Effects of Inherent Electric and Anisotropic Forces on Raman Spectra in α-Quartz†

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Measurements with improved precision of the width, intensity, and position of all the Raman-active lines of α-quartz have been made; the results are more extensive than those previously reported. With the accuracy achieved, we can for the first time quantitatively determine the relative values of the Raman tensor elements for all lines, and the relative importance of the long-range electric force and the force due to the crystal anisotropy. The effect of the inherent electrooptic contribution to the scattering is studied for various E vibrations.

IN this paper we report the results of a complete measurement of the positions, intensities, and widths of all the Raman-active lines in α-quartz. This work is more extensive and is an improvement over previous investigations[1,2] in several ways; the parameters of all the lines were measured under identical experimental conditions; a He-Ne laser was used for excitation, giving a controllable, intense source which was monochromatic, directional, and linearly polarized; the detection system was totally digital facilitating the use of a digital computer in removing the effects of the instrument function by a combination of a least-squares fit and deconvolution routine.[3] The results of these measurements were used to calculate the relative magnitudes of the elements of the Raman tensor and to deduce for the E vibrations the relative magnitude of the forces due to crystal anisotropy as compared with the long-range electric forces. The effect of the inherent electrooptic contribution to the scattering is studied for various E vibrations.

Quartz is a complex piezoelectric crystal having D_3 symmetry and nine atoms per unit cell. Group theory predicts that, of the 27 normal modes, four will be totally symmetric (A_1 modes) and eight will be doubly degenerate (E modes). The remainder are the four infrared-active A_2 modes and the three acoustic modes. The E vibrations are simultaneously infrared and Raman active, leading to frequencies, intensities, and widths which are dependent on the orientation of the sample. The theory of Raman scattering in piezoelectric crystals has been described by Poulet,[4] and a general review article was published by Loudon.[5] Loudon's treatment deals with a single infrared-active mode, but if the E lines are well separated in frequency, his results may be easily modified to handle the many-mode situation.

The scattered intensity is given by[5]

$$S=[\sum \hat{e}_\sigma{}^i R_{\sigma\rho}{}^{(\tau)}(A\hat{\xi}^\tau+B\hat{k}^\tau)\hat{e}_\rho{}^s]^2, \quad \rho,\sigma,\tau=x,y,z, \tag{1}$$

where $\hat{e}^i$ and $\hat{e}^s$ are the directions of the electric field vector of the incident and scattered light, respectively. A is a scattering coefficient related to the lattice deformation, and B gives the contribution due to the electrooptic effect associated with the E vibration; $\hat{k}$ is the direction of propagation of the phonon and $\hat{\xi}$ is the mechanical polarization of the phonon in question. $R_{\sigma\rho}{}^{(\tau)}$ is the element of the Raman tensor, and group theory predicts that for D_3 symmetry it must have the following form:

$$\underset{A_1}{\begin{bmatrix} a & & \\ & a & \\ & & b \end{bmatrix}} \quad \underset{E(x)}{\begin{bmatrix} c & & \\ & -c & d \\ & d & \end{bmatrix}} \quad \underset{E(y)}{\begin{bmatrix} & -c & -d \\ -c & & \\ -d & & \end{bmatrix}}. \tag{2}$$

For the symmetric A_1 vibrations, B in Eq. (1) is zero and $\hat{\xi}$ may be dropped from the equation since all directions of the phonon polarization are equivalent.

Experimentally, a 50-mW He-Ne laser was focused into cubes of synthetic quartz which were about 2 cm on edge. The scattering was observed at right angles for all four possible polarizations, i.e., two for the incident beam and two for the scattered light. Two samples were prepared, one with all the sides normal to the crystallographic axes, and the other cut so that the x and z axes were at 45° to the sides of the sample. This allowed three orientations corresponding to three directions of phonon propagation with respect to the z axis, viz., $\theta=90°$ or x into y scattering, $\theta=45°$ or x into z, and $\theta=0°$. Each Raman-active line was measured for all orientations and polarizations.

