Observation of the Silent Soft Phonon in β-Quartz by Means of Hyper-Raman Scattering

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(Received 3 December 1990)

By means of hyper-Raman scattering, a silent soft phonon was observed in β-quartz for the first time. The soft phonon was found to become underdamped at high temperatures. Both the square of the frequency ω_0^2 and the integrated intensity I_0 of the soft phonon were found to obey Landau-Cochran's soft-mode theory. The α-β phase transition of β-quartz is found to be well described by a simple displacive-type phase transition with the silent soft phonon, in contrast to many studies which suggest an order-disorder phase transition.

PACS numbers: 64.70.Kb, 78.30.Hv

Quartz (SiO_2) is one of the most important materials for science and technology. Although a number of studies on quartz have been made, the mechanism of its phase transition is not understood clearly. Quartz undergoes a phase transition[1] at $T_c = 573\,°C$ from a high-temperature hexagonal β phase with point-group symmetry D_6 into a low-temperature trigonal α phase with point-group symmetry D_3. It is known that there is an incommensurate phase in a very narrow temperature range between T_c and $T_i = T_c + 1.8\,°C$.[2,3] From group-theoretical analysis, the soft mode of the α-β phase transition in the β phase is the B_1 silent mode, which is inactive for both Raman scattering (RS) and infrared (ir) measurements, while that in the α phase is the Raman-active A_1 mode. The displacements of atoms in the soft mode can be approximately described by the rotation of SiO_4 tetrahedra along the crystal a axis.[4]

In the α phase, the soft phonon with A_1 symmetry was found by Scott[5] from measurements of RS and the phase transition was well described by a displacive-type phase transition. But, since the α-β phase transition at T_c is first order,[1] the phase-transition mechanism in the β phase is not necessarily the same as that in the α phase. In fact, there is confusion about the phase-transition mechanism in β-quartz. From the studies of electron-diffraction[6] and neutron-diffraction[7] measurements, it was pointed out that the structure of β-quartz is an average of α_1 and α_2 structures which are different from each other only by the direction of the a axis, with 180° rotation around the c axis. Furthermore, Tsuneyuki, Aoki, and Tsukada recently performed a molecular-dynamics calculation and obtained the same result for the β-quartz structure as those described above.[8] From the study of inelastic neutron scattering, on the other hand, Axe and Shirane observed the central soft mode in the β phase, whose intensity varied as the Curie-Weiss law.[1] However, it could not be determined whether the origin of this central soft mode is a phonon or relaxational model, since this soft mode shows one peak at 0 cm^{-1} in the entire temperature range from T_c to about $T_c + 200\,°C$ and the line-shape fitting by a model function could not be performed.

Quartz contains three SiO_2 molecules in a unit cell and the irreducible representations of optical phonons in the β phase with point group D_6 are given as follows:

$$\Gamma_{opt} = A_1(R) + 3B_1(HR) + 2A_2(ir,HR) + 2B_2(HR) + 4E_1(ir,R,HR) + 4E_2(R,HR),$$

where ir, R, and HR in parentheses show activity for these measurements, respectively. The silent soft mode with B_1 symmetry in the β phase is active for the hyper-Raman scattering (HRS) measurement alone. The HRS tensor of the B_1 mode has only two components, $\beta_{xxx} = a$ and $\beta_{yyx} = -a/3$. Since the E_1 mode has the same HRS tensor components as those of the B_1 mode, it is difficult to observe only the B_1 mode. However, the contribution of the E_1 mode to the spectra of the B_1 mode is negligible, because the intensity of the E_1 mode is too weak. It should be noted that second-harmonic generation (SHG) is forbidden in point group D_6 irrespective of its acentric symmetry. Therefore, it is convenient to observe the soft mode of β-quartz in the low-energy region.

