

## High-pressure Raman study of the vibrational modes in $\text{AlPO}_4$ and $\text{SiO}_2$ ( $\alpha$ -quartz)

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The pressure dependence of the optical-phonon frequencies in berlinite ( $\text{AlPO}_4$ ) and  $\alpha$ -quartz has been investigated by high-pressure Raman scattering experiments, using a diamond cell; berlinite was studied up to 12 GPa and  $\alpha$ -quartz to 20 GPa. The  $A_1$  soft phonon mode at  $216\text{ cm}^{-1}$  in  $\text{AlPO}_4$  and the corresponding mode in  $\alpha$ -quartz at  $206\text{ cm}^{-1}$  exhibit similar but anomalously large and non-linear pressure dependences. Further, these two modes exhibit striking decreases in their widths with increasing pressure. These changes appear to be connected with the decoupling of the strong anharmonic interactions of the  $A_1$  soft mode phonon with the two-phonon (acoustic) states in  $\alpha$ -quartz and with one-phonon (optical) and two-phonon (acoustic) states in  $\text{AlPO}_4$ . Pressure experiments help in distinguishing the relative strength of these interactions in the two materials. The mode-Grüneisen parameters have been obtained and, again, the  $A_1$  soft mode has a large  $\gamma_i$ , namely, 3.45 in  $\text{AlPO}_4$  and 4.32 in  $\alpha$ -quartz. Using refractive-index matching with  $\alpha$ -quartz and  $\text{AlPO}_4$ , the  $n(P)$  of a 4:1 methanol-ethanol mixture has been evaluated.

### INTRODUCTION

Berlinite ( $\text{AlPO}_4$ ) is isomorphic to  $\alpha$ -quartz ( $D_3^4$ ) and undergoes the same temperature-induced  $\alpha$ - $\beta$  transition as quartz near 850 K.<sup>1-3</sup> Further,  $\text{AlPO}_4$  can be prepared in the other well-known crystalline modifications of  $\text{SiO}_2$ ,<sup>1,2</sup> viz., tridymite and cristobalite, by high-temperature treatment. In view of these close structural similarities between  $\text{AlPO}_4$  and  $\text{SiO}_2$  at ambient pressure,<sup>1,2</sup> a close correspondence in high-pressure behavior may also be expected for the two systems.

High-pressure Raman studies offer a very sensitive method to probe phase changes as well as subtler changes in bonding induced by pressure, apart from enabling one to collect information of interest to lattice dynamics. Therefore, we undertook a high-pressure Raman study of  $\text{AlPO}_4$  and have studied the optical phonons to 12 GPa. To our knowledge no high-pressure Raman investigation has been reported for  $\text{AlPO}_4$  in the literature. We have also investigated  $\alpha$ -quartz ( $\text{SiO}_2$ ) to 20 GPa, although this system has been previously studied by others.<sup>4-6</sup> Our purpose was to determine the high-pressure behavior of the Raman modes in quartz for a close comparison with  $\text{AlPO}_4$ . These results will be presented and discussed in this paper.

### EXPERIMENTS

Pressure was generated using the diamond-anvil cell<sup>7</sup> and calibrated using the ruby-fluorescence technique.<sup>8</sup> For the pressure medium, a 4:1 methanol-ethanol mixture was used. Raman spectra were obtained with a Spex double monochromator equipped with a conventional photon-counting system. For excitation the 488.0-nm line from an argon-ion laser was used. The laser power was in the range of 100–200 mW.

Samples of synthetically grown  $\text{AlPO}_4$  in the form of crystal plates were available to us.<sup>9,10</sup> Fragments from

the crystal plates were loaded into the diamond cell for recording the Raman spectra. Since the fragments were of unknown orientation with respect to the crystal axes, polarization measurements were not attempted. Excellent Raman spectra, with peaks in the expected positions,<sup>11</sup> were obtained with 488-nm excitation.

