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Light Scattering Study of α-β Transition of Quartz

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Coupled mode analysis of Raman spectrum of soft mode has given the temperature dependence of its frequency

$$\omega_l = 41\,|\mathrm{T}-\mathrm{T}_0|^{0.20\pm0.02}\,(\mathrm{cm}^{-1})$$

with $T_0 = T_c + 5$ K. The critical index $\gamma/2 = 0.20$ is significantly smaller than those for other structural phase transitions. Direct observation of phase boundary region near T_c has revealed that there exist linear inhomogeneities elongated along Z-axes (optic axes), which are the 'source' of opalescence. Change in T_c with an uniaxial stress along X-axes was found to be $\mathrm{d}T_c/\mathrm{dp} = +9.3 \pm 1.0$ K/kb, violatineg the rule by Samara et al.

§1. Introduction

The $\alpha-\beta$ phase transition of quartz at 573°C ($D_3^4 - D_6^4$) has been extensively studied since the first observation of the transitional opalescence by Yakovlev et al.[1] One of the reasons for the continueing investigations is that quartz is an excellent candidate for studying critical behavior of structural phase transitions, in particular, still puzzling phenomena of opalescenece and the underdamped soft mode behavior are peculiar to quartz.

As for the opalescence, Shapiro and Cummins have first shown[2] that it originates from static microdomains. From the correlation of scattered intensity we have confirmed that there are no frequency components in the range of 1 Hz ~ 50 MHz,[3] while recently, Bartis[4] has pointed out intrinsic defects may cause the transitional opalescence with an estimated lower frequency bound of 50 MHz. Apart from the frequency spectrum, careful investigation on the right and small angle scattering intensity from the phase boundary region has been performed by Dolino.[5] It is interesting that his results, as well as those of Shustin et al.[6] and ours,[3] indicate that the opalescence does not emerge equally in all directions but has strong directionality.

On the other hand, the soft mode behavior of quartz has been studied by several authors.[7,8] Scott[8] has taken into account the phonon hybridization and determined [9] the critical exponent for the soft mode frequency to be $\beta = 0.31 \pm 0.05$, which is almost the same as that of order parameter. However, no detailed coupled mode analysis has been performed yet to obtain the exponent, which should be represented not by β but by $\gamma/2$ (γ: critical exponent for susceptibility).

In this paper, we present some results on direct observation of transition region (§2), analysis of Raman spectrum (§3) and finally briefly comment on the effect of uniaxial stress. Detailed results on Raman spectrum will be published elsewhere.

§2. Observation of the Phase Boundary Region

Artificial quartz crystals of selected quality made by Kinseki-sha Co., Ltd. have been used throughout the experiment. A 6×6×6 mm³ sample was enclosed by a thin platinum plate with apertures and also by boron nitride to keep the temperature gradient less than 0.2 K/mm. It was then set in a stainless piston, which enables one to apply an uniaxial stress.

With a configuration shown in Fig. 1 (a), phase boundary region was observed along Z-axis (optic axis) by illuminating the sample with a tungsten lamp and simultaneously scattered light of He-Ne laser into Y-direction was measured to see the opalescence. As has been reported by Dolino,[5] near the transition temperature T_c, two layers of about a half millimeter thick were observed between the homogeneous α and β phases and they move as

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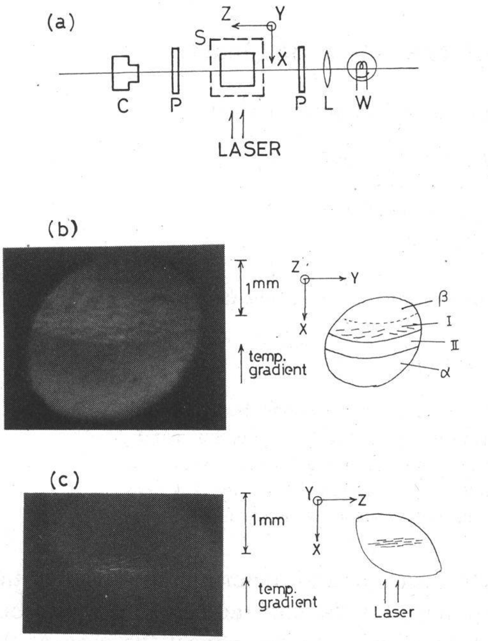

