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LETTER TO THE EDITOR

Dynamical central peak near the incommensurate phase transition of quartz

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Abstract. The central peak of quartz near the incommensurate (INC) phase was investigated by means of the high-resolution light-scattering technique. It was found that the observed central peak includes a broad dynamical component in addition to the previously reported narrow static component. The linewidth (approximate range 1.5–5 GHz) of the broader component decreases in proportion to $\Delta T = T - T_i$ in the β phase (T_i is the β–INC phase transition temperature), and its intensity shows a maximum at T_i. It becomes very weak when the temperature is close to T_c (INC to α phase transition temperature), while the linewidth is within the instrumental linewidth of 0.6 GHz throughout the INC phase. Possible origins of the peaks are briefly discussed.

The incommensurate (INC) phase of quartz near the α–β transition at $T_c = 573$ °C has been studied since 1983 by a number of researchers (Gouhara *et al* 1983, Dolino *et al* 1983, Van Landuyt *et al* 1985). The lower transition at T_c from the INC phase to the α phase is a first-order phase transition, which is easily recognised, since a strong elastic scattering of light, the so-called critical opalescence, appears at T_c (Yakovlev *et al* 1956). The higher transition from the β to the INC phase at $T_i = T_c + \Delta T_i$ ($\Delta T_i = 1.3$–1.8 K) is a second-order phase transition. The condensation of a soft mode with a wavevector $k_i \simeq 0.03a^*$ (a^* is the reciprocal lattice vector along the x axis) at T_i generates a modulated structure in the INC phase, which was confirmed by x-ray and neutron diffraction experiments and also directly by electron microscopic observations (Gouhara and Kato 1984, 1985, Dolino *et al* 1984a, b). Besides the discommensuration lattice, a few modulated structures with a different scale were reported in the INC phase, for example the $\pm\varphi$ domain structure and the super-modulation structure (Gouhara and Kato 1985).

In light-scattering studies, both amplitude and phase modes are expected to be observed in the low frequency region from phenomenological theory (Golovko and Levanyuk 1983, Shionoya *et al* 1986). However, only a few light-scattering studies on the dynamical behaviour in the INC phase of quartz have been performed up to now. A-symmetry and E-symmetry amplitude modes were observed around 10 cm^{-1} in the Raman spectra of the INC phase (Berge *et al* 1984, Shigenari *et al* 1987), while the

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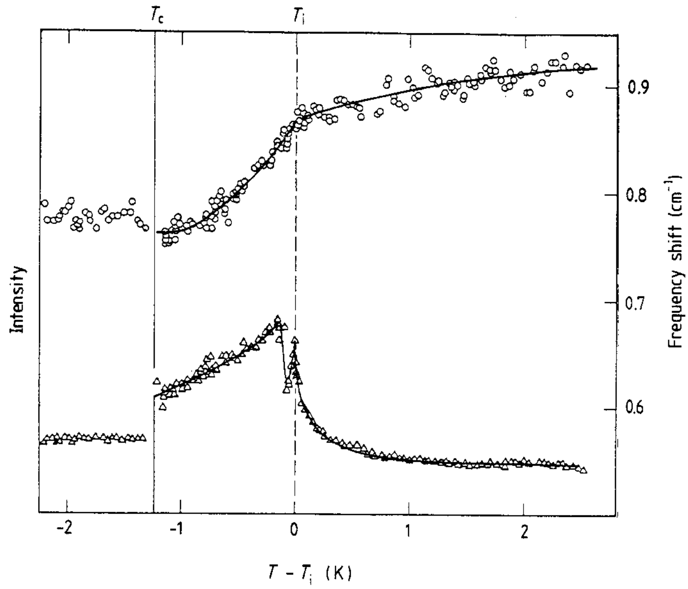

Figure 1. Temperature dependence of the central-peak intensity (▲) and the frequency shift of the LA mode (○) in Brillouin–Rayleigh spectra near the incommensurate phase. The temperature is given by the difference from T_i, at which the central peak intensity has a maximum and the frequency shift of the LA mode has a kink.

observation of a phase mode has not yet been reported. The existence of the temperature-dependent central peak of quartz has been reported first by Berge *et al* (1984), and then by Shigenari and Shionoya (1985). It was found that the central peak shows an apparently strange dependence on the direction of the $\boldsymbol{q}$-vector (Shigenari and Abe 1989). As for the width of the central peak, no broadening exceeding the resolution of the spectrometer has been reported.

