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Complete set of elastic and piezoelectric coefficients of α-quartz at low temperatures

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A complete set of low temperature elastic constants \( C_{ij} \) and piezoelectric coefficients \( e_{ij} \) of α-quartz single crystal has been investigated by resonance ultrasound spectroscopy coupled with a laser-Doppler interferometry. Most elastic constants showed monotonic elastic stiffening, while \( C_{66} \) continuously softened as the temperature decreased. Two piezoelectric coefficients \( e_{ij} \) showed monotonic decreasing upon cooling, and we found a strong correlation between \( e_{11} \) and \( C_{66} \), representing that thermal contraction induced internal strain plays an important role in their temperature behaviors. Group theoretical lattice dynamics analysis revealed that the elastic softening and the correlation can be attributed to an optical-mode-phonon-type internal strain having doubly degenerated \( E \) symmetry in the point group of \( D_3 \), © 2007 American Institute of Physics. [DOI: 10.1063/1.2816252]

I. INTRODUCTION

α-quartz (α-SiO\(_2\)) has a trigonal crystal structure with the space group symmetry of \( P3_21 \) (or \( P3_121 \) in its chiral pair). Since the discovery of piezoelectric effect by the Curie brothers in 1880, its moderate piezoelectricity, high temperature stability of resonance frequencies, and low internal friction have provided a variety of applications to acoustic devices such as filters, oscillators, sensors, etc. Up to now, intensive measurements on elastic constants \( C_{ij} \) and piezoelectric coefficients \( e_{ij} \) of α-quartz are carried out. \(^{1-11}\) On the other hand, α-quartz undergoes a \( \alpha-\beta \) structural phase transition at high temperature, \(^{12-14}\) and solid-state amorphization under high pressure. \(^{2,15-17}\) Being related to these phase stability of α-quartz, evaluations of higher-order elasticity, \(^{18}\) negative Poisson’s ratio, \(^{19}\) lattice vibrations, \(^{20,21}\) and internal frictions \(^{11}\) are also interesting issues.

Independent studies \(^{11,15}\) showed that currently used \( C_{ij} \) and \( e_{ij} \) of α-quartz are inconsistent with each other even at ambient temperature. Needless to say, the disagreement becomes marked about their temperature dependences. \(^{1}\) A part of this origin can be attributed to the experimental procedure; previous methods require many independent measurements for different crystals and need to solve simultaneous equations. In addition, they include various measurement errors due to crystal misorientations, resonance-frequency shift by attached electrodes and coupling agents, ambiguous electric boundary conditions, etc. \(^{11}\) Resonance ultrasound spectroscopy (RUS) is a state of the art technique because it simultaneously determines both \( C_{ij} \) and \( e_{ij} \) from only one single crystal specimen with high accuracy. \(^{22-26}\) Recently, Ogi et al. reinvestigated \( C_{ij} \) and \( e_{ij} \) of α-quartz by the RUS coupled with a laser-Doppler interferometry (RUS/LDI) and provided a reliable result at ambient temperature. \(^{11,26}\) However, low temperature measurements have not been performed by the method. Generally, elastic constants \( C_{ij} \) are defined as the fourth-rank coefficient tensor to the second derivative of internal energy with respect to Lagrange strains; a complete set of low temperature \( C_{ij} \) is therefore, indispensable to derive an accurate thermodynamic equation of state. Furthermore, both low temperature \( C_{ij} \) and \( e_{ij} \) are required to account for the theoretical calculation accuracies, such as density functional ab initio studies and lattice dynamics calculations, \(^{15,21}\) as well as most research works mentioned above.

Motivated by the current status, we investigated the complete set of elastic constants \( C_{ij} \) and piezoelectric coefficients \( e_{ij} \) of the α-quartz single crystal by the RUS/LDI method from ambient temperature to 5 K. The first-order temperature coefficients of elastic constants showed quantitative agreements with previous values supporting the accuracy of the present study. \( C_{66} \) and \( e_{11} \) continuously decrease as the temperature decreases and are found to show a strong correlation with each other; the Pearson product-moment correlation coefficient becomes 0.98, which is remarkably close to unity. The origin of softening of \( C_{66} \) and the strong correlation with \( e_{11} \) have been discussed on the basis of a group theoretical lattice dynamics approach. \(^{27}\)

