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► To cite this version:

J.P. Bachheimer. An anomaly in the β phase near the α - β transition of quartz. Journal de Physique Lettres, 1980, 41 (23), pp.559-561. 10.1051/jphyslet:019800041023055900 . jpa-00231846

HAL Id: jpa-00231846

<https://hal.science/jpa-00231846>

Submitted on 1 Jan 1980

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Classification
 Physics Abstracts
 62.20D — 67.40K — 91.60

An anomaly in the β phase near the α - β transition of quartz

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(Reçu le 23 juillet 1980, accepté le 15 octobre 1980)

Résumé. — Des mesures détaillées de dilatation thermique, de module d'élasticité et de biréfringence, en phase β , près de la transition (1^{er} ordre) α - β du quartz révèlent une anomalie qui suggère l'existence d'une transition du 2^e ordre à une température légèrement supérieure à celle de la transition α - β .

Abstract. — Detailed measurements of thermal expansion, elastic compliance and birefringence in the β phase of quartz around the α - β first order transition show an anomaly which suggests the existence of a second order transition slightly above the usual α - β transition.

1. Introduction. — Since the discovery of the α - β first order ($T_1 \sim 573$ °C) phase transition of quartz by Le Chatelier (1889) much work [1] has been performed on the α (low temperature) and β (high temperature) phases.

However the microscopic mechanism of this transition is not precisely known. There is even some doubt regarding the β phase structure : from neutron diffraction, Wright and Lehmann [2] are in favour of a disorder type (corresponding to Dauphiné twins of α phases) structure contrary to Young's [3] conclusion of a displacive transition from X-ray data. Inhomogeneous structure resulting from phase coexistence or Dauphiné twinning has been observed at the transition [4, 5]. A zone centre soft mode has been observed in the α phase by Raman spectroscopy [6] and in the β phase by neutron scattering [7]. Recently a detailed study has been made of very low frequency phonons around the α - β transition [8].

Relatively few detailed measurements of macroscopic properties have been made in the α - β region with good temperature resolution. We have only found the following papers in which the hysteresis cycle is evident [9, 10] : thermal expansion [11, 4] birefringence and [6] adiabatic elastic constant c_{ij} by Brillouin scattering. Furthermore some ambiguities [12, 13] have been reported when one tries to compare data from different authors. So we have built an apparatus which allows simultaneous measurements of the isothermal and adiabatic elastic constants (s_{ij}) and of the thermal expansion (α_i) coefficients on the same sample. Further we can measure the birefringence. We have already shown [14] that in the α

phase the results obey Pippard's relations well while in the β phase further investigations are necessary.

The aim of this letter is to give only the most remarkable new results we have obtained in the β phase in the vicinity of the transition. (A complete discussion of Pippard's relations in this phase will be made in a future paper with more experimental detail.)

2. Samples and apparatus. — The measurements are made along the long dimension of single crystal parallelepipeds ($30 \times 7.5 \times 7.5$ mm³) of natural quartz with faces perpendicular to crystal axes.

For the furnace we have paid special attention to obtaining uniform and constant temperature. It was built with 3 independent heating coils in order to minimize the thermal gradient on the sample, which is measured by a differential thermo-couple (0.025° resolution). The crystal temperature is measured with better than 0.01 °C resolution, with a 50 Ω platinum resistor coupled to the sample by a gold foil using a 5 1/2 digit multimeter for readout.

For the elastic constants a uniaxial stress (σ_{ii}) obtained with a level and weights is applied to the sample through stainless steel pistons and gold foils. The relative pistons displacements are measured by a differential transformer transducer (LVDT) which gives a resolution of 2.5×10^{-5} mm. Just after a stress application the adiabatic value of the deformation is measured (Fig. 1). The sample goes back (in few minutes) to its equilibrium temperature, after which the isothermal value is obtained. When the stress is constant and the temperature varies we mea-

Fig. 1. — Measured deformation *versus* time under sudden stress application. The arrows indicate the adiabatic deformation (example shown for $T - T_i = +0.9^\circ\text{C}$, $\Delta\sigma_{xx} = 0.21 \text{ kg/mm}^2$).

sure with the same device the thermal expansion. The residual instrumental dilatation coefficient is about $2.5 \times 10^{-6}/^\circ\text{C}$.