Since HRS is a second-order nonlinear process of the electric field of laser light, the scattering intensity of HRS is very weak compared with that of RS. Especially, HRS intensity in quartz is very weak. So, in order to measure the HRS spectra of quartz, we employed a photon-counting level multichannel detector PIAS (HAMAMATSU K.K.) with a single grating monochromator HR320 (Jobin Yvon).[9] As the source of exciting radiation of the HRS measurements, an acoustic Q-switched Nd-doped yttrium-aluminum-garnet laser whose wavelength is 1064 nm was used with a peak power about 17 kW at a pulse repetition rate of 1 kHz. A focusing lens with $f = 100$ mm was used. An optically polished natural quartz with dimensions $6\times4\times5$ mm^3 was set in a furnace with a temperature stability better than $\pm 0.5\,°C$. A right-angle scattering configuration $Z(XXX)Y$ was employed to measure the light scattering by the strongest HRS tensor component of the B_1 mode. Quartz has a rotatory power along the crystal c axis, but the rotation angle of the polarization vector is within 10° for the wavelength of 1064 nm. The measurement of the HRS spectra was tried in all scattering configurations, but HRS intensity in the β phase is found to be too weak to be detected except for the configurations $*(XXX)*$ and $*(YYX)*$ which include the B_1 soft mode.

Figure 1 shows HRS spectra in the β phase measured at various temperatures with the scattering configuration $Z(XXX)Y$. These spectra clearly show that a central peak at low temperature becomes two peaks at high temperatures except for a very weak residual central peak. Since all of these spectra can be well fitted with a damped harmonic oscillator (DHO) from near T_c to $T_c+200\,°C$ as shown in Fig. 1 except for the central part, the spectra are suggested to be caused by the soft phonon. On the other hand, since the residual central peak at high temperatures seems not to vary with decreasing temperature, it might be SHG caused by an impurity and/or defect which partly breaks the D_6 symmetry. Further, the intensity of this SHG is negligible compared with that of the soft phonon at low temperatures, because this intensity is almost constant while the soft-phonon intensity rapidly increases at low temperature, where HRS spectra are well fitted by the DHO curve calculated without this SHG spectra.

As seen in Fig. 1, hyper-Raman spectra at low temperatures show a single peak. Therefore, it is a serious problem whether these spectra are the overdamped soft phonon or the relaxational mode. In order to decide about the line shape of HRS spectra at low temperature, line-shape analyses of $I(\omega)\omega^2$ are performed following the method in Ref. 10. As shown in the inset of Fig. 1, the $I(\omega)\omega^2$ plot of the HRS spectrum clearly shows the DHO spectrum, because the $I(\omega)\omega^2$ spectrum has a peak at ω_0 and decreases in the high-frequency region. That is, the soft mode is the DHO and the relaxational mode is thought to be negligible in the temperature region above 590 °C, if it exists.

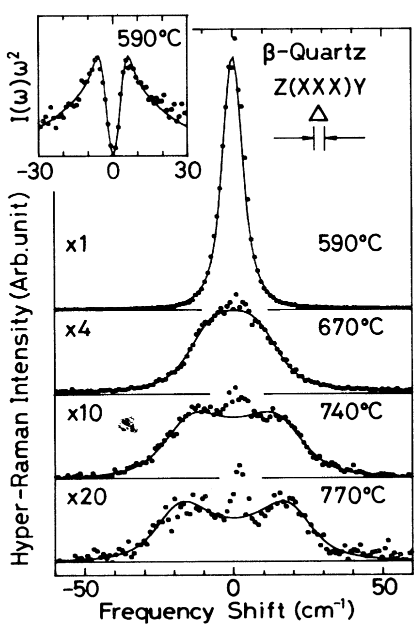

FIG. 1. Hyper-Raman spectra of β-quartz at various temperatures. Solid circles are observed data. Solid curves are the spectral line shape fitted by a damped harmonic oscillator. Residual central peak might be the SHG caused by impurities and/or defects. Inset: $I(\omega)\omega^2$ plot at 590 °C.