II. EXPERIMENTAL PROCEDURE

A. Material

The material studied is a 4.8 × 5.2 × 5.8 mm\(^3\) rectangular parallelepiped right-handed α-quartz (\( P3_21/\overline{D_3^1} \)) single crystal cut along crystallographic \( X, Y, \) and \( Z \) orientations. The accuracies of size and orientations are ±1 \( \mu \)m and ±1°, respectively. Mass density \( \rho \) determined from the dimension and mass of the specimen is \( \rho=2643.51 \) kg/m\(^3\), which is almost consistent with the x-ray result (\( \rho=2648.6 \) kg/m\(^3\)). \(^{28}\) α-quartz has a threefold screw axis along the \([0,0,Z]\) direction and three twofold rotation axes within the \(X-Y\) plane. It includes three SiO\(_2\) molecules in a unit cell; the O atoms are located at the 6c Wyckoff position (general position) and Si
atoms are located at the 3b position. As a result, it is constructed from SiO₄ tetrahedra sharing their 6c corners with each other.

According to the point group of D₃, α-quartz has six independent elastic constants Cᵢⱼ and two piezoelectric coefficients eᵢⱼ,

\[
C_{ij} = \begin{bmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\
C_{12} & C_{11} & C_{13} & -C_{14} & 0 & 0 \\
C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\
C_{14} & -C_{14} & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & C_{14} & C_{66}
\end{bmatrix},
\]

(1)

\[
e_{ij} = \begin{bmatrix}
e_{11} - e_{11} & 0 & e_{14} & 0 & 0 \\
0 & 0 & 0 & 0 & e_{14} - e_{11} \\
0 & 0 & 0 & 0 & 0
\end{bmatrix}.
\]

(2)

Here, C₆₆=(C₁₁−C₁₂)/2. The superscript E for Cᵢⱼ is abbreviated for simplicity. In addition to Cᵢⱼ and eᵢⱼ, it has two dielectric coefficients εᵢⱼ. In this work, we fixed the e₁₁/e₀ and e₃₃/e₀ to be 4.424 and 4.632 (Ref. 11) since the reported temperature coefficients of εᵢⱼ are less significant compared with eᵢⱼ about one to two orders in magnitude.¹

B. Resonance ultrasound spectroscopy

The free vibration resonance frequencies of a specimen depend on dimensions, mass density, and independent material constants of Cᵢⱼ, eᵢⱼ, and εᵢⱼ. Thus, we can inversely calculate Cᵢⱼ and eᵢⱼ from a given εᵢⱼ and measured resonance frequencies fᵢ by solving stationery point of the Lagrangian L,

\[
L = \frac{1}{2}(S_{ijk}S_{jk} - \phi_{mn}\phi_{mn} + 2\phi_{mn}\phi_{mn}S_{jk} - \rho\omega^2u_{ij}).
\]

(3)

Here, S denotes the engineering strain in contracted notation. ρ and ω show the mass density and the angular frequency, respectively. For the inverse calculation, the displacement uᵢ and the electric potential φ are expanded by Legendre polynomials of the order of 18 and Eq. (3) is numerically solved with the Rayleigh-Ritz method.

The temperature dependence of free vibration resonance frequencies fᵢ is measured by a tripod-type RUS measurement system.²⁶ The RUS unit and specimen are set into a cryogenic chamber, and low temperature measurements have been carried out from 5 K to ambient temperature with ΔT=5 K. Temperature inaccuracy is approximately ±0.1 K throughout the study. Free vibration resonance spectra have been obtained from 0.3 to 1.1 MHz, and the resonance frequencies are determined by the Lorentzian-function fitting procedure; more than 60 peaks are obtained at each temperature step. The average rms error between experimental and theoretical resonance frequencies is approximately 0.15%. The symmetry of the macroscopic free vibration of a parallelepiped-shaped α-quartz specimen is given by the point group C₂ᵥ, which has four irreducible representations: Aᵥ, Bᵥ, A₃ᵥ, and B₃ᵥ.²⁹ Resonance frequencies are unambiguously matched by comparing surface displacement distributions measured by laser-Doppler interferometer with those of calculations.¹¹²⁶

III. EXPERIMENTAL RESULTS

Figure 1 shows a temperature dependence of normalized resonance frequencies. We find no distinctive difference due to the macroscopic free vibration symmetries. Most frequency changes fall into the range of 1% to −0.5% and some modes show extremely high temperature stability with only ±0.02% change. Ohno reported an exchange of vibration symmetry if resonance frequencies of two different modes approach each other.³⁰ According to Ohno, this phenomenon is interpreted as the mode coupling induced by lattice defects such as orientational and/or chiral twinnings.¹ A crystallographic misorientation of the specimen also causes this effect. As seen from Fig. 1, however, we did not find such effect over the entire modes, indicating that a combination of defects and orientation errors is negligible in this work.