In this Letter, we report a first observation of a dynamical central peak in polarised Brillouin–Rayleigh spectra. The scattering configuration is $XY(Z, Z)X\bar{Y}$, so that the scattering vector $\boldsymbol{q}$ is parallel to the Y axis, which is the direction of propagation of the modulation wave. Brillouin–Rayleigh spectra were obtained using the triple-pass Fabry–Perot interferometer with the finess of 42 and FSR = 49.5 GHz. A single-mode Ar^+ laser (514.5 nm) with a power of about 500 mW was used for the excitation. A natural quartz crystal with dimensions $3 \times 8 \times 8$ mm^3 was carefully polished and set in an oven with temperature stability better than ± 0.02 K. The Rayleigh component of the spectra could be observed without using an I_2 filter because of the high purity and optical homogeneity of the quartz crystal. This enabled us to detect subtle changes in spectra in the low-frequency region.

Figure 1 shows a temperature dependence of the peak intensity of the central component and the Brillouin shift of the LA mode in and near the INC phase, obtained by slowly cooling from the β phase. It was measured with a relatively low-resolution spectrometer, so that the central-peak intensity includes the contribution from two components described in the following. The frequency shift of the LA mode monotonously decreases with temperature in the β phase. Then it starts to decrease steeply at about $T_c + 1.42$ K for this sample and gradually approaches the value of the α phase;

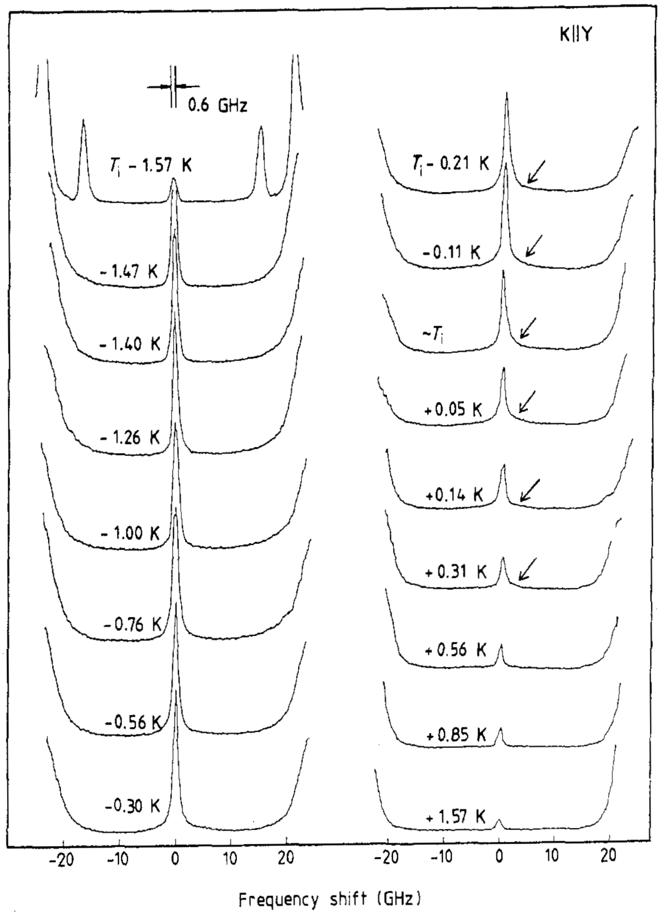

Figure 2. The temperature dependence of the $XY(Z, Z)X\bar{Y}$ Brillouin–Rayleigh spectra in the region $T_c - 0.05\ \mathrm{K} < T < T_i + 1.57\ \mathrm{K}$, where $T_c = T_i - 1.52$ K. The temperature decreases from the bottom of the right-hand side to the top of the left-hand side. The increase of intensity at both sides of each spectrum is due to the Brillouin line of the LA mode.

it shows no anomaly at T_c. Far above T_i, the central peak is hardly detectable. As the temperature is decreased, the intensity of the central peak increases considerably and makes a weak maximum just at a temperature where the shift of the LA mode shows an anomaly. Thus we take this temperature as the β–INC phase-transition point, T_i. The temperature determined by this method agrees with the temperature at which the linewidth of the satellite peak starts to decrease abruptly in the neutron scattering study after Dolino *et al* (1984a, b). On further cooling, it was observed that the intensity jumps abruptly and shows another maximum at about 0.2 K below T_i in the INC phase. This jump of intensity is reproducible for repeated temperature cycles. In the INC phase it decreases gradually with temperature decrease and loses its intensity suddenly at T_c.

