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Raman Spectrum of α Quartz at High Pressures*

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Raman spectra of single crystals of α quartz at pressures as high as 40 kbar are reported. The frequencies of the Raman lines located at 128, 207, 265, 464, 697, 795, and 807 cm^{-1} at atmospheric pressure increase with increasing pressure by about 0.6, 1.8, 0.5, 0.9, 0.8, 0.8, and 0.8 cm$^{-1}\cdot$kbar^{-1}, respectively, with a probable accuracy of about 20% due to an uncertainty about the pressure scale. These frequencies of the α-quartz spectrum also are significantly sensitive to temperature. The frequencies of all other Raman lines of α quartz, except three at 145, 450, and 509 cm^{-1} that could not be studied, are independent of pressure.

This paper describes a technique for determining the pressure dependences of the frequencies of Raman-active optical phonons of single crystals at pressures as high as 40 kbar. Results are presented of an investigation of the laser-excited Raman spectrum of α quartz that was made while developing techniques for high-pressure laser Raman spectroscopy. The relationship between these results and other properties of quartz are briefly discussed.

α quartz is a trigonal crystal, of symmetry D_3, and has nine atoms per primitive cell.[1] It is stable at atmospheric pressure at temperatures below 574°C, at which it transforms reversibly to hexagonal β quartz. The threefold optic axis of α quartz corresponds to the sixfold axis of β quartz, the transformation arising primarily from a cooperative distortion of atomic positions in planes normal to the sixfold axis of β quartz. The temperature of the α–β transition increases nearly linearly with increasing pressure at about 26°C kbar^{-1} according to Cohen and Klement.[2]

The vibrational Raman spectrum of α quartz has been studied by many investigators, and this work has recently been summarized in detail by Scott and Porto.[3] Their paper includes many references to earlier studies, among which that of Saksena[4] is particularly relevant to this work; only a few pertinent results of previous investigations will be summarized here. The temperature dependence of the atmospheric-pressure Raman spectrum of quartz has been studied to above the α–β transition by Nedungadi[5] and recently by Shapiro, O'Shea, and Cummins[6] in order to identify the vibrational mode which softens at the α–β transition. The results of the earlier study suggested that the 207-cm^{-1} mode[7] was the soft mode; however, the work of Shapiro *et al.* suggests that a weak line at 145 cm^{-1}, whose origin is closely related to that of the 207-cm^{-1} line, corresponds to the soft mode.

When classified into representations of the symmetry group D_3, the 24 optical vibrations of α quartz are divided into four modes of A_1 symmetry, four modes of A_2 symmetry, and eight, doubly degenerate modes of E symmetry. The degeneracies of the modes of E symmetry may be split by long-range electrostatic interactions that are discussed by Scott and Porto.[3] The modes of A_1 and E symmetries are predicted to be Raman active. The symmetry of the normal mode associated with each line of the Raman spectrum can be determined by observing the polarization dependence of its intensity. Whether it is appropriate to use the group D_3 to analyze the vibrational Raman spectrum of α quartz has been the subject of some discussion because five (instead of four) lines of the spectrum are observed to have polarization selection rules for modes of A_1 symmetry. However, Shapiro *et al.*[6] have demonstrated how this apparent discrepancy can be resolved.

Assignment of the Raman frequencies belonging to either class of vibrational modes to the appropriate normal coordinate motions, however, depends upon indirect evidence including, e.g., studies of intensities of Raman and related transitions, and of possible correlations of Raman frequencies of closely related materials (see, e.g., Ref. 4). The frequencies of the various normal modes of α quartz have not been assigned rigorously. Relationships between pressure dependences of Raman frequencies and phase equilibria at high pressures may be an asset for assigning normal mode frequencies, while studies of the pressure dependences of Raman frequencies of crystals whose normal modes have been analyzed may provide the information needed to describe in detail local distortions of the structures of compressed materials. High-pressure Raman spectra also may be able to suggest new phase instabilities. Except for a few qualitative comparisons of the observations reported here with relevant proper-

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[7] Unless explicitly stated otherwise, all frequencies herein refer to the room-temperature, atmospheric-pressure spectrum reported in Ref. 3.

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