In the case of quartz, platelets from a thin cross-cut quartz-crystal plate  $75\text{ }\mu\text{m}$  in thickness, originally prepared for ultrasonic generation at 40 Mc, were loaded into the diamond cell. With  $75\text{-}\mu\text{m}$ -thick platelets, we could only go up to 60 kbar, before the diamond flats contacted the quartz sample. For experiments at higher pressure, small fragments were obtained from a synthetically grown large quartz crystal. These fragments were again of random orientation, and pieces that were  $20\text{--}30\text{ }\mu\text{m}$  in thickness and  $50\text{--}70\text{ }\mu\text{m}$  in linear dimensions were selected for mounting inside the diamond cell. Gasket blanks of full hard T301 stainless steel were indented to a thickness of  $75\text{--}90\text{ }\mu\text{m}$  and then a  $200\text{-}\mu\text{m}$ -diam hole drilled in it.

### RESULTS AND DISCUSSION

Although berlinite is isomorphous with quartz, its unit cell is doubled along the  $c$  axis, owing to the substitution of Al and P ions in alternate Si sites.<sup>12</sup> This situation brings the  $\mathbf{q}=(0, 0, \pi/c)$  quartz zone-boundary phonons nons into the zone center in the case of  $\text{AlPO}_4$ , resulting in a richer Raman spectrum for  $\text{AlPO}_4$  compared to quartz. Scott<sup>11</sup> has identified these features in the spectrum of  $\text{AlPO}_4$ . Group theory predicts<sup>11</sup>  $8\Gamma_1+17\Gamma_3$  Raman-active modes for  $\text{AlPO}_4$  and  $4\Gamma_1+8\Gamma_3$  modes for quartz. Inclusion of electrostatic splittings result in  $8\Gamma_1+17\Gamma_3(\text{TO})+17\Gamma_3(\text{LO})$  modes for  $\text{AlPO}_4$  and  $4\Gamma_1+8\Gamma_3(\text{TO})+8\Gamma_3(\text{LO})$  for quartz.<sup>11</sup> (The  $\Gamma_1$  correspond to the totally symmetric  $A_1$  modes and the  $\Gamma_3$  to the doubly degenerate  $E$  modes, in the chemical notation for describing the mode symmetry.)

The pressure dependence of the observed Raman peaks in  $\text{AlPO}_4$  and  $\alpha$ -quartz are shown in Figs. 1 and 2. In the case of  $\text{AlPO}_4$ , we are able to follow 11 Raman peaks up to 12 GPa, while in quartz 8 peaks were followed up to 20 GPa. Table I lists the observed Raman peaks, their  $d\nu_i/dP$ , and the mode-Grüneisen parameters  $\gamma_i$  for both  $\text{AlPO}_4$  and  $\alpha$ -quartz from the expression  $\gamma_i = B_0 / \nu_i (d\nu_i/dP)$ , where  $B_0$  is the bulk modulus,  $\nu_i$  is the phonon frequency, and  $d\nu_i/dP$  is its pressure dependence evaluated from low-pressure data.

It has been pointed out in the case of quartz<sup>4-6</sup> that the modes which exhibit a strong temperature dependence are precisely those that show a strong pressure dependence; the modes in question being the ones at 128, 206, and 465  $\text{cm}^{-1}$ . The same is true for  $\text{AlPO}_4$ , and the corresponding modes are the 116, 216, and 460  $\text{cm}^{-1}$ . A rather remarkable feature in Figs. 1 and 2 is the strikingly similar pressure sensitivities exhibited by the 216- $\text{cm}^{-1}$  mode of  $\text{AlPO}_4$  and the 206- $\text{cm}^{-1}$  mode of quartz. These modes show a large initial increase in frequency with pressure and rapidly flatten out at higher pressures. The  $\nu_i$ -vs- $P$  behavior is thus highly nonlinear, as noted in the very recent pressure Raman study of quartz.<sup>6</sup> Previous high-temperature investigations at ambient pressure<sup>13,14</sup> have shown that these modes behave anomalously as the  $\alpha$ - $\beta$  phase transition is approached; they exhibit unusual line shapes, broaden unsymmetrically, and soften with temperature. The detailed behavior of these modes with temperature has been interpreted in terms of anharmonic interaction between one-phonon states and one-phonon and two-phonon states,<sup>13,14</sup> to which we will return later in this paper.