Table I lists the width of each of the Raman lines and the relative magnitudes of the Raman tensor. The identification of the lines is that of Scott and Porto,[6]

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TABLE I. Experimental positions, widths, and relative magnitudes of the elements of the Raman tensor for the lines in α-quartz.

Frequency shift (cm^{-1})	Width (cm^{-1})	Tensor elements[a]				
I A_1 modes		a^2		b^2		b^2/a^2
207 (206±0.5)	21.6±0.5	484		619		1.3
356 (355±1)	2.2±0.3	38		55		1.5
464 (464.5±1)	6.3±0.1	906		1000		1.1
1085 (1082±2)	5.3±0.6	2.3		31		13.5
II Degenerate E modes		c^2		d^2		c^2/d^2
128 (128±0.5)	3.3±0.2[b]	125		62		2.0
265 (264.5±1)	3.0±0.5[b]	<1		29		<0.03
697 (696±2)	5.5±1.3					>1.0
1162 (1159±2)	7.5±0.9[b]	23		5.5		4.2
III Nondegenerate E modes		c^2	$c^2(\mathrm{LO})/c^2(\mathrm{TO})$	d^2	$d^2(\mathrm{LO})/d^2(\mathrm{TO})$	c^2/d^2
394 (394±1)	2.0±0.9	11		<1		>11
401 (403.5±1)	2.0±0.9	6	0.55	2	>2	>6
450 (450±1)	2.0±0.5	<1		13		<0.07
509 (508.5±1)	1.5±0.5	<1		10	0.79	<0.1
795(796±2)	7.5±1.0	<1		14		<0.07
807 (809±2)	6.0±1.0	<1		20	1.43	<0.05
1072 (1067±2)	4.0±2.0	<1		2.7		<0.4
1235 (1230±2)	8.0±2.0	3.7	>3.7	<1	<0.37	>3.7

[a] Calculated from the integrated intensities and normalized so that b^2 (464 cm^{-1}) = 1000.
[b] Width corresponding to $\theta = 0°$.

and given in parentheses are our experimental[7] line positions at room temperature. The widths as given are the full width at half-maximum intensity of a Lorentzian function which, when convoluted with a Gaussian instrument function, best fits the data.[3] The 207-cm^{-1} line is much broader owing to the fact that it is the line which is responsible for the α-β transition.[8] These width values, although they do not agree in every case with those reported earlier,[1] are more accurate, mainly because of the photon-counting detection system and the deconvolution procedure used.[3] The elements of the Raman tensor were calculated by comparing the integrated intensity of each line with the intensity predicted from Eq. (1). For this purpose, the integrated intensity data of $\theta = 45°$ and $\theta = 90°$ scattering were used; the $\theta = 0°$ data, obtained from a different sample, provide a check for the determination of the tensor elements. Compensation was made for the spectral sensitivity of the photomultiplier tube and the polarizing effect of the monochromator. The depolarizing effects due to the birefringence and optical activity were also taken into consideration. The values shown in Table I have been normalized so that b^2 for the 464-cm^{-1} line is 1000. The 697-cm^{-1} line was too weak for an accurate determination of the elements, although it was strong enough to conclude that $c^2 > d^2$ for this mode.

It is seen from Table I that in general the A_1 modes are more intense than the E modes, and that they fall into two types; the 207-, 356-, and 464-cm^{-1} lines all have b^2 just slightly larger than a^2, while for the 1085-cm^{-1} line, b^2 is much larger than a^2, in qualitative agreement with previous work.[2] The E modes are divided into two groups. For the degenerate E modes deformation scattering and polar scattering[5] may be separated and the values of c^2 and d^2 can be consistently determined by more than one way. For the nondegenerate E modes, the contribution due to deformation scattering cannot be easily separated from that due to polar scattering, the values c^2 and d^2 for the high-frequency (longitudinal) components (401, 509, 807, and 1235 cm^{-1}) in Table I include the electrooptic contribution as well. The fact that the ratio c^2/d^2 is different for transverse and longitudinal component of the "same" mode agrees with the qualitative results of some recent observations.[9] That the relative magnitudes of c and d are reversed for the two components of the 1072-1235-cm^{-1} doublet is probably due to the fact that another E line (1161 cm^{-1}) falls in between.