Table I summarizes the low temperature elastic constants Cᵢⱼ, bulk modulus B, and piezoelectric coefficients eᵢⱼ of the α-quartz. Θₛ represents the acoustic Debye temperature calculated from the complete set of Cᵢⱼ by numerically solving the Christoffel equation. From Table I, we see that most Cᵢⱼ changes by only a few percent while the changes in C₁₂ and e₁₂ are notable; C₁₂ increases by about 30% and e₁₂ decreases

<table>
<thead>
<tr>
<th>T (K)</th>
<th>C₁₁</th>
<th>C₁₂</th>
<th>C₁₃</th>
<th>C₁₄</th>
<th>C₃₃</th>
<th>C₄₄</th>
<th>C₆₆</th>
<th>e₁₁</th>
<th>e₁₄</th>
<th>B</th>
<th>ε₁₁</th>
<th>ε₁₄</th>
<th>Θₛ</th>
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<tbody>
<tr>
<td>275</td>
<td>86.76</td>
<td>7.06</td>
<td>11.90</td>
<td>-17.98</td>
<td>105.41</td>
<td>58.27</td>
<td>39.85</td>
<td>37.37</td>
<td>0.149</td>
<td>-0.026</td>
<td>590.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>87.65</td>
<td>9.42</td>
<td>12.80</td>
<td>-17.83</td>
<td>107.65</td>
<td>59.60</td>
<td>39.12</td>
<td>38.75</td>
<td>(0.066)</td>
<td>-0.026</td>
<td>590.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FIG. 1. (Color) Temperature dependence of free vibration resonance frequencies obtained by RUS. Resonance frequencies are normalized by their ambient temperature values and classified into four irreducible representations: Aᵥ, Bᵥ, A₃ᵥ, and B₃ᵥ.
by a factor of 0.5. The violation of the Cauchy relation, $C_{12} = C_{66}$, $C_{13} = C_{55}/H_20849 = C_{44}/H_20850$, is still significant at 5 K. Figure 2 presents the temperature dependence of elastic constants $C_{ij}$. Most elastic constants show monotonic elastic stiffening, while $C_{66}$ shows continuous softening upon cooling. Following the previous work, the temperature dependence of elastic constants $C_{ij}(T)$ is analyzed by means of the third-order Taylor series expansion,

$$
\frac{\Delta C_{ij}}{C_{ij}(0)} = T^{(1)}_{Ci}(\Delta T) + T^{(2)}_{Ci}(\Delta T)^2 + T^{(3)}_{Ci}(\Delta T)^3,
$$

with

$$
T^{(n)}_{Ci} = \frac{1}{n! C_{ij}(0)} \frac{\partial^n C_{ij}}{\partial T^n} \bigg|_{T=T_0},
$$

where $\Delta C_{ij} = C_{ij} - C_{ij}(0)$ and $\Delta T = T - T_0$. $C_{ij}(0)$ represents the elastic constants at $T_0 (=275$ K). The temperature coefficients $T^{(n)}_{Ci}$ are summarized in Table II. Present results showed reasonable agreements with previous works on the first-order coefficients $T^{(1)}_{Ci}$, while slight inconsistencies have been confirmed in the higher-order terms. The discrepancies can be attributed to the difference in measurement tempta-

![Figure 2](image-url) (Color online) Temperature dependence of elastic constants $C_{ij}$ and bulk modulus $B$. $C_{66}$ continuously softens throughout the temperature range, and $C_{14}$ shows weak softening below 100 K. Solid curves in the figures show the least-squares fitting results to Varshni’s function (Ref. 32).