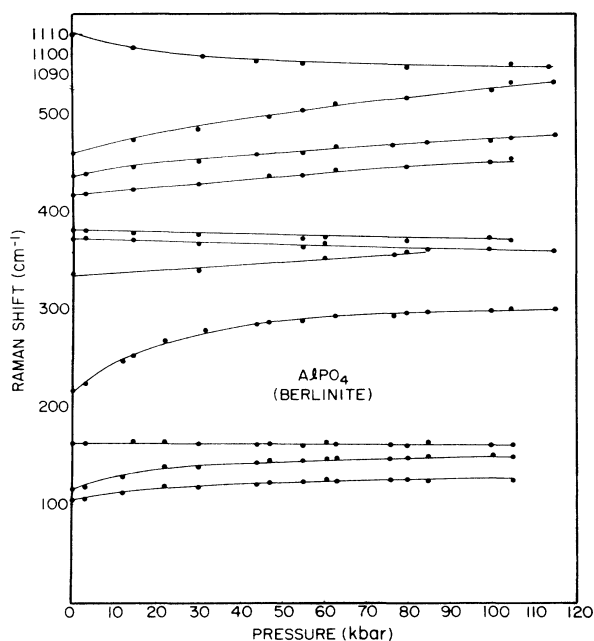


FIG. 1. Pressure dependence of the phonon frequencies in berlinite ( $\text{AlPO}_4$ ).

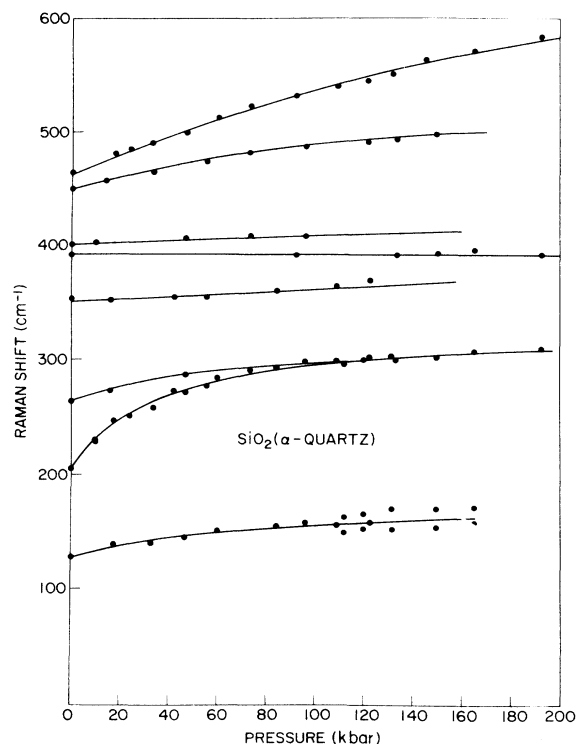


FIG. 2. Pressure dependence of the phonon frequencies in  $\alpha$ -quartz.