In addition to the results given in Table I and from the detailed measurements on each line for the three orientations, we can make several observations. For the degenerate case the line should become narrower[5,7] as one goes from $\theta = 90°$ to $\theta = 0°$, and experimentally this was found to be true. For the 128-cm^{-1} line the width decreased by about 0.7 cm^{-1} and by about 2.0 cm^{-1} for the 265- and 1162-cm^{-1} lines. This observed linewidth dependence on phonon orientation should be compared with Zubov's results,[1] where he reported the measured widths to be independent of crystallographic direction. Another point of departure is that the numerical values of the Zubov widths were grouped close to 4, 6, 8, and 12 cm^{-1}. From this he concluded that the Raman-active modes have only four different lifetimes and that these

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are connected with the four axes of symmetry of quartz. His reasoning is by no means obvious and no such grouping is apparent in our data.

Of the resolved E modes it was observed that for the 394–401- and 795–807-cm^{-1} doublets, the high-frequency component moved down in frequency by 20 and 25%, respectively, and that for the 450–509-cm^{-1} doublet, it moved up by 50% of the splitting as θ was changed from 90° to 45°. These are examples of the case where both the anisotropy and electric forces are large and comparable.[5–7] The frequency shift of the 807-cm^{-1} line has been determined by Couture-Mathieu *et al.*[10] by infrared reflection measurements. For the 1072-1235-cm^{-1} doublet, the frequency shifts with θ were found to be negligible, leading to the conclusion that for this mode the anisotropy is much smaller than the electric forces. Our observed orientational dependence of the line positions agrees with the recent calculations of the polariton spectra of α-quartz.[11]

From Eq. (1) it can be seen that the ratio of the scattered intensity for a purely longitudinal vibration to that of a purely transverse vibration ($B=0$) is $\eta=(A+B)^2/A^2$. Since A and B, in general, depend on the scattering polarization and can have the same or opposite signs, the electric field contribution depending on individual modes may either add to or detract from the scattering intensity. For the degenerate E modes, the $\theta=45°$ intensity of the $x(yx)z$ and $x(zx)z$ scattering depend only on c^2 and d^2, and the $\theta=90°$ scattering intensity depends on η as well. This fact enables us to determine η simultaneously with c^2 and d^2. We can determine one value of η for each of these modes; they are approximately 0.8, 0.7, ~1.0, and 0.9 for the 128-, 265-, 697-, and 1162-cm^{-1} modes, respectively. For the nondegenerate E modes, the electric field contribution to the scattering intensity depends very much on individual modes. The scattering intensity of a longitudinal component may be either greater or smaller[9] than that of its corresponding transverse components as shown in Table I. For these modes, we report the ratios of the scattering intensities of the two components, $c^2(\mathrm{LO})/c^2(\mathrm{TO})$ and $d^2(\mathrm{LO})/d^2(\mathrm{TO})$, for each of the four degenerate pairs, with the exception of the c^2 ratio for the 450–509- and 795–807-cm^{-1} pairs, for which the intensities were too weak.

In conclusion, we may summarize the work as follows. The widths and intensities of all the lines were measured under identical conditions using a laser source and compensating for effects due to the instrument and the complicating optical properties of quartz. The changes in frequency and linewidth as a function of orientation and the relative size of the electric forces and the forces due to crystal anisotropy were discussed. The experimental results were shown to agree with the predictions. We also report the effect of the electric field accompanying a longitudinal vibration on the scattering intensity for E vibrations.

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