<table>
<thead>
<tr>
<th>$C_{ij}$</th>
<th>$T^{(1)}_{Ci}$ (10^6/K)</th>
<th>$T^{(2)}_{Ci}$ (10^{-9}/K^2)</th>
<th>$T^{(3)}_{Ci}$ (10^{-12}/K^3)</th>
</tr>
</thead>
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<tr>
<td>$C_{11}$</td>
<td>$-53.9\pm0.6$</td>
<td>$50.8\pm7.2$</td>
<td>$390.5\pm19.6$</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>$-2200\pm11.7$</td>
<td>$-2141.1\pm133$</td>
<td>$5079.4\pm361$</td>
</tr>
<tr>
<td>$C_{13}$</td>
<td>$-500.7\pm5.9$</td>
<td>$-365.2\pm67.3$</td>
<td>$1531.1\pm183$</td>
</tr>
<tr>
<td>$C_{14}$</td>
<td>$83.9\pm1.8$</td>
<td>$29.5\pm20.8$</td>
<td>$-602.9\pm56.4$</td>
</tr>
<tr>
<td>$C_{33}$</td>
<td>$-136.5\pm1.3$</td>
<td>$-206.4\pm14.8$</td>
<td>$31.1\pm40.2$</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>$-146.2\pm0.9$</td>
<td>$-243.3\pm10.8$</td>
<td>$-49.8\pm29.2$</td>
</tr>
<tr>
<td>$C_{66}$</td>
<td>$136.2\pm1.0$</td>
<td>$245.2\pm11.3$</td>
<td>$-24.5\pm30.8$</td>
</tr>
</tbody>
</table>
ture range between the present (5–275 K) and previous works (218–363 K). Thus, the quantitative consistency of $T^{(1)}_c$ supports our measurement accuracies and the present higher-order terms would be useful for theoretical and/or practical applications at low temperatures.

Let us discuss the low temperature lattice dynamics of α-quartz from $C_4(T)$ behaviors. The solid curves in Fig. 2 show the least-squares fitting result to Varshni’s function: $C_4(t) = C_4^0 - s/[\exp(t/T) - 1]$, where $t$ represents the Einstein temperature $\Theta_E$. The estimated $t$ becomes $t_{c11} = 228$ K, $t_{c33} = 240$ K, $t_{c12} = 289$ K, $t_{c13} = 280$ K, $t_{c44} = 236$ K, $t_B = 270$ K, and $t_{c14} = 637$ K. Compared with the original definition of $\Theta_E = 0.750 T_d = 443$ K, the temperature dependence of $C_{14}(T)$ is obviously far from being usual because the estimated Einstein temperature is too high. The zone-center-mode mean Grüneisen parameter $\gamma$, estimated from the temperature slope of the bulk modulus $dB/dT$, becomes 1.15.

Piezoelectric coefficients $e_{ij}$ also provide attracting material properties. Our measurement reveals that both $e_{111}^2 / e_{11}$ and $e_{11}^2 / e_{11}$ monotonically decreases with temperature (see Fig. 3). As is well known, the piezoelectricity appears by the loss of inversion symmetry in the point group operation (20 of 32 point groups show this effect). Continuous decreasing of $e_{ij}$ therefore, suggests the formation of internal strain associated with macroscopic thermal contraction. As mentioned above, α-quartz is constructed from SiO$_4$ tetrahedra sharing their corners with each other. Since the covalent bond in the tetrahedron is sufficiently high, low temperature volume contraction will be mainly caused by the rigid body rotation of the tetrahedra. Such a microscopic picture has been confirmed by the previous work and a high temperature α-β phase transition is driven by a soft mode phonon associated with the rotation. The internal strain can be ascribed to the static optical-mode phonons, which disturb the crystal field around ions and will eventually affect the piezoelectricity.

Another notable feature is found between $C_{66}$ and $e_{111}^2 / e_{11}$; namely, these independent coefficients show an almost linear relation especially below 200 K. The Pearson product-moment correlation coefficient becomes 0.98, which is remarkably close to unity and represents a strong correlation between these coefficients. The correlation suggests that a single mode internal strain affects both $C_{66}$ and $e_{111}^2 / e_{11}$ simultaneously. In the next section, the origins of the unusual elastic behaviors and the correlation between $C_{66}$ and $e_{111}$ will be discussed from a group theoretical lattice dynamics perturbation approach.

IV. DISCUSSION

A. Normal modes of α-quartz at the Π point

First of all, we briefly summarize the crystallography of α-quartz from a group theoretical point of view. In the trigonal unit cell, six O atoms are located at the following 6c Wyckoff positions: (1) $[x,y,z]$, (2) $[-y,x,y,z+2/3]$, (3) $[-x+y,-x,z+1/3]$, (4) $[x,y,-y,z]$, (5) $[x+y,-x,-z+1/3]$, and (6) $[-x,-y,-z+2/3]$. Since these are general positions, the vectors (1)–(6) represent the symmetry operations $G_i$ in the space group. The group elements can be divided into three classes $C_1 = \{G_1\}$, $C_2 = \{G_2, G_3\}$, and $C_3 = \{G_4, G_5, G_6\}$, representing identical, screw, and π-rotation operations, respectively. Three Si atoms are located at the 3b site, one of which is left unmoved by an operation in $C_3$.

