 \left(1 - \exp \left(- \frac{t}{\tau}\right)\right)$ with $\tau = 1.9$ h. Similar variations were observed in samples S5 and N(Al). In these 3 samples, for which detailed measurements were performed, the short time step is around 10 mK while the values at saturation are rather different (18 mK for S3, 50 mK for S5 and 115 mK for N(Al)). Pinning steps were found in

![Graph](image_url)  
**Fig. 6.** — Pinning step, observed between $T_s$ and $T_f$, on sample S3 after a waiting time $t_s = 12$ h at temperature $T_s$. The insert shows the increase of the pinning step $T_s - T_f$, as a function of the waiting time $t_s$. 

the 9 samples investigated. The values of the step width $\delta T_s$ measured after a waiting time of 12 h are given in table III: for 6 samples the width of this step was between 7 and 24 mK. It was larger for only 3 samples (50 mK for S5, 90 mK for S(Ge) and 80 mK for N(Al) which was not at saturation). It seems that different mechanisms (may be related to different impurities) are at the origin of short and long time pinning: the existence of the short time pinning, which has not been reported in other inc materials, may be due to some kind of solid friction force [35].

Table III. — Characteristic parameters of the staircase variations observed at low rates of temperature variation: $\left( \frac{dT}{dt} \right)_c$ is the critical rate of temperature variation, below which the staircase variation is observed. $\delta T_c$ and $\delta T_0$ are respectively the step widths, just below $\left( \frac{dT}{dt} \right)_c$ and at low rate $\left( \frac{dT}{dt} < 5 \text{ mK/h} \right)$. For comparison we have included the values of $\delta T_s$, the width of the pinning step measured after a waiting time $t_s = 12$ h. (For S3, line (a) gives the results obtained in the first week of experiment, while line (b) gives results obtained 1 month later.)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta T_s$ (mK)</th>
<th>$\left( \frac{dT}{dt} \right)_c$ (mK/h)</th>
<th>$\delta T_c$ (mK)</th>
<th>$\delta T_0$ (mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>7</td>
<td>&lt; 2.4</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>S2</td>
<td>12</td>
<td>No investigation</td>
<td>12,5</td>
<td>14</td>
</tr>
<tr>
<td>S3(a)</td>
<td>18</td>
<td>90</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>S3(b)</td>
<td>10</td>
<td>30</td>
<td>30</td>
<td>14</td>
</tr>
<tr>
<td>S4</td>
<td>10</td>
<td>60</td>
<td>20</td>
<td>16</td>
</tr>
<tr>
<td>S5</td>
<td>50</td>
<td>250</td>
<td>50</td>
<td>29</td>
</tr>
<tr>
<td>S(Ge)</td>
<td>90</td>
<td>90</td>
<td>50</td>
<td>90</td>
</tr>
<tr>
<td>N'</td>
<td>15</td>
<td>5</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>N''</td>
<td>24</td>
<td>15</td>
<td>irregular</td>
<td>24</td>
</tr>
<tr>
<td>N(Al)</td>
<td>80</td>
<td>10</td>
<td>17</td>
<td>80</td>
</tr>
</tbody>
</table>

The existence of a pinning step increasing with time suggests the presence of mobile defects, a feature which is indeed confirmed by the observation of memory effects: when the waiting time at a constant temperature $T_s$ exceeds some critical value (6 h for S3) a step, shown in figure 7, is observed at $T_s$ in a subsequent cycle performed with a constant rate of temperature variation. This is an example of the memory effect first observed in SC (NH$_2$)$_2$ [4] and in Rb$_2$ZnCl$_4$ [5]: the sample remembers that it has remained for a long time at a temperature $T_s$. The width $\delta T_m$ of the memory steps also increases as a function of the waiting time (above the threshold value) with a time constant similar to that of the time dependent pinning. In sample S3, the memory effect decreases as a function of time as shown in the insert of figure 7: the starting value (18 mK at $t = 0$) corresponds to the pinning step after a waiting time of 24 h. The first memory step of 11 mK was observed 1.5 h after the start of the measurement. The data points are well represented by an exponential decay with $\delta T_m(\text{mK}) = 4.4 + 13.5 \exp \left( -t/\tau \right)$ where $\tau = 2.1$ h. The time constant of 2.1 h for the decay is nearly the same as that of 1.9 h found for the time dependent pinning. The possibility
1949

Fig. 7. — Memory effect observed during a continuous temperature variation after a waiting time $t_w = 24 \, \text{h}$ at $T^*$ for sample S3.