The  $E$  modes of  $\text{AlPO}_4$  at 372 and 382  $\text{cm}^{-1}$  have a small negative slope and consequently have a negative Grüneisen parameter. The corresponding modes in quartz at 394 and 401  $\text{cm}^{-1}$  behave similarly. But the high-frequency  $A_1$  mode of  $\text{AlPO}_4$  at 1110  $\text{cm}^{-1}$  and the corresponding quartz mode at 1085  $\text{cm}^{-1}$  appear to behave differently. Whereas the former has an initial negative slope and a broad minimum, the latter has a positive slope at all pressures. On the other hand, the 1160- $\text{cm}^{-1}$  mode of quartz decreases in frequency with pressure initially and then increases, exhibiting a broad minimum, according to Hemley.<sup>6</sup> Thus, in terms of the pressure behavior, the 1110- $\text{cm}^{-1}$  mode of  $\text{AlPO}_4$  and the 1160- $\text{cm}^{-1}$  mode of quartz seem to be the corresponding modes and not the 1085  $\text{cm}^{-1}$  of quartz and the 1110  $\text{cm}^{-1}$  of  $\text{AlPO}_4$ . At pressures above 12 GPa it was impossible to obtain a spectrum with  $\text{AlPO}_4$ , although in the case of quartz there was no problem in following the Raman peaks up to 20 GPa, the limit of pressure in the present study. (The experiments were terminated at 20 GPa only because the methanol-ethanol pressure medium turned so nonhydrostatic above 20 GPa that the Raman peaks showed splittings and line-shape changes. Splittings due to uniaxial stress<sup>15</sup> can be seen in Fig. 2 even above 12 GPa; see particularly the 128- $\text{cm}^{-1}$  Raman peak above 12 GPa.) Hemley<sup>6</sup> has reported amorphization of quartz under pressures above 30 GPa, and apparently this happens even with Ar as a pressure medium, as judged by the Raman spectrum of the sample. Because of the difficulty in

TABLE I. Observed Raman modes, and mode-Grüneisen parameter  $\gamma_i$  for  $\text{AlPO}_4$  and  $\alpha$ -quartz.  $\text{AlPO}_4$ ,  $B_0=287.0$  kbar, calculated from the elastic constants.  $\alpha$ -quartz,  $B_0=371$  kbar. The values in parentheses are from Ref. 6.

| $\text{AlPO}_4$ (berlinite)     |   |            | $\text{SiO}_2$ (quartz)         |   |              |
|---------------------------------|---|------------|---------------------------------|---|--------------|
| $\nu_i$<br>( $\text{cm}^{-1}$ ) | $d\nu_i/dP$<br>( $\text{cm}^{-1}/\text{kbar}$ ) | $\gamma_i$ | $\nu_i$<br>( $\text{cm}^{-1}$ ) | $d\nu_i/dP$<br>( $\text{cm}^{-1}/\text{kbar}$ ) | $\gamma_i$   |
| <i>A</i> <sub>1</sub> modes     |   |            | <i>A</i> <sub>1</sub> modes     |   |              |
| 160                             | 0.0   | 0          |                                 |   |              |
| 216                             | 2.6   | 3.45       | 206                             | 2.4   | 4.32 (3.63)  |
| 334                             | 0.2   | 0.17       | 355                             | 0.05  | 0.05 (0.03)  |
| 460                             | 1.0   | 0.62       | 464                             | 0.8   | 0.64 (0.66)  |
| 1110                            | -0.5  | -0.13      |                                 |   |              |
| <i>E</i> modes                  |   |            | <i>E</i> modes                  |   |              |
| 105                             | 0.7   | 1.9        |                                 |   |              |
| 116                             | 0.8   | 1.98       | 128                             | 0.6   | 1.7 (1.64)   |
|                                 |   |            | 264                             | 0.6   | 0.84 (0.65)  |
| 372                             | -0.1  | -0.07      | 394                             | 0   | 0            |
| 382                             | -0.1  | -0.07      | 401                             | 0.1   | 0.09 (-0.03) |
| 416                             | 0.4   | 0.27       |                                 |   |              |
| 436                             | 0.9   | 0.59       | 450                             | 0.05  | 0.04 (0.52)  |

observing any Raman peaks in  $\text{AlPO}_4$  at pressures above 12 GPa, we suspected a change to a glassy state in  $\text{AlPO}_4$ . However, on release of pressure the original crystalline spectrum reappeared, but somewhat reduced in intensity. Although we do not know the reason for the reduced intensity, the experiment weakens the argument for a change to a glassy state, in the case of  $\text{AlPO}_4$ .