It is useful to employ normal modes to describe lattice vibration. Elastic and piezoelectric properties are related to long-wavelength vibrations (or wave number $k=0$ in a reciprocal lattice); we thus restrict our considerations to the center of the Brillouin zone (Π point). Then, the space group of the α-quartz $P\bar{3}21$ becomes isomorphic to the point group of $D_3$. The character table and basis functions of the $D_3$ group are summarized in Table III. It has three irreducible representations, where $A_1$ is Raman active, $A_2$ is infrared active, and both are active in the $E$ mode, as expected from the basis functions.

The displacement vectors in the α-quartz unit cell have $3 \times 9 = 27$ degrees of freedom. Expressing the number of atoms that are left unmoved by an operator $G_i$ by $N_i$, it becomes $N_1 = 9$, $N_{2,3} = 0$, and $N_{4,5,6} = 1$. On the other hand, the character $\chi_i$ of an operation $G_i$ is simply given by $\chi_i = 1 + 2 \cos \theta$, where $\theta$ represents the rotation angle of $G_i$. Then, the characters of the 27 dimensional displacements $\chi = N_i \chi_i$ become

| $A_1$ | 1 | 1 | 1 | $x_1^2, x_1^2 + x_2^2$ |
| $A_2$ | 1 | 1 | -1 | $x_2$ |
| $E$ | 2 | -1 | 0 | $\{x_1, x_2, (x_1^2 - x_2^2)/2\}$ |

Ref. 36
\( \chi = 27G_1 - G_4 - G_5 - G_6. \) \tag{6}

Note that \( \chi \) includes the following translational motions: \( \chi = 3G_1 - G_4 - G_5 - G_6. \) Now, we reduce Eq. (6) to a direct sum of irreducible representations. From a great orthogonality theorem, coefficient \( q_\alpha \) for an irreducible representation \( \alpha \) is given by

\[
q_\alpha = \frac{1}{g} \sum G^a(G)^* \chi^a(G), \tag{7}
\]

where \( g \) is the order of the group and the asterisk represents a complex conjugate. By Eq. (7) and Table II, Eq. (6) can be decomposed into the following form:

\[
\chi = (A_2 + E) + 4(A_1 + A_2 + 2E). \tag{8}
\]

The term in the first parentheses represents the three acoustic modes, and that in the second shows other 24 optical modes. The optical mode includes all three symmetries, while only \( A_2 \) and doubly degenerated \( E \) are included in the acoustic mode. The totally symmetric \( A_1 \) acoustic mode is forbidden at the \( \Gamma \) point.

**B. Effect of internal strain on elastic constants and piezoelectric coefficients**

We discuss the effect of internal strains on elastic constants \( C_{ij} \) and piezoelectric coefficients \( e_{ij} \) from a group theoretical lattice dynamics approach. By means of a perturbation analysis for a long-wavelength equation of motion, \(^{37}\) Miller and Axe introduced a second rank tensor \( F_{\alpha j}(j) \) to define the coefficient of the normal optical-mode vibration \( j. \) \(^{27}\) By using \( F_{\alpha j}(j) \), they formulated the effect of the optical-mode-type internal strain on elastic constants and piezoelectric coefficients as follows:

\[
C_{\alpha \gamma \mu \delta} = - \sum_j \frac{1}{\omega^2(j)} F_{\alpha j}(j) F_{\mu \delta}(j), \tag{9}
\]

\[
e_{\mu \alpha} = - \sum_j \frac{1}{\omega^2(j)} P_{\mu}(j) F_{\alpha j}(j), \tag{10}
\]

where \( C_{\alpha \gamma \mu \delta} \) and \( e_{\mu \alpha} \) show the internal strain part of the elastic constants and of the piezoelectric coefficients, respectively. \( \omega(j) \) and \( P_{\mu}(j) \) represent the vibration frequency and polarization of mode \( j \). Since \( F_{\alpha j}(j) \) and \( P_{\mu}(j) \) transform as second and first rank tensors by a given point group operation, Eqs. (9) and (10) represent that only the Raman active mode contributes to the internal strain part of elastic constants and only modes that are both Raman and infrared active contribute to piezoelectric coefficients. Note that the effect of the acoustic mode is taken to vanish in the formula.