A memory effect has been observed in 8 of the 9 samples investigated, (only $N''$ shows no memory effect although pinning steps were observed). For most samples the amplitude of the memory effect was about $10 \, \text{mK}$; larger memory effects have been found only in the 3 samples with large pinning steps and the two effects have similar amplitude ($50 \, \text{mK}$ for S5, about $90 \, \text{mK}$ for N(Al) and S(Ge)). Memory effects are observed only if the writing time exceeds some threshold value. On the other hand when a memory effect exists it is very stable and can be observed for several days in the inc phase. (Only sample S3 shows a decrease of the memory effect in the inc phase).

A remarkable property of the memory effect in quartz is its asymmetry. In figure 7 the memory effect is observed only on the side of the hysteresis cycle where the writing was performed. However in most samples after longer writing times a memory effect can be observed on both sides of the cycle, as shown in figure 8 for sample S5. Curve (a) shows the asymmetric memory effect observed at P1 after a writing time of 2 h at P1. After a supplementary writing time of 2 h at P1, the memory effect at P1 has increased and another memory step appears at P2, on the other side of the hysteresis cycle, on curve (b). Finally after a total writing time of 12 h at P1, 2 symmetric memory effect are observed at P1 and P2 on curve (c). (The 3 curves of figure 9 were obtained during identical temperatures cycles of 2 h heating, followed immediately by 2 h cooling). Recently a similar asymmetry of the memory effect has been observed in thiourea [36]. As this material has a single modulation wave, this shows that the asymmetry of the memory effects is not related to the particular 3 $q$ structure of quartz, but to some unknown difference in the process of modulation variations, between heating and cooling.

Except for sample S3, the memory effect is stable in the inc phase. We have made further study of this stability by heating in the $\beta$ phase. The results of such annealing are shown in
Fig. 8. — Evolution of the memory effect in sample S5 for various writing time $t_s$.
(a) After $t_s = 2$ h, an asymmetric memory effect is observed with a single plateau $P_1$ on the side of the writing.
(b) After $t_s = 4$ h, the memory effect becomes symmetric, a second plateau $P_2$ appears on the opposite side of the cycle.
(c) After $t_s = 12$ h, larger memory effects are observed at $P_1$ and $P_2$.
(For clarity, the cycles have been translated along the vertical axis.)

Figure 9 for sample S5. Curve (a) shows the initial symmetric memory effect obtained after a writing time of 24 h. Curve (b) was obtained after heating for 2 h at $T_i + 0.5$ K: the step at $P_2$ has disappeared, while the step at $P_1$, on the side of the writing is reduced. Curve (c) was obtained after a further heating of 2 h at $T_i + 6.5$ K showing a further decrease of the step at $P_1$. Finally, curve (d) shows that the memory effect has completely disappeared after a 12 h heating at $T_i + 6.5$ K.

The effect of annealing in the $\beta$ phase has been observed in other quartz samples and shows large variations; for the pure sample S3 there is already a decrease of the memory effect in the inc phase. S5 shows a complete annealing after a few hours at $T_i + 6.5$ K. In a previous paper [10] we have presented the annealing of the synthetic sample, now called S1. There was a partial annealing after 6 h at $T_i + 10.5$ K. Finally sample N(Al) was very stable and shows no annealing even after 10 h at $T_i + 60$ K. These differences in the stability of the memory effect are probably related to the nature of the various impurities: in the pure S3 sample, with very few metallic impurities, one can probably attribute all irreversible effects to the presence of H. In other samples the origin of the memory effect may also be influenced by metallic impurities Na$^+$ or Li$^+$, as in N(Al). However it is difficult to understand why it is so difficult to erase the memory effect in this sample.