Hyper-Raman spectra of the β quartz are well fitted in the temperature region from 590 to 770 °C by the DHO spectrum which is convoluted by the instrumental function. Figure 2 shows the temperature dependences of the squared frequency ω_0^2 and damping constant Γ of the soft phonon. Since the line shape of the DHO strongly depends on ω_0/Γ as well as ω_0, ω_0 and Γ can be determined with an accuracy of about ± 1 and ± 2 cm^{-1}, respectively. As seen in Fig. 2, the ω_0^2 obeys Landau-Cochran's soft-mode theory based on mean-field approximation; $\omega_0^2 \sim |T-T_0|^\gamma$, $\gamma=1$, where T_0 is a temperature slightly lower than T_c as discussed later. The frequency of the soft phonon in the β phase is found to be much lower than that in the α phase, which is consistent with the results of lattice-dynamical calculations obtained by Elcombe.[11] Γ shows almost a constant value of 26 ± 2 cm^{-1} in the temperature range from T_c to 710 °C ($T_c+137\,°C$) and slightly decreases with increasing temperature in the high-temperature region above 710 °C.

Scott observed a soft phonon in α-quartz obeying $\omega_0^2 \sim |T-T_c|^\gamma$, $\gamma=\frac{2}{3}$, which is not in agreement with the result by the mean-field approximation theory. These critical exponents in both high- and low-temperature phases are also reported to be $\gamma=1$ (Ref. 12) and $\gamma=\frac{2}{3}$,[13] respectively, in hexagonal $BaTiO_3$ which also shows a silent soft phonon in the high-temperature phase. Furthermore, the value of $\gamma=\frac{2}{3}$ is also reported for SbSI (Ref. 14) and $SrTiO_3$,[15] and this value of $\gamma=\frac{2}{3}$ is explained by a "cigarlike" cluster model, which includes a weak uniaxial anisotropic interaction between clusters.[16] From the electron-microscopy obser-

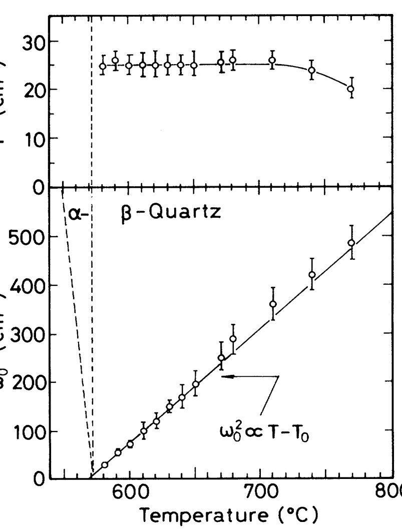

FIG. 2. Temperature dependence of ω_0^2 and Γ of soft phonon. Open circles are fitting parameters obtained from Fig. 1. Solid line for ω_0^2 is $\omega_0^2 \sim T-T_0$ ($T_0=T_c-5\,°C$). Broken line for α phase is given by Ref. 5.

vation of Dauphiné twins in α-quartz by von Tendeloo, van Landuyt, and Amelinckx,[6] it was found that the domain of Dauphiné twins forms a roughly triangular prism with the edge parallel to the c axis and the walls of this domain vibrate. Furthermore, the uniaxial anisotropy of the interaction is thought to be weak in α-quartz, because there is no strong long-distance force such as the electric field by spontaneous polarization in ferroelectrics. Therefore, the cigarlike cluster model might possibly apply to α-quartz.

Figure 3 shows the temperature dependence of the integrated intensity I_0 which is measured by using a slit width with the resolution of $\pm 50\ \mathrm{cm}^{-1}$. The temperature of the sample was raised slowly by 0.24 °C/min and the intensity was integrated over 5 min per point. The measurement was also done for the cooling process, but any intrinsic difference was hardly noticed. The temperature calibrated by critical opalescence[17] appeared at $T_c = 573\,^\circ\mathrm{C}$. In the β phase, I_0 is mainly the integrated intensity of HRS by the soft phonon since SHG is very weak. The temperature dependence of I_0 clearly shows that the soft-phonon HRS intensity increases gradually as the temperature approaches T_c from the high-temperature side. But, at about $T_c + 2\,^\circ\mathrm{C}$, I_0 increases rapidly and then suddenly disappears at T_c. Since the temperature $T_c + 1.8\,^\circ\mathrm{C}$ is T_i, the temperature region of rapid increase may correspond to an incommensurate phase. This rapid increase of I_0 may be due to SHG which is induced by the ordering of lattice displacements in the incommensurate phase, because the order parameter is not zero in this phase. Furthermore, an amplitudon or phason may be thought to be responsible for this rapid increase. Because they are proportional to the square and biquadratic of the order parameter, respectively,[3] the temperature dependence of I_0 may be able to be elucidated. In order to clarify the origin of the rapid increase of I_0, it is necessary to observe the HRS spectra in the incommensurate phase as well as the detailed measurement of I_0. In the α phase, we could not discuss I_0 in detail, because the sample has a Dauphiné twin. But, it is suggested that the intensity of both the soft phonon and SHG are very weak in the α phase.