To perform birefringence measurements, a small hole through the furnace allows a laser beam ($\lambda = 0.6328 \mu$) to pass through the middle of the sample perpendicular to the long dimension. Values of the phase angle $\varphi = \pi \Delta n \frac{l}{\lambda}$ (where Δn is the birefringence and $l = 7.5 \text{ mm}$ the thickness) are provided continually by the De Senarmont method using an automatic device.

Both expansion and birefringence (φ) values are recorded on an $X - Y_1, Y_2$ recorder with the temperature on the X axis.

3. Results. — The results of measurements from a sample along the X axis direction are shown in figure 2 (these curves were obtained with a constant stress of 0.7 kg/mm^2 which does not modify the conclusions because the main effect of this stress is to shift the transition temperature [14]). Another similar sample but from a different origin shows the same behaviour. Measurements on a third sample along the Z axis direction exhibit the essential features we have found in the X direction (with $\alpha_z \sim 0.53 \alpha_x$ in all the β region studied here). Figure 1a shows the thermal expansion we have obtained from the $X.Y$ recorder with a typical drift of 0.03°C/min . and a thermal gradient on the sample $\lesssim 0.1^\circ\text{C}$. The $\alpha \rightarrow \beta$ transition in heating appears abruptly whereas for the $\beta \rightarrow \alpha$ transition in cooling there is a premonitory length decrease in agreement with birefringence observation [11, 4]. We can observe small superheating and supercooling. In looking attentively we find a discontinuity of the slope around $\tilde{T} \sim T_{i\beta \rightarrow \alpha} + 1.3^\circ$. This anomaly is made more obvious by proper magnification of the dilatation curve (Fig. 2a bis). We can see it as well on the thermal expansion curve coefficients

Fig. 2. — Temperature dependence of the expansion and elastic modulus measured along the X axis of quartz in the vicinity of the α - β transition. *a*) Thermal expansion. *a bis*) Same as above, but focus on a special zone magnified by 4. In addition, the birefringence variations $\Delta\varphi$ are reported. *b*) Thermal expansion coefficient (calculated from *a*). *c*) • adiabatic (--- interpolated line) and + isothermal (— calculated, see text) Young's $(s_{11})^{-1}$ modulus of elasticity in β phase. (— — values in α phase from [14].)

(Fig. 2b). To check that this particularity is not due to an inhomogeneous crystal we have performed birefringence measurements which are local : figure 2a bis shows the same discontinuous character (in fact the birefringence is nearly proportional to the expansion in the transition region). Both birefringence and expansion curves have been verified to be reversible when cooling and heating, down to the $\beta \rightarrow \alpha$ transition (the heterophase structures appear in the dashed parts of the hysteresis cycle and are not reversible [4]). In figure 2c the temperature variation of the adiabatic and isothermal $(s_{11})^{-1}$ Young's modulus are reported. The main variation of the adiabatic value takes place slightly above the $\alpha \rightarrow \beta$ transition, around the $\tilde{T}$ region but the variation at the $\beta \rightarrow \alpha$ transition is lost in the scatter of the experimental points (around $\pm 3\%$ precision). (On the contrary the adiabatic values along the Z direction show a clear disconti-

nuity.) For the isothermal elastic coefficient we distinguish also two steps in going back to the α phase : a rapid softening around the $\tilde{T}$ region followed by a nearly linear temperature decrease to values several time lower than those of the α phase curve.

So in three independent measurements (Δl , Δn , s_{ii}) the existence of a new anomaly in macroscopic properties of quartz is observed. We think that this anomaly is intrinsic because we have observed it in three samples.

4. Discussion and conclusion. — In the previous published results on thermal expansion and birefringence, we think that generally either the lack of temperature resolution, or the thermal drifts or the thermal gradient on the sample were too great to allow the discernement of this anomaly which takes place in only a $\sim 0.15^\circ$ interval. Although it is difficult to compare the c_{ij} values of Shapiro [6] with our s_{ii} measurements we can note on his curves, in the β phase, certain inflexion points which might be related to the anomaly observed here.