Although very interesting by itself, the memory effect has a disturbing influence on some measurements and in particular for the study of time dependent variations at a given temperature. For sample S3 where the memory effect appears only after a threshold time of
Fig. 9. — Annealing of the memory effect of sample S5 obtained by heating in the β phase.

(a) Initial symmetric memory effect obtained after a writing time \( t_w = 24 \) h.
(b) Suppression of the step \( P_2 \) and reduction of the width of step \( P_1 \) after a 2 h heating at \( T_i + 0.5 \) K.
(c) Further reduction of the width of the step \( P_1 \) after heating 2 h at \( T_i + 6.5 \) K.
(d) Suppression of the memory effect after heating 12 h at \( T_i + 6.5 \) K.

6 h this is not too disturbing. However for sample S5 and even more for sample N(Al) the study of the time dependence is strongly affected by the existence of the memory effect. To have meaningful data it would be necessary to perform an annealing before each measurements.

2.4 DISCONTINUOUS VARIATIONS. — The effects described above (pinning steps, memory effects...) can now be considered as classical ones for inc phases. However we have recently discovered a new spectacular effect in quartz: for slow rate of temperature variation the change of physical properties becomes discontinuous. This phenomena which was first observed during the simultaneous measurement of γ-ray diffraction and of birefringence [37] has now been observed in most of our samples: we have already published some results [11] obtained on S3; here figure 10 shows the similar behavior observed on S5, when the rate of temperature variation \( \frac{dT}{dt} = 60 \) mK/h. Instead of the continuous variation observed in figure 3 for \( \frac{dT}{dt} = 300 \) mK/h, we now observe a discontinuous variation starting around point (A) and giving a staircase curve in the lower half of the inc phase. In the same way on the heating curve, a staircase behavior is observed below point (B). This discontinuous behavior is observed only below a critical rate of temperature variation as shown in figure 11: curve (a) obtained at \( \frac{dT}{dt} = 300 \) mK/h is continuous. For \( \frac{dT}{dt} = 240 \) mK/h some periodic accidents
Fig. 10. — Discontinuous variation of the birefringence of sample S5 as a function of the temperature for a slow rate of temperature variation \( \left( \frac{dT}{dt} = 60 \text{ mK/h} \right) \). On cooling the staircase behavior appears at point (A) and on heating it disappears at point (B). The insert shows the increase of the step width when the rate of temperature variation decreases below the threshold of 250 mK/h. Similar phenomena were observed in most of the present samples but with different values of the parameters. In table III we give the value of the critical rate \( \left( \frac{dT}{dt} \right)_c \) below which the staircase variation is observed, the width of the steps \( \delta T_c \) observed just below this critical rate and the width \( \delta T_o \) of the limiting step at small rate (for comparison we have also indicated the width of the pinning step \( \delta T_s \) observed after a waiting time of 12 h). For S3 we give two values, as a change of the staircase behavior was observed during the duration of the experiment: line S3 (a) corresponds to the results already published [11] which were obtained during the first week of the experiment. After 1 month of experiments in the inc phase, the staircase parameters have changed to the values of line S3 (b). The threshold rate has decreased as well as the starting step width. However the limiting step width at small rate takes the same value of 14 mK. For S1 no oscillation was observed even at the smaller rate of 2.4 mK/h while S2 was not measured at slow rate. For N(Al) at slow rate, the duration of a step becomes so long that memory effects are produced: after a slow scan with \( \frac{dT}{dt} = 4.8 \text{ mK/h} \) a staircase is observed with steps of 40 mK; in a subsequent rapid scan with \( \frac{dT}{dt} = 100 \text{ mK/h} \) the same staircase is observed but now as a memory effect. The stability of the memory effect in N(Al) can also produce a lock-in between staircases obtained with different rates of temperature variation.
The results of table III show some correlation between the widths of the staircase steps and of the pinning steps, often found between 10 and 20 mK. Only three samples S5, S(Ge) and N(Al) have larger steps of 30, 50 and 80 mK respectively, corresponding to the existence of larger pinning steps. By analogy with the behavior of the memory effect (observed directly in a γ-ray experiment [10]), one can suppose that each step of the staircase corresponds to a plateau of constant \( q \). (Recent diffraction experiments using synchrotron radiation at LURE (Orsay) have indeed shown that the staircase behavior is produced by successive pinning and depinning of modulation waves [38].) The steps of figure 10 correspond to change of \( q \) between 1 and \( 5 \times 10^{-4} \) a\(^*\); the observed steps are due to cooperative effects: for a 1 cm\(^3\) sample, about 5000 extra modulation periods appear (or disappear) along each modulation direction at each step. Finally we present some preliminary measurements on a «swept» sample, obtained by high temperature electrolysis of quartz [13]: this is an industrial process used to improve the performance of quartz oscillator, by changing the nature of the charge necessary to compensate a substitutional Al\(^{3+}\). We have performed birefringence measurements on a sample S5\(_v\) which has been swept in vacuum by J. P. Bachheimer and P. Palleau in our laboratory. After a careful vacuum sweeping, one expects that the ions (Na\(^+\), Li\(^+\)) will be eliminated in the vicinity of the Al\(^{3+}\) and replaced by an electronic hole (h\(^+\)). Indeed the birefringence measurement plotted in figure 12 shows a spectacular modification of the hysteresis cycle for this swept sample S5\(_v\), which comes from the same stone as S5: on cooling one observes only 6 large steps — the first one of 200 mK width. The thermal hysteresis on plateau (A) of 500 mK is the largest one observed in quartz and is 4 times greater than the thermal hysteresis of sample S5. Furthermore the rate of
temperature variation has now a small influence: large staircase steps are observed even at 600 mK/h, the only effect of slower rates is that the staircase steps are a little larger, so that there is one step less between $T_i$ and $T_c$. Further studies are under way to clarify the effect of sweeping. At the present time we can only mention that the behavior of S5v is so different from that of the other samples that in this case a new explanation of the staircase behavior appears necessary. The small influence of the rate of temperature variation suggests that the friction force is no more dependent on the velocity of discommensurations. Indeed the observed behavior is rather similar to the effect of a dry friction producing relaxation oscillations [35].