An interesting observation in connection with pressurization experiments on  $\text{AlPO}_4$  and quartz in methanol-ethanol is the vanishing of the crystals in the pressure medium due to the refractive-index matching. This is so remarkable that even the birefringence of the crystal could be distinguished and matched from the movement of the Becke line which gives a very good indication of the relative differences in the refractive indices between the medium and the crystals. At room temperature the  $\epsilon_D$  index of quartz can be perfectly matched at 72 kbar and similarly, the  $\epsilon_D$  of  $\text{AlPO}_4$  (berlinite) can be matched at 56 kbar pressure. When the quartz index is adjusted for 72 kbar using the low-pressure data,<sup>16</sup> we obtain  $n=1.59$  for the index of the 4:1 methanol-ethanol mixture at 72 kbar.

Polian *et al.*<sup>17</sup> have evaluated the  $n(P)$  for 4:1 methanol-ethanol mixture by first fitting the density data of Bridgman to Tait's equation of state (EOS) and then using the function relating Eulerian strain to the  $n(\rho)$ . To a very good approximation

$$n(\rho) = n(\rho_0) - 0.571[1 - (\rho/\rho_0)^{2/3}] .$$

In Fig. 3 we show  $n(P)$ , by following the same procedure, but putting the constraint that the refractive index ( $n$ ) of the mixture should equal 1.59 at 72 kbar. This necessitated using  $B_0=0.7$  GPa and  $B_0^1=10.1$  in the Tait EOS to match the above point. We believe that the  $n(P)$  given in Fig. 3 may be useful in optical measurements at high pressures.

#### PRESSURE AND THE *A*<sub>1</sub> SOFT MODE

The temperature dependence of the low-frequency *A*<sub>1</sub> mode in quartz has been of great interest from the standpoint of the mechanism triggering the  $\alpha$ - $\beta$  transition in quartz near 850 K. Raman and Nedungadi<sup>18</sup> discovered in 1940 that this mode underwent anomalous broadening, and decreased in frequency as the  $\alpha$ - $\beta$  quartz transition was approached. Since then, the connection between soft-mode behavior and phase transitions in crystalline solids has received much attention, both experimentally and theoretically.<sup>19</sup>

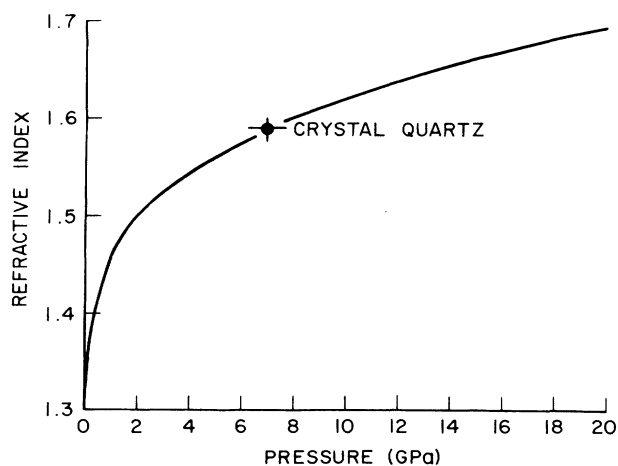


FIG. 3. Refractive index of 4:1 methanol-ethanol mixture as a function of pressure computed from  $n(\rho)$  relationship and Bridgman's  $\rho$ -vs- $P$  data. The  $\alpha$ -quartz constraint point is shown.