The dilatation curves are found nearly invariant under small uniaxial stresses. This supports the validity of the cylindrical approximation made by Pippard so that the elastic isothermal compliances and expansion coefficients are related by the Pippard-Garland [15] relation :

$$s_{11} = \frac{\partial T_t}{\partial \sigma_{xx}} \alpha_x + s_{11}^0$$

taking

$$\frac{\partial T_t}{\partial \sigma_{xx}} = 1.04 \text{ } ^\circ\text{C/kg/mm}^2 \text{ } ^{(1)}$$

from our measurements and the values of α_x (Fig. 2b) with $s_{11}^0 = (11\,250 \text{ kg/mm}^2)^{-1}$ to obtain a good fit with the measured value [16, 17] some degrees above the transition we obtain the continuous line of $(s_{11})^{-1}$ we have plotted on figure 2c. The agreement with the experimental points shows the coherence of the measurements.

Expansion coefficients and elastic constants show sharp variation in the $\tilde{T}$ region ; this suggests the existence of a second order transition just above the well known $\alpha \rightarrow \beta$ transition. Indeed Aslanian and Levanyuk [18] have shown the theoretical possibility of an incommensurate phase in the β phase of quartz. This intermediate modulated phase type is not unusual and has been observed in several cases : NaNO_2 [19] for example. So in quartz we could have the same situation.

Acknowledgments. — Thanks are due to Dr. G. Dolino for stimulating conversations and clarifying comments and to Prof. Joseph Lajzerowicz and Dr. M. Vallade for fruitful discussions.

⁽¹⁾ For the $\alpha \rightarrow \beta$ transition the value is somewhat lower : $0.97 \text{ } ^\circ\text{C/kg/mm}^2$.

References

- [1] BACHHEIMER, J. P., DOLINO, G., *Phys. Rev.* **B 12** (1975) 3195 and references therein.
- [2] WRIGHT, A. F. and LEHMANN, M. S., *J. Solid State Chem.*, to be published.
- [3] YOUNG, R. A., Defense Documentation Center, Report n° AD 276 235 (1962), unpublished.
- [4] DOLINO, G., *J. Phys. Chem. Solids* **40** (1979) 121-128.
- [5] VAN TENDELOO, VAN LANDUYT, J. and AMELINCKX, S., *Phys. Status Solidi (a)* **33** (1976) 723.
- [6] SHAPIRO, S. M., Thesis, Johns Hopkins University U.S.A. (1969).
- [7] AXE, J. D., SHIRANE, G., *Phys. Rev.* **B 1** (1970) 342.
- [8] BOYSEN, H., DORNER, B., FREY, F. and GRIMM, H. G., to be published.
- [9] SORELL, C. A., ANDERSON, H. U., ACKERMANN, R. J., *J. Appl. Crystallogr.* **7** (1974) 468.
- [10] BANDA, E. J., CRAVEN, R. A., PARKS, R. D., HORN, P. M., BLUME, M., *Solid State Commun.* **17** (1975) 11.
- [11] DE MANDROT, R., *Mem. Soc. Vaudoise Sci. Nat.* **62** (1950) 1.
- [12] COE, R. S., PATERSON, M. S., *J. Geophys. Res.* **74** (1969) 4921.
- [13] KLEMENT, W., COHEN, C. H., *J. Geophys. Res.* **73** (1968) 2249.
- [14] BACHHEIMER, J. P., DOLINO, G., *Ferroelectrics* **25** (1980) 423.
- [15] GARLAND, C. W., *J. Chem. Phys.* **41** (1964) 1005.
- [16] MAYER, G., Rapport C.E.A. (France) (1960) 1330.
- [17] PERRIER, A., DE MANDROT, R., *Mem. Soc. Vaudoise Sci. Nat.* **7** (1923) 333.
- [18] ASLANIAN, T. A., LEVANYUK, A. P., *Solid State Commun.* **31** (1979) 547.
- [19] HAMANO, K., EMA, K., *J. Phys. Soc. Japan* **45** (1978) 923 and references cited therein.