All the previous measurements show the great influence of impurities on the detailed behavior of the inc phase of quartz. It seems that H impurity is most important in several of these effects, but metallic impurities can also influence some effects in particular those which have a long time dependence.

3. Discussion.

In this last part, we will discuss the results obtained on quartz in relation to the general understanding of inc materials. After considering the effect of static impurities, we will turn to the effect of mobile impurities, and then discuss the phenomenon of discontinuous variations.

3.1 Static impurities. — It is now well known that metastable states are very usual in inc materials. Following the initial observation in TTF-TCNQ [39], a global hysteresis has been observed in nearly all the materials where there is a variation of the modulation wavevector as a function of temperature: most observations are related to insulating materials [2] but
similar effects have also been observed in several conducting CDW materials such as TaS$_3$ and K$_{0.3}$MoO$_3$ [1].

The common occurrence of a global hysteresis has sometimes been attributed to an intrinsic origin such as the effect of pinning by Peierls lattice forces which lead to various devil's staircase behavior; then the close succession of first order transitions may lead to an irreversible temperature behavior [40]. Another intrinsic explanation is related to the necessity of nucleation of linear defects in order to change the modulation period. Such deperiodization lines, first suggested by McMillan [41] for CDW and developed later by Janovec [42] for insulating materials, have indeed been observed directly by electron microscopy in several materials [43]. (One may note that such defects were already observed in 1976 in quartz [44] although the relation to an inc phase was only understood later.) Theoretical calculations of the effect of such nucleation process on the global hysteresis have been reviewed by Natterman [45] but as usual with nucleation theory comparison with experimental results is difficult, as critical parameter values are not well-known. Another support to the nucleation model is found in the recent computer simulation of Parlinski [46]: a 2D molecular dynamic calculation shows indeed nucleation of defects in the bulk or on the surfaces, which change the modulation period. In small samples these discrete events produce a discontinuous variation of the period, similar to the staircase behavior of quartz. But for large samples, one expects a continuous variation, due to the averaging of many uncorrelated nucleation events. (It is interesting to note that several works have developed models where the conduction of CDW is due to the nucleation of linear defects and that the analogy with the plastic behavior of metals has been emphasized [47].)

Although the nucleation of linear defects, either in the bulk or at the surface, is a topological necessity to change the modulation period of an inc phase, the relation with macroscopic global hysteresis is not clear, and in fact in most experiments described in the review paper of Hamano [3] it appears that the global hysteresis is rather due to the pinning by chemical impurities.

Prelovsek has recently published a review [48] of theoretical works related to the effect of impurity pinning, mostly in relation with the non-linear conduction of CDW. Few studies of the global hysteresis have been performed: we can cite the 1-D computer simulation of Littlewood and Rice [49] who have reproduced the irreversible variation of the modulation wavevector, and the phenomenological work of Lederer et al. [6], leading to a finite hysteresis at $T_i$, in agreement with experimental results on thiourea [50].

3.2 MOBILE IMPURITIES. — In almost all the studies presented above, only static impurities were considered. However it is clear that the memory effect can only be explained by a change in defect states, as this effect is observed even after heating in the normal phase. The memory effect can then be produced either by a diffusion of mobile impurities as considered by Lederer et al. [6] or by the reorientation of some defects as suggested by Unruh and Levstik [51]. As the diffusion model has been most developed, it will be briefly presented here. Lederer et al. [6] considered that there is a local interaction $V_0 \rho^2(r) \delta(r - r_0)$ between a point defect at $r_0$ and a sinusoidal modulation of amplitude $\rho(r)$ and of wavevector $q_m$ at a temperature $T_m$. (A linear coupling with $\rho$ would lead to a shift of $T_i$ [6], which has not been observed neither in quartz nor in thiourea.) Considering the impurity as mobile with a diffusion constant $D$, Lederer et al. [6] solved the diffusion equation in the sinusoidal potential of the inc wave. Then a Defect Density Wave (DDW) appears with a wavevector $2q_m$ and a time dependent amplitude $b(t)$ given by

$$b(t) = \frac{C_0 V_0 \rho^2}{k_B T} (1 - \exp(-4Dq_m^2t))$$

(1)
where $C_0$ is the concentration of mobile impurities. The lock-in energy $F_d$ between the DDW and a modulation wave of wavevector $q(T)$ is then

$$F_d = V_0 \rho \beta b(t) \delta (q(T) - q_m) = \frac{C_0 V_0^2 \rho^4}{k_B T} (1 - \exp(-4 D q_m^2 t)) \delta (q(T) - q_m).$$

(2)

There is a lock-in with $q(T) = q_m$ as long as this interaction energy is larger than the elastic energy $F_{el}$ due to the distortion of the modulation wave. Around the equilibrium value $q_e$, the elastic energy $F_{el}$ is given by a quadratic expression

$$F_{el} = \hbar \rho^2 (q(T) - q_e)^2.$$

(3)

When the initial modulation $q_m$ is equal to the equilibrium value $q_e$, one obtains the width $\delta q_d$ of the pinned steps from the equality of the lock-in energy given by equation (2) with the elastic energy of equation (3). Then assuming a linear temperature variation, $q(T) = q_m + \alpha (T - T_m)$ one obtains the temperature width $\delta T_d$ of the pinned step:

$$\delta T_d = \frac{V_0 \rho}{\alpha} \left[ \frac{C_0}{\hbar k_B T} (1 - \exp(-4 D q_m^2 t)) \right]^{1/2}.$$

(4)

This expression also gives the width of the memory step observed in subsequent cycles, if the amplitude of the DDW does not decrease during the elapsed time. One must point out that the $1/2$ power of equation (4) is a direct consequence of the quadratic expression of the elastic energy of equation (3) which is valid only when the initial modulation wave vector $q_m$ is equal to the equilibrium value $q_e$.