The temperature behaviour of the Brillouin–Rayleigh spectra obtained near the INC phase is shown in figure 2. In the spectra at $T_i + 1.57$ K, i.e. well above T_i, the central component is very weak and it remains so for higher temperatures. Thus, it is simply due to the residual elastic scattering from the surface and/or defects. The background between the LA mode and the central peak is flat, indicating the absence of interaction between the modes at $T \gg T_i$.

As the temperature approaches T_i, the central-peak intensity gradually increases. In addition to the increase in the peak intensity, we notice that a broad component appears around the tail of the central peak, as indicated by the arrows in figure 2. Its intensity increases and the linewidth becomes sharp as the temperature approaches T_i from the β phase. In contrast to the tail, the narrow central peak grows in intensity and no change was observed in the INC phase with respect to the linewidth. Both the broad and narrow components disappear in the α phase, except for the spurious elastic scattering.

In order to analyse the lineshape, we have tried to separate the spectrum into two components by simply assuming a superposition of a certain relaxational mode and a elastic, but still closely related to the phase transition, component.

$$I = I_B \Gamma/[(\omega - \omega_0)^2 + \Gamma^2] + I_N\{1/[1 + F(\sin^2\delta/2)]\}^3 + \text{background} \qquad (1)$$

$$F = 4R/(1 - R)^2. \qquad (2)$$

The first Lorentzian term represents the broad component and the second term represents the narrow component, which is the instrumental function of the Fabry–Perot interferometer (called Airy's formulae). Γ is the inverse of the relaxation time and represents the half-width at the half maximum (HWHM), ω_0 is the frequency of the incident beam. $\delta = (\omega/c)(1/\text{FSR})$ and R are the phase difference and the reflection coefficient of the Fabry–Perot interferometer, respectively. In the analysis the F was treated as a parameter.

The calculated curve agrees fairly well with the observed central peak, as shown in figure 3. The results evidently show that both the linewidth and the intensity of the broader component are temperature dependent. Use of a single term, either of those in equation (1), could not reproduce the overall lineshape.

Figure 4 shows the temperature dependence of the linewidth (HWHM) and the intensity. The linewidth of the narrow peak is less than the resolution (0.6 GHz) of the Fabry–Perot interferometer for the entire temperature range (figure 4(*a*)). In contrast, the linewidth of the Lorentzian decreases in proportion to T–T_i and reaches about 1.5 GHz at T_i in the β phase. In the INC phase, no conceivable change in the linewidth was detected and the value was scattered around 2 GHz. As for the intensity, it turns out that the first weak maximum shown in figure 1 is due to this broad dynamical central peak, while the second maximum or jump comes from the narrow central peak, the behaviour of which has been described recently (Shigenari and Abe 1989). In the α phase, both central peaks disappear.

At the present stage, it is hard to identify the origin of the central peaks observed. From the fact that the linewidth of the broad peak gets narrow toward T_i, this mode has a dynamical origin related to the β–INC phase transition. However, it cannot be the phason in the INC phase, since the intensity of the phason is expected to be proportional to the square of the order parameter, while the broad peak has a significant intensity only near T_i.

In other materials undergoing the structural phase transition, central peaks have been observed and various interpretations have correspondingly been proposed. Comparing our results on quartz with other crystals, we note that the linewidth 1.6 GHz at T_i is larger than those observed in KH_2PO_4 (Courtens 1978) and KTS ($K(H_xD_{1-x}(SeO_3)_2)$ (Tanaka *et al* 1978), and it is rather close to that of $BaMnF_4$ (Bechtle *et al* 1978) which also shows an INC phase transition. It is well known that in the former two cases the

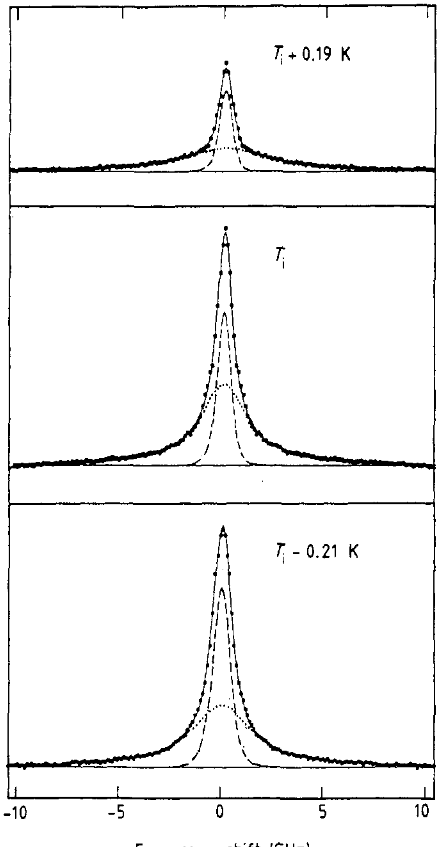

Figure 3. Computer fitting to the observed central-peak spectra at three temperatures close to T_i. Dots represent the experimental data points. Full curves represent the calculations. Broken and dotted curves represent the Airy's and Lorentzian components, respectively.