Fig. 1. (a) Experimental setup. W: tungsten lamp, L: lens, P: polarizer, C: camera, S: sample crystal in furnace. (b) Observation of transmitted light along Z-axis (optic axes). Two layers (I) and (II) are seen horizontally due to the approximately vertical temperature gradient. (I) is the coexistence region of α and β phases and (II) is supposed to be composed of microtwinnings of Dauphine type. (c) Observation from Y-direction of the scattered light (opalescence) of He-Ne laser incident along X-axis. The linear stripes are the source of 'opalescence' which corresponds the layer (II) in (b).

temperature is slowly raised (Fig. 1 (b)). The first layer with coarse grain structure locating at higher temperature side, is a region where α and β phase coexist, while the second more homogeneous layer is considered to be composed of microtwinnings.[10] The opalescence (Fig. 1 (c)) emerges only from the second layer, i.e. α-phase side of the boundary region.

It is interesting that, as shown in Fig. 1 (b), the 'source' of opalescence is neither homogeneous nor random grainy but it consists of linear stripes with a dimension of several tens of micron in width and a few tenths of millimeter in length. Such linear inhomogeneity explains the directionality of opalescence reported before.[3] Though the microscopic origin is not known,* the existence of such an inhomogeneity may change the nature of the phase transition.

* Dolino[5] has suggested the possibility that the minimum elastic energy is required for inclusion elongated along the Z-axis.

§3. Raman Scattering from Soft Mode

Raman spectra were measured using 514.5 nm Ar laser and a double-monochromator. In Fig. 2, spectra for lowfrequency A_1 modes in X(ZZ)Y configuration are given. Note that the raw data have been divided by the thermal factor $\{n(\omega)+1\}$ reducing them to $\chi''(\omega)$, imaginary part of the susceptibility.

First, static susceptibility has been estimated from the data using Kramers-Kronig relation $\chi(0)=\int_0^\infty\{\chi''(\omega)/\omega\}d\omega$. Since the soft mode contribution to $\chi(0)$ is expected to have a temperature dependence of $\chi_{SM}(0)\propto<\eta>^2<\Delta\eta^2>\propto|T_c-T|^{2\beta-\gamma}$, γ can be estimated if the temperature dependence of order parameter is known. Using the data on the second harmonic generation of light (SHG),[11] $\beta=1/3$, it was found that the lower mode contribution $\chi_l(0)/\langle\eta\rangle^2$ to static susceptibility *increases* slightly faster than $\langle\eta\rangle^{-2}$, that is, $\gamma\gtrsim2\beta$ for $15\text{K}<T_c-T<100\text{K}$. In contrast, the higher mode $\chi_h(0)$ is almost temperature independent, This method of analysis, however, has some ambiguities which prevented us determining the value of the critical index γ.

Next, we analysed the spectra as two damped harmonic oscillators coupled through a real

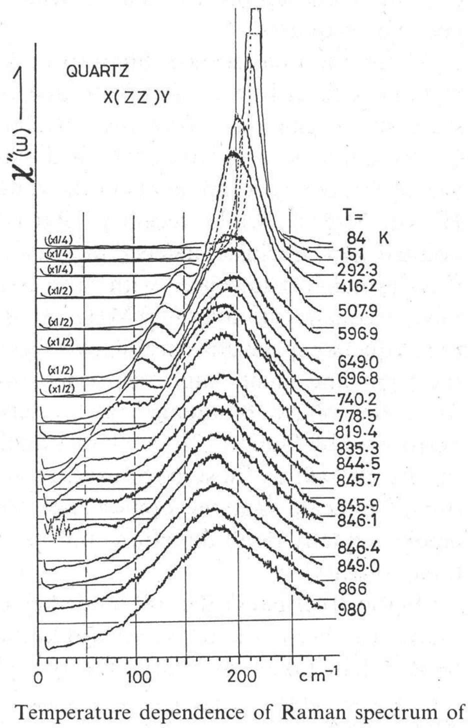

Fig. 2. Temperature dependence of Raman spectrum of low frequency A_1 modes in the configuration of X(ZZ)Y. Note that the raw data have been converted into $\chi''(\omega)$.