In the presence of global hysteresis, $q_m$ is no longer equal to $q_e$, but as shown by Lederer et al. [6] impurity pinning leads to different values, $q_-(T)$ upon cooling and $q_+(T)$ upon heating. When this global hysteresis effect is small relative to the memory effect, the previous calculation remains valid, at least for long writing times. However a different regime is observed when the lock-in effect is small relative to the global hysteresis. We start again with the elastic energy given by the quadratic expression of equation (3), but now we make a linear expansion around the initial value $q_m = q_+$ for small value of $q(T) - q_+$

$$F_{el} = \hbar \rho^2 (q(T) - q_e)^2 = \hbar \rho^2 (q(T) - q_+ + q_+ - q_e)^2 + 2 \hbar \rho^2 (q_+ - q_e) (q(T) - q_+).$$

(5)

Then one can assume that the width of the pinned step $\delta q_d = q(T) - q_+$ is given by the equality of the lock-in energy of equation (2), with the increase of the elastic energy corresponding to the distortion $q(T) - q_+$. Keeping the same linear temperature dependence, $q(T) = q_m + \alpha (T - T_m)$ one obtains the width $\delta T_d$ of the pinned step

$$\delta T_d = \frac{V_0 \rho C_0}{2 \alpha \hbar k_B T (q_+ - q_e)} (1 - \exp(-4 D q_m^2 t)).$$

(6)

So when the memory effect is small relative to the global hysteresis, one gets a simple exponential variation for the width of the pinned step. It appears that our results in quartz, at least on sample S3, are in agreement with the simple exponential behavior of equation (6) while those of Jamet in Thiourea [52] are in better agreement with those of equation (4). However the distinction between these two regimes when the memory effect and the global hysteresis are of the same order may be experimentally difficult.
Nevertheless, from either formula one gets an order of magnitude of the time constant \( \tau \) from which one can evaluate a diffusion coefficient \( D \). Taking our experimental value \( \tau = 7000 \) s, and a modulation period of 20 nm, one gets

\[
D = \frac{1}{4 \times 7000 \times \left( \frac{20 \times 10^{-9}}{2 \pi} \right)^2} = 3 \times 10^{-22} \text{ m}^2/\text{s}
\]

which is of the same order as the value found by Jamet [52] in thiourea but at a temperature of 200 K. In quartz this value can be compared with several experimental results, recently reviewed by Kronenberg and Kirby [53]: around the \( \alpha-\beta \) transition temperature, Na\(^+\) and H\(^+\) have diffusion constant parallel to \( OZ \) axis of the same order, \( D = 10^{-13} \) m\(^2\)/s, while for Li\(^+\), \( D \) is larger by about one order of magnitude. (For directions perpendicular to the \( OZ \) axis, the diffusion constants for Na\(^+\) and Li\(^+\) are smaller by at least 3 orders of magnitude, while the diffusion of H\(^+\) appears to be rather isotropic.) The strong disagreement between these values and the present result in the inc phase can be explained in several ways:

- There is a DDW, but produced only by the diffusion of impurities with a very low mobility. (The effect produced by impurities with normal mobility will disappear too quickly to be observed in the present experiment.)
- There is a DDW, but produced by the local reorientation of impurities, as suggested by Unruh and Levstik [51] and not by diffusion.
- There is a diffusion, not in the potential of the modulation wave, but in the long range field of defects of the modulation waves (deperiodisation lines, rotation grain boundaries...) as suggested by Snoeck et al. [31]. Then with \( D = 10^{-13} \) m\(^2\)/s one gets the good time constant (\( \tau = 7000 \) s) for lengths of \( 10^{-4} \) m which are of the order of magnitude of rotation domains observed by X-ray topography [54].
- Finally due to the strong anisotropy of the diffusion of alkali ions, it may be impossible to reduce this problem to a unidimensional one as the modulation vectors are perpendicular to \( OZ \) while alkali diffusion is mainly parallel to \( OZ \).