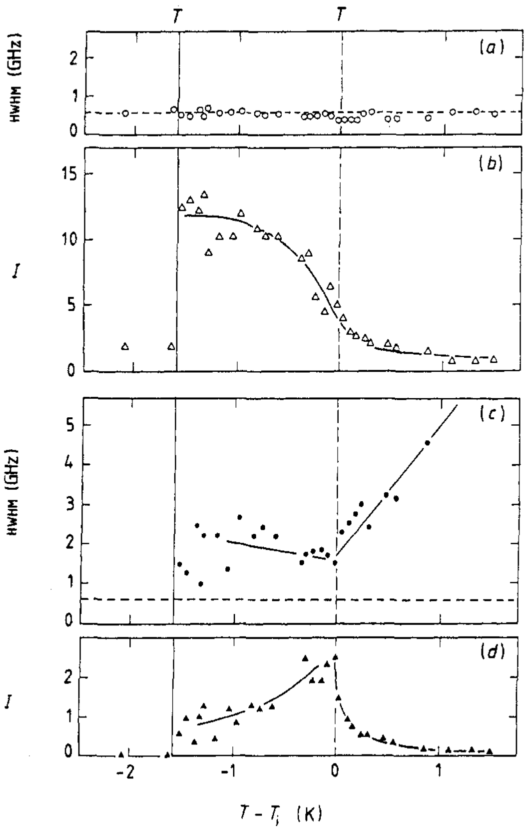

Figure 4. Temperature dependences of linewidth (HWHM) and peak intensities of the two central peak components: (*a*) and (*b*) are those for the narrow central peak; (*c*) and (*d*) are those for the broad central peak (dynamical central peak). The broken curves represent the instrumental linewidth (0.6 GHz) dominated by the finess of the Fabry–Perot interferometer. Full curves are guides for the eye.

narrow central peaks originate from dislocations and/or impurities, which are essentially static, but couple with soft modes. Thus the linewidth is much narrower than those of crystals like $Pb_3Ge_5O_{11}$ (Lyons and Fleury 1978) and NH_4Cl (Andrews and Harley 1981). It has been proved also that such central peaks disappear in annealed crystals. In the quartz case, samples used in the experiment have a high purity, and reproducibility among a number of samples is good. So, it is not likely that the central peak in quartz is caused by the scattering from impurities.

The other possible mechanism is the 'two phonon difference' scattering of the soft phonon modes at $\boldsymbol{k}_i$: in other words, phonon density fluctuation of the soft phonon near T_i. Its temperature dependence ($T > T_i$) reflects the fluctuation of the soft phonon mode at $\boldsymbol{k}_i$. In the case of entropy fluctuation, a characteristic frequency (HWHM) is expected to be proportional to q^2 (Fleury and Lyons 1983). However, the measurement of the dependence on the magnitude of the scattering vector $\boldsymbol{q}$ has not yet been performed.

The origin of the narrow peak has not yet been definitely made clear, either. It is considered that the narrow peak is an elastic scattering from the static scattering object. According to a possible mechanism proposed by Shigenari and Abe (1988), it is the scattering due to the $\pm\varphi$ domain walls. In the INC phase of quartz, the modulation waves propagating along the three equivalent Y axes form a triangular discommensuration lattice. These discommensurations split into $\pm\varphi$ domains where the modulation lattice tilts from the X axis by a temperature-dependent angle φ (Walker 1983, Van Landuyt *et al* 1985). Due to the formation of these tilted domains, strain will be concentrated near domain boundaries. Spatial inhomogeneity of the dielectric constant $\Delta\varepsilon$ induced by this strain would be responsible for the elastic scattering. Based on this idea, the directional dependence of the central-peak intensity was explained.

In conclusion, we have found a dynamical central peak near the β–INC phase transition T_i, in addition to a narrow central peak. The mode, probably the two phonon difference scattering of the soft mode at k_i, cannot be attributed to a phason.

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