Figure 4 shows the temperature dependence of T/I_0. In this figure, T/I_0 shows a linear temperature dependence as $T/I_0 \sim |T - T_0|$, where T_0 is 568 °C, lower than $T_c = 573\,^\circ\mathrm{C}$ which is the first-order phase-transition temperature. This value of T_0 is higher than $T_0 = T_c - 10\,^\circ\mathrm{C}$ reported by Axe and Shirane.[1]

It is said that the frequency dependence of RS spectra, which is active for both RS and ir, is proportional to the imaginary part of the electric susceptibility $\chi(\omega)$ caused by ion displacements.[18] In the case of a ferroelectric phase transition where the soft mode is intrinsically ir active, T/I_0 should obey the Curie-Weiss law.[9] However, the temperature dependence of T/I_0 in β-quartz would not follow this law which means a divergence of the dielectric constant, because the electric susceptibility does not diverge toward T_0 in quartz. But, the temperature dependence of T/I_0 does show the Curie-Weiss law. We will discuss this temperature dependence of T/I_0 by introducing a generalized susceptibility.

First, electronic polarization $P(\omega)$ induced by radiation in materials develops from the incident electric field as

$$P_i(\omega) = \sum_j \alpha_{ij}(\omega) E_j + \tfrac{1}{2} \sum_{jk} \beta_{ijk}(\omega) E_j E_k + \cdots ,$$

where $i,j,k = X,Y,Z$. The $\alpha(\omega)$ and the $\beta(\omega)$ are the electronic polarizability and the hyperpolarizability, respectively. Since $\alpha(\omega)$ and $\beta(\omega)$ are generally a function of the position of atoms in a crystal, differentials of the $\alpha(\omega)$ and the $\beta(\omega)$ by normal coordinates give the RS and HRS tensor, respectively.[19] That is to say, the fluctuations of $\alpha(\omega)$ and $\beta(\omega)$ give RS and HRS spectra, respectively. The fluctuation of electronic polarizability is induced by the relaxational or vibrational mode with quadrupole character, while the fluctuation of hy-

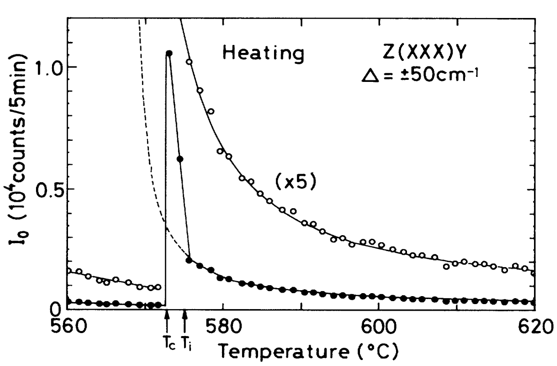

FIG. 3. Solid circles are the temperature dependence of integrated intensity I_0 in the frequency range of $\pm 50\ \mathrm{cm}^{-1}$, which reflects the intensity of the soft phonon in the β phase. Solid line in the temperature region above T_i is $I_0 \sim T/(T - T_0)$, where $T_0 = T_c - 5\,^\circ\mathrm{C}$.

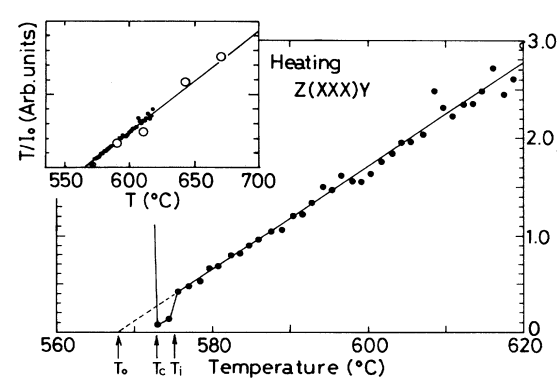

FIG. 4. Solid circles are the temperature dependence of T/I_0 where I_0 is given in Fig. 3. Open circles in the inset are T/I_0 where I_0 is obtained from integrating the intensity of the spectrum using the DHO. Solid line in the temperature region above T_i is $T/I_0 \sim T - T_0$.

perpolarizability is induced by that with dipole and octupole character.