Let us consider the transformations of \( F_{\alpha j}(j) \) and \( P_{\mu}(j) \) in the present \( D_3 \) group under the \( x, x, x \)-Cartesian coordinate system. With the help of basis functions (see Table III), nonvanishing \( F_{\alpha j}(j) \) components for the \( A_1 \) mode \( F_{\alpha j}(A_1) \) are \( F_{11}(A_1) = F_{22}(A_1) \) and \( F_{33}(A_1) \). Similarly, \( E \) allows \( F_{33}(E) \), \( F_{12}(E) \), and \( F_{11}(E) = -F_{22}(E) \). On the other hand, the nonvanishing polarization \( P_{\mu}(j) \) for the \( A_2 \) mode is \( P_3(A_2) \), and those for the \( E \) mode are \( P_1(E) \) and \( P_3(E) \).

The full fourth-rank tensor notation of \( C_{66} \) is \( C_{1212} \) so that \( F_{12}(E) \) doubly contributes to the coefficient. As seen from Eq. (8), the \( E \) symmetry is included in the optical mode and \( F_{12}(j) \) exists only in \( E \). Thus, the low temperature softening in \( C_{66} \) can be realized by the effect of the optical-phonon-type internal strain, which has a symmetry of \( E \). On the other hand, piezoelectric coefficients are affected only by the \( E \) mode since it requires both Raman and infrared active. From Eq. (2), nonzero components of the third rank tensor are \( e_{111} = -e_{222} = e_{212} \) (= \( \pm e_{11} \)) and \( e_{123} = -e_{223} \) (= \( \pm e_{14} \)). Thus, the possible combinations of \( P_{\mu}(E) F_{\alpha j}(E) \) are \( P_1(E) F_{11}(E) \), \( P_1(E) F_{22}(E) \), and \( P_1(E) F_{12}(E) \) for \( e_{11} \), and \( P_1(E) F_{23}(E) \) and \( P_3(E) F_{31}(E) \) for \( e_{14} \). Clearly, \( F_{12}(E) \) contributes to \( e_{11} \) as \( C_{66} \) too. This would explain the strong correlation between \( C_{66} \) and \( e_{11}^2 / e_{11} \). Similarly, we also see the effect of \( F_{12}(E) \) on the unusual softening in \( C_{14} \) below 100 K. From Eq. (1), \( C_{14} = C_{26} = C_{2212} \) so that the contributing coefficients are \( F_{22}(E) \) and \( F_{12}(E) \). Thus, the effect of \( F_{12}(E) \) on \( C_{14} \) is straightforward.

Finally, we mention the \( A_2 \) mode internal strain. The present results cannot access this mode since it does not influence \( C_{ij} \) and \( e_{ij} \). Thus, the existence of the thermal contraction induced \( A_2 \) mode internal strain is unclear. Here, theoretical calculations such as molecular dynamics would be useful. The present low temperature \( C_{ij} \) and \( e_{ij} \) are helpful to evaluate the accuracy of these theoretical calculations.

**V. CONCLUSIONS**

In summary, we investigated the low temperature elastic constants \( C_{ij} \) and piezoelectric coefficients \( e_{ij} \) of the \( \alpha \)-quartz single crystal using the RUS/LDI method. Conclusions of the present study are summarized as follows.

(i) Most elastic constants showed monotonic stiffening, while \( C_{66} \) continuously softens with decreasing temperature.

(ii) The elastic constant change between 5 K and ambient temperature is only a few percent while \( C_{12} \) increases by a factor of 1.3 upon cooling.

(iii) Cauchy relations are severely violated throughout the present temperature range.

(iv) Compared with ambient temperature values, piezoelectric coefficients, \( e_{11} \) and \( e_{14} \), decrease by about a factor of 0.5 at 5 K. Such notable decrease in \( e_{ij} \) suggests the formation of internal strains associated with macroscopic thermal contraction.

(v) We find a strong correlation between \( C_{66} \) and \( e_{11}^2 / e_{11} \) especially below 200 K. The group theoretical lattice dynamics analysis revealed that the elastic softening found in \( C_{66} \) and \( C_{14} \) and the correlation between \( C_{66} \) and \( e_{11}^2 / e_{11} \) can be explained from the formation of an optical-mode-phonon-type internal strain, which has a doubly degenerated \( E \) symmetry in the point group of \( D_3 \).