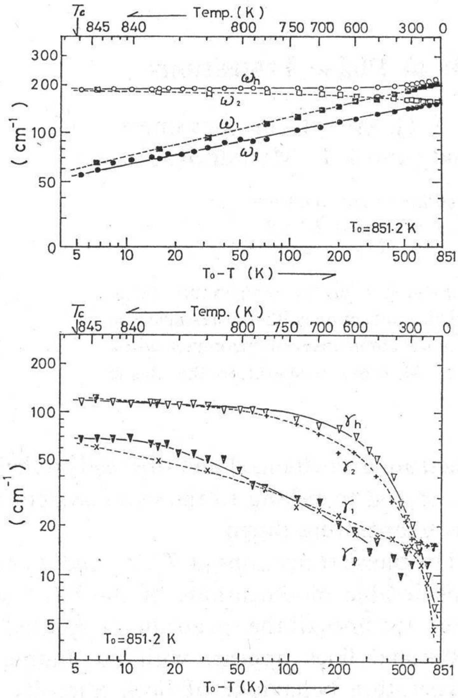

Fig. 3. Mode parameters obtained from the coupled mode analysis. $\omega_{l,\mathrm{h}}$ and $\gamma_{l,h}$ are frequencies and damping constants for the decoupled modes, respectively while $\omega_{1,2}$ and $\gamma_{1,2}$ are those for modes in the absence of the coupling.

coupling constant. Figure 3 shows the uncoupled mode parameters ($\omega_{1,2}$ and $\gamma_{1,2}$) and the decoupled mode parameters ($\omega_{l,\mathrm{h}}$ and $\gamma_{l,\mathrm{h}}$). It should be mentioned that decoupled modes are generally no more simple damped harmonic oscillators and the frequency $\omega_l(\omega_\mathrm{h})$ is the most important parameters representing the distance of poles of $\chi(\omega)$ in complex ω plane.[12] From Fig. 3, we obtain $\omega_l=41|T_0-T|^{0.20\pm0.02}$ cm^{-1} with $T_0=T_\mathrm{c}+5$K for a very wide temperature range.* The critical exponent of the soft mode $\gamma/2=0.20\pm0.02$, being much less than the classical value of 0.5, is still significantly smaller than that obtained by Höchli and Scott[10] as $\beta=0.31\pm0.05$. Since for various models of phase transitions, the exponent γ is known to be larger than unity, such a small value of γ is rather puzzling. It is speculated, however, that linear inhomogeneity along Z-axis mentioned above (§2), may affect the soft mode behavior either through the lowering of dimensionality or the strain field around the inhomegeneity.

Finally we briefly present the preliminary result on the effect of uniaxial stress. Variation of the transition temperature with the applied stress along X-axis was determined to be $\mathrm{d}T_\mathrm{c}/\mathrm{d}p=+9.3\pm1.0$ K/kb, which is slightly less than the reported value of 10.6 ± 0.4 K/kb.[13] Softening of the lowest mode similar to that of Fig. 2 was observed when one approaches the $T_\mathrm{c}(p)$ line from the α-phase side.

It should be noticed that the positive value of $\mathrm{d}T_\mathrm{c}/\mathrm{d}p$ of quartz violates the rule given by Samara et al.[14] Which says that the sign of $\mathrm{d}T_\mathrm{c}/\mathrm{d}p$ for displacive type structural phase transitions is positive or negative depending on whether the relevant soft mode is located on Γ point or zone boundary in reciprocal space, respectively. Here, taking into account of the result for quartz, we propose a revised expression: "$\mathrm{d}T_\mathrm{c}/\mathrm{d}p$ is positive or negative depending on whether the soft mode is infrared active or inactive, respectively." If the lack of dipolar long-range force for the Z.B. soft phonon is essential for the rule of $\mathrm{d}T_\mathrm{c}/\mathrm{d}p$, this expression seems reasonable since the long-range force is always accompanied with an infrared active lattice mode but not necessarily with all modes at Γ point.

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* Uncoupled mode frequency ω_1 has the temperature dependence of $\omega_1=41|T_0-T|^{0.25\pm0.05}$ cm^{-1}.

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