Scott investigated the temperature behavior of the soft  $A_1$  mode in quartz<sup>13</sup> as well as  $\text{AlPO}_4$  (Ref. 14) up to the  $\alpha$ - $\beta$  transition point and proposed that in quartzlike structures there is a strong anharmonic interaction between one-phonon states and between one-phonon and two-phonon states. In the model for quartz, the  $206\text{-cm}^{-1}$   $A_1$  mode decreases in energy with increasing temperature and overlaps a two-phonon (TA zone-edge phonon) band centered around  $147\text{ cm}^{-1}$ , interacting with it strongly. The anharmonic coupling between the optic mode and the two-phonon state broadens the optic phonon anomalously, by providing a relaxation mechanism for decay into acoustic-phonon pairs. A Fermi-resonance-like interaction that occurs in gas molecules such as  $\text{H}_2\text{O}$  has been suggested for the anharmonic resonance between the one-phonon and the two-phonon states.

In the case of  $\text{AlPO}_4$ , Scott<sup>14</sup> discovered softening of the  $216\text{-cm}^{-1}$  mode with increasing temperature and anomalous changes in line shape and linewidth, as the  $\alpha$ - $\beta$  transition was approached. To explain the results, he invoked two mechanisms: a strong anharmonic coupling of the  $216\text{-cm}^{-1}$   $A_1$  mode with another one-phonon state near  $160\text{ cm}^{-1}$  of the same symmetry, and also an anharmonic interaction with a two-phonon (zone-boundary acoustic-phonon) continuum. Accordingly, above 400 K a striking anharmonic interaction between the soft mode and the  $A_1$  phonon near  $160\text{ cm}^{-1}$  occurs which is describable via a Green's-function treatment,<sup>20</sup> or in terms of a Fano-type formalism.<sup>21</sup> The interaction between the optical phonons apparently is via the anharmonic terms linking each of the phonons to the two-phonon (acoustic) continuum. The second anharmonic coupling arises from an interaction of the same type as in quartz, between the one-phonon state at  $216\text{ cm}^{-1}$  and a two-phonon (acoustic) band centered around  $\sim 140\text{ cm}^{-1}$ . Using a Green's-

function technique, Zawadowski and Ruvalds<sup>20</sup> calculated the spectrum for two optic phonons interacting via anharmonic coupling to two acoustic phonons, and demonstrated the antiresonance characteristics in the single-phonon density of states, which is in excellent agreement with the observed features in the first-order Raman spectrum of  $\text{AlPO}_4$ .<sup>14</sup> In Fig. 4 the different phononic interactions discussed above are shown schematically for normal pressure and at high pressure ( $\sim 5.5\text{ GPa}$ ). The point to recognize here is that quartz and  $\text{AlPO}_4$  present somewhat different coupled-mode interactions and we believe that the pressure behavior of the soft mode ( $216\text{ cm}^{-1}$  of  $\text{AlPO}_4$  and  $206\text{ cm}^{-1}$  of quartz) reflects this difference, particularly the effect of pressure on the linewidth.

In Figs. 5 and 6 are shown the pressure behavior of the  $216\text{-cm}^{-1}$  mode in  $\text{AlPO}_4$  and the corresponding mode in quartz at  $20\text{ cm}^{-1}$  recorded at room temperature. The  $206\text{-cm}^{-1}$  mode in quartz sharpens somewhat and shifts rapidly to higher frequency with increasing pressure. (Similar changes in linewidth have been noted by Dean *et al.*<sup>5</sup> in a recent low-temperature Raman study of quartz. They found a considerable narrowing of the  $206\text{-cm}^{-1}$  peak on lowering the temperature to 77 K and a small shift to higher frequency due to thermal contraction accompanying cooling.) By comparison, the effect of pressure on the  $216\text{-cm}^{-1}$  peak in  $\text{AlPO}_4$  is much more striking (see Fig. 5). The linewidths at half maximum are marked on the right-hand side of the peak in Fig. 5. There appears to be also a change in the background scattering continuum in the low-frequency region of the spectrums, which is also seen in Fig. 6 for quartz. The effect of pressure on the phonon energies is shown schematically in Fig. 4. We believe from our results that the anharmonic interaction between the two  $A_1$  optical phonons in  $\text{AlPO}_4$  is there even at room temperature and