Therefore, it is reasonable that the RS and HRS spectra are the imaginary parts of a generalized susceptibility caused by the induced quadrupole and the induced dipole and octupole, respectively. Let the generalized susceptibilities which give RS and HRS spectra be denoted $\chi^{R}(\omega)$ and $\chi^{HR}(\omega)$, respectively. Then, the χ^{R} includes quadrupole mode susceptibility, while the χ^{HR} includes dipole and octupole mode susceptibility.[10] By the fluctuation-dissipation theorem, I_0/T is proportional to the static susceptibility $\chi(0)$.[20] In the case of β-quartz, however, the soft mode is a silent mode, so the electric dipole susceptibility does not diverge, but $\chi^{HR}(0)$, which arises only from the octupole fluctuation of SiO_4, can diverge at the phase transition temperature. This is the reason why I_0/T, which reflects χ^{HR}, diverges like the Curie-Weiss law.

In conclusion, we observed a silent soft phonon in β-quartz for the first time by means of HRS. This result may be the first direct evidence that the α-β phase transition is a simple displacive-type phase transition. The soft phonon is confirmed to be the silent mode, because it is active only for HRS.

This result is consistent with those from inelastic neutron measurements by Axe and Shirane,[1] except for the result that the soft phonon is overdamped at temperatures above $T=T_c+200\,^\circ C$. Since their experiment was performed by using incident neutron energy $E=19$–78 meV and energy resolution of about $\Delta E=0.4$ meV (corresponding to about 3 cm^{-1}), the momentum resolution Δk is estimated to be $\Delta k=0.03$–0.016 Å^{-1}, while that of optical measurements is much smaller, $\Delta k\leq 10^{-4}$ Å^{-1}. On the other hand, the softening of the acoustic branch occurs at $k_i\sim 0.03a^*=0.006$ Å^{-1} for the incommensurate phase transition in the β phase,[2] where a^* is a reciprocal lattice constant along the a axis with $a=4.9977$ Å at 590 °C.[5] Therefore, the dispersion of soft-phonon branches around k_i might become complex at higher temperatures than T_i as well as at the temperature T_i. Since their observation does not have a sufficient momentum resolution, the soft phonon might be observed as an overdamped oscillator. Further, this low-momentum resolution might prevent an accurate analysis of the spectral line shape.

A relaxational mode is observed in $SrTiO_3$ (Ref. 21) and $BaTiO_3$ (Ref. 22) which show a typical displacive-type phase transition. Therefore, there is a possibility to observe a relaxational mode in quartz, even if the phase transition of quartz is displacive type. Such a relaxational mode cannot be excluded in the HRS spectra of β-quartz in the vicinity of T_c below 590 °C.

Recently, Tsuneyuki, Aoki, and Tsukada reported a molecular-dynamics calculation[8] for quartz where they suggest that the structure of β-quartz is a time average of α_1 and α_2 structures. If there is such a fluctuation as the time average of two structures, a relaxational mode should appear in HRS. From their results, the linewidth of the relaxational mode could be estimated to be about 5.5 cm^{-1} of FWHM (corresponding to a relaxation time of 12 psec) just above T_c, which is wider than the resolution 4 cm^{-1} of our observation. However, the width of the residual central peak in the HR spectrum does not become wider than the resolution even at higher temperatures. Since its intensity does not vary with temperature as mentioned before, it must be SHG of a static origin. Because no relaxational mode is observed in this study, we conclude that a structural fluctuation between α_1 and α_2 in β-quartz does not exist in the temperature region above 590 °C ($T_c+17\,^\circ C$). A structural fluctuation between α_1 and α_2 may occur in the vicinity of the phase transition temperature.

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