At the present time it seems difficult to make a choice between these different hypothesis and it will be necessary to accumulate more experimental results to understand the microscopic mechanism of the memory effect in quartz.

### 3.3 DISCONTINUOUS VARIATIONS

The regular staircase variations of physical properties, below a threshold rate of temperature variations, is a new phenomenon in the field of inc materials which at the present time has been observed only in quartz [11, 37] and in thiourea [36]. (A staircase behavior has also been observed in small TaS\(_3\) samples, with cross sections of a few \( \mu \)m\(^2\) but without any dependence on the rate of temperature variation [55].)

On the other hand, the existence of discontinuous steps due to defect pinning, has been reported in many materials, either in the presence of large impurity concentrations as in (Rb\(_{1-x}\)K\(_x\))\(_2\) ZnCl\(_4\) [56] or of irradiation induced defects [57-59]. In thiourea also, the existence of high order commensurate steps observed by Moudden et al. [60], has latter been attributed to X-ray irradiation damage [50].

Unruh [5] has also observed discontinuous variations of the dielectric constant in Rb\(_2\)ZnCl\(_4\) during temperature variations. However the coherence length of this phenomenon is very different from that observed in quartz: Unruh found no correlation for 2 electrodes distant by 1 mm, while in quartz the discontinuous variations are coherent on a sample of 1 cm length. The high coherence of the staircase variation in quartz is rather remarkable: recent results obtained after partial electrolysis, show that the coherence of the discontinuous steps is probably due to long range elastic effects [61].

In our previous paper [11], we have developed a model analogous to the phenomenological theory of the Portevin-Le Chatelier effect in alloys [62]. Both models are based on the
existence of a nonlinear friction force, showing a S-shaped dependence as a function of the velocity of the moving object (discommensurations (DC) for inc materials, lattice dislocations for alloys). Indeed Srolovitz et al. [63] have found such a S-shaped dependence for the friction force of a moving DC interacting with mobile impurities: at low velocity there is a large friction force as the impurities follows the DC motion, while at larger velocity of DC, when the impurities cannot follow the DC, the friction force is smaller. However a different explanation of the staircase variation has recently been proposed by Parlinski and Denoyer [65]: in a computer simulation of a 3D model, they obtained a staircase variation from correlated nucleation of several stripples.

New interesting features could appear from a study of the spatial dependence: the discontinuous steps observed as a function of time, are probably associated to spatial discontinuities, as already detected in the case of the Portevin-Le Chatelier effect [64]; similar spatial structure can probably be observed by optical or X-ray measurements in the inc phase of quartz.

This systematic study of the irreversible properties of the inc phase of quartz has shown surprising variations among different samples. However a result is now clearly established: these effects are related to the presence of chemical impurities. Furthermore it appears that H is probably the most important impurity for these effects. In addition to the global hysteresis observed in most inc materials, quartz (as thiourea) shows several time dependent phenomena (pinning steps, memory effect, discontinuous variations) which reveal the large effect of mobile impurities. Finally the possibility of changing the nature of these defects by electric sweeping can help to elucidate the mechanisms of these effects. The drastic change observed after vacuum sweeping is very encouraging for future work. But progress must also be made on the theoretical side in particular on the microscopic theory of the global hysteresis. We hope that the present results will push in this direction.

Acknowledgements.

We acknowledge J. P. Bachheimer and P. Palleau for building the furnace used in this experiment and for performing the vacuum sweeping of sample S5v. We thank Mr. D. F. Croxall from GEC (UK) and X. Buisson from SICN (France) for giving us characterized samples and Mr. B. Viard from Besançon University for the chemical analysis of sample S5.

References