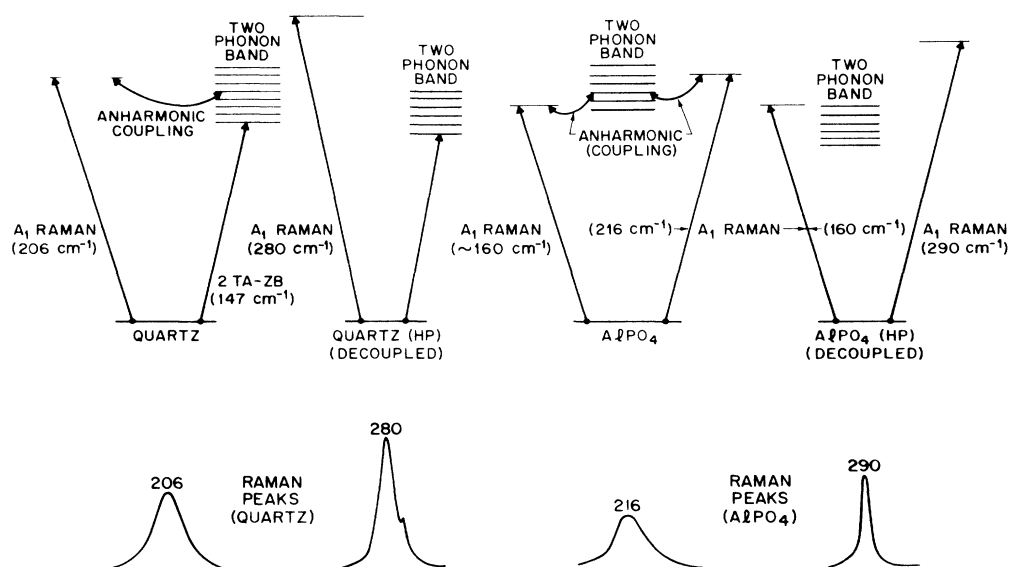


FIG. 4. Phononic interactions involving the  $A_1$  soft mode and one- and two-phonon states in quartz and  $\text{AlPO}_4$ . The effect of pressure on the levels are shown on the right in each case and the observed linewidths at the bottom. High pressure is indicated by HP.

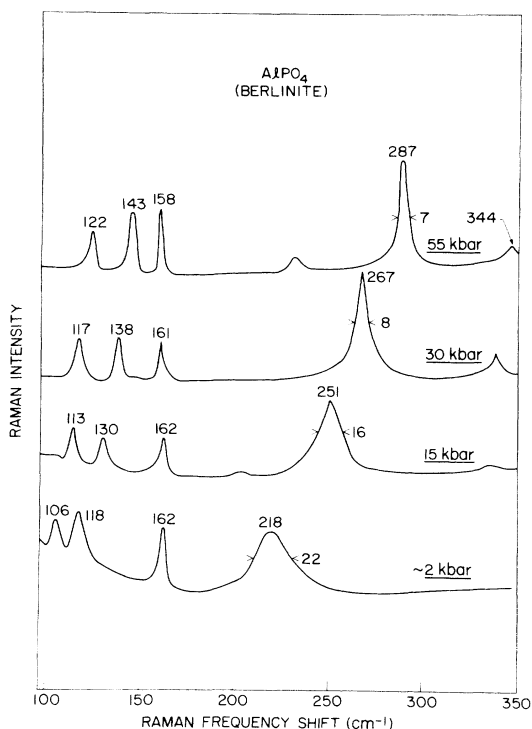


FIG. 5. Effect of pressure on the low-frequency phonons in  $\text{AlPO}_4$ . The striking changes and shift of the soft  $A_1$  mode ( $216 \text{ cm}^{-1}$  at 1 bar) is to be noted. The half-width at half maximum is marked on the peak.

this is the dominant mechanism that contributes to the linewidth of the  $A_1$  soft mode ( $216 \text{ cm}^{-1}$ ) at normal pressure. With increasing pressure the soft  $A_1$  phonon and the  $A_1$  phonon near  $160 \text{ cm}^{-1}$  move rapidly away from each other and consequently get decoupled. Further, this would be true even if the two optic phonons interact via the two-phonon continuum, since the overlap of the optic-phonon state with the latter also rapidly decreases with increasing pressure (see Fig. 4). In the case of quartz, there is no low-frequency  $A_1$  phonon and the line shape is mainly determined by the interaction with the two-phonon band. It is also to be noted here that the  $\alpha$ - $\beta$  transition temperature is moving farther away rapidly with increasing pressure, since  $dT/dP$  for the  $\alpha$ - $\beta$  phase transition is very large and positive.<sup>22</sup> The observed changes would be quite consistent with this.

#### SUMMARY AND CONCLUSIONS

We conclude the following:

(1) From the pressure dependence of the optical phonons in  $\text{AlPO}_4$  and  $\text{SiO}_2$ , it is clear that the modes which exhibit a strong temperature dependence are also strongly pressure dependent.

(2) The pressure dependence of the soft  $A_1$  mode in  $\text{AlPO}_4$  and in  $\alpha$ -quartz are strikingly similar. Both show a large initial increase in frequency and rapidly flatten out

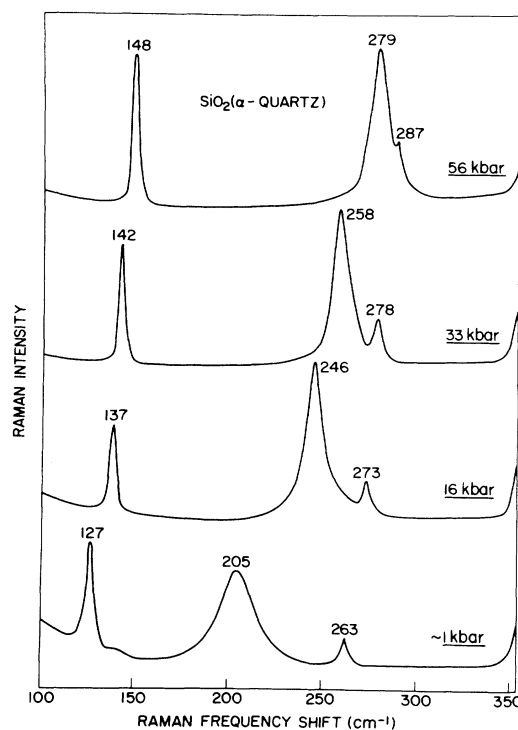


FIG. 6. Effect of pressure in the low-frequency phonons in  $\alpha$ -quartz. Note the change in the linewidth of the  $A_1$  mode near  $205 \text{ cm}^{-1}$ .

at pressures above 5 GPa. Thus, the frequency-versus-pressure behavior is highly nonlinear.

(3) Further, these two modes exhibit striking changes in width with increasing pressure. In  $\text{AlPO}_4$ , the half-width at half maximum decreases from about 20 to  $7 \text{ cm}^{-1}$ .  $\alpha$ -quartz also exhibits a large change, although not to the same extent.

(4) Pressure decouples the strong anharmonic interaction of the soft  $A_1$  mode with one-phonon (optic) and two-phonon (acoustic) states in  $\text{AlPO}_4$ , and two-phonon (acoustic) states in  $\alpha$ -quartz. However, from the more striking changes in the observed linewidth with pressure in the case of  $\text{AlPO}_4$ , we conclude that the anharmonic interaction with the one-phonon state ( $A_1$  optic phonon at  $160 \text{ cm}^{-1}$ ) is the dominant mechanism responsible for the line broadening in  $\text{AlPO}_4$ . In quartz there is no low-frequency optic phonon of the same symmetry and the only mechanism influencing the linewidth is the anharmonic interaction with the two-phonon (acoustic) state. Thus, pressure helps to discriminate the difference in the two cases.

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