

Raman Spectra and Lattice Dynamics of α -Berlinite (AlPO_4)

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Using the Born-von Karman and rigid-ion models of Elcombe for the optical phonons in α -quartz, we have analyzed the Raman spectra of isomorphous AlPO_4 (berlinite). The resulting analysis yields several physical parameters which are not accessible to any other experimental measurement; for example, the dispersion of phonon branches in the high-frequency region. Since the AlPO_4 Brillouin zone is halved in the $[00\zeta]$ direction compared with that of quartz, phonons characteristic of critical point A in quartz are Raman active in AlPO_4 . The near equivalence of $\text{Al} + \text{P}$ and 2Si masses and of phonon frequencies experimentally determined in SiO_2 and AlPO_4 demonstrates that a significant amount of charge compensation exists in AlPO_4 , such that Al and P each have a nominal valence of $\sim +4$, rather than $+3$ and $+5$. This is confirmed by the measured LO/TO splitting of modes which would be described as having wave vector $(0, 0, \pi/c)$ in quartz: If Al and P charges and masses were identical, these degeneracies would remain unsplit by the lattice Coulomb field. The small splittings we observe ($7\text{--}19 \text{ cm}^{-1}$) for each transverse/longitudinal doublet allow us to determine the difference in effective charge for Al and P ions. An estimate of $Z(\text{P}) - Z(\text{Al}) \approx 0.2e$ is obtained from the rigid-ion expression $4\pi^2 \sum_j (\omega_{\text{LO},j}^2 - \omega_{\text{TO},j}^2) = (4\pi/V) \sum_k Z_k^2/m_k$, and values $Z(\text{P}) = 2.4e$, $Z(\text{Al}) = 2.2e$, $Z(\text{O}) = -1.15e$ deduced.

I. INTRODUCTION

α -berlinite (AlPO_4) is isomorphous to quartz.¹ It has space group D_3^4 with Al and P ions at C_2 sites and oxygen ions at C_1 sites. The AlPO_4 unit cell consists of three formula groups (18 atoms). It is twice as long as that of quartz in the C direction, owing to the replacement of silicons with nonequivalent Al and P atoms. Because the mass of $\text{Al} + \text{P}$ (atomic numbers 13 and 15) is about the same as that of two silicon atoms (atomic number 14), the phonon frequencies in α - SiO_2 and α - AlPO_4 are very nearly the same for all modes, in striking contrast to α - GeO_2 ,² and the temperatures for the α - β transition are very nearly equal³ (846 and 852 °K). This near equivalence of AlPO_4 and SiO_2 lattices suggests the use of an "extended-zone scheme" for the description of optical phonons in the two crystals. Such analyses have proved useful in the past in interpreting the spectra of polytypes, such as SiC ⁴ and ZnS .⁵ In the case of quartz, a phonon having wave vector $(0, 0, \pi/c)$ is at critical point A at the zone boundary. The symmetry at A happens to be the same as at Γ , the Brillouin-zone center, and consequently there exist three symmetry representations for phonons at A , one of which is twofold degenerate, just as at Γ . Phonons having the same numerical wave vector in AlPO_4 [$\vec{q} = (0, 0, \pi/c)$ (quartz)] are, however, at a Brillouin-zone center, since

$$\frac{\pi}{c(\text{quartz})} = \frac{\pi}{\frac{1}{2}c(\text{AlPO}_4)} = \frac{2\pi}{c}.$$

Hence, one may expect to describe the modes

which appear in the infrared (IR) or Raman spectra of AlPO_4 at frequencies where nothing is manifest in SiO_2 as due to quartz phonons at $(0, 0, \pi/c) \equiv A$.

Neglecting Coulomb effects at finite wave vector, we may determine the symmetries and number of phonon branches at Γ and A in AlPO_4 in the usual way. There are no atoms on the C_3 axis, so $X(3) = 0$. There is one Al ion and one P ion on each C_2 axis, so $X(2) = n(C_2)(-1) = -2$. The identity matrix character is $3n$, which is 54. Hence, from Koster's tables⁶ we find

	E	C_3	C_2
Γ_1 (or A_1)	1	1	1
Γ_2 (or A_2)	1	1	-1
Γ_3 (or A_3)	2	-1	0
$X(\Gamma)$	54	0	-2

Hence

$$n(\Gamma_1) + n(\Gamma_2) + 2n(\Gamma_3) = 54,$$

$$n(\Gamma_1) + n(\Gamma_2) - n(\Gamma_3) = 0,$$

$$n(\Gamma_1) - n(\Gamma_2) + 0 = -2.$$

The simultaneous solution to the three equations above is $8\Gamma_1 + 10\Gamma_2 + 18\Gamma_3$ zone-center phonon branches, of which $1\Gamma_2 + 1\Gamma_3$ are acoustic and $8\Gamma_1 + 9\Gamma_2 + 17\Gamma_3$ are optic. Thus, including the electrostatic splittings, $8\Gamma_1 + 17\Gamma_3$ (TO) + $17\Gamma_3$ (LO) Raman lines are predicted.

In comparison, quartz has $4\Gamma_1 + 4\Gamma_2 + 8\Gamma_3$ optic branches at Γ and $4A_1 + 5A_2 + 9A_3$ at A .⁷ The Γ_3 degeneracies are removed at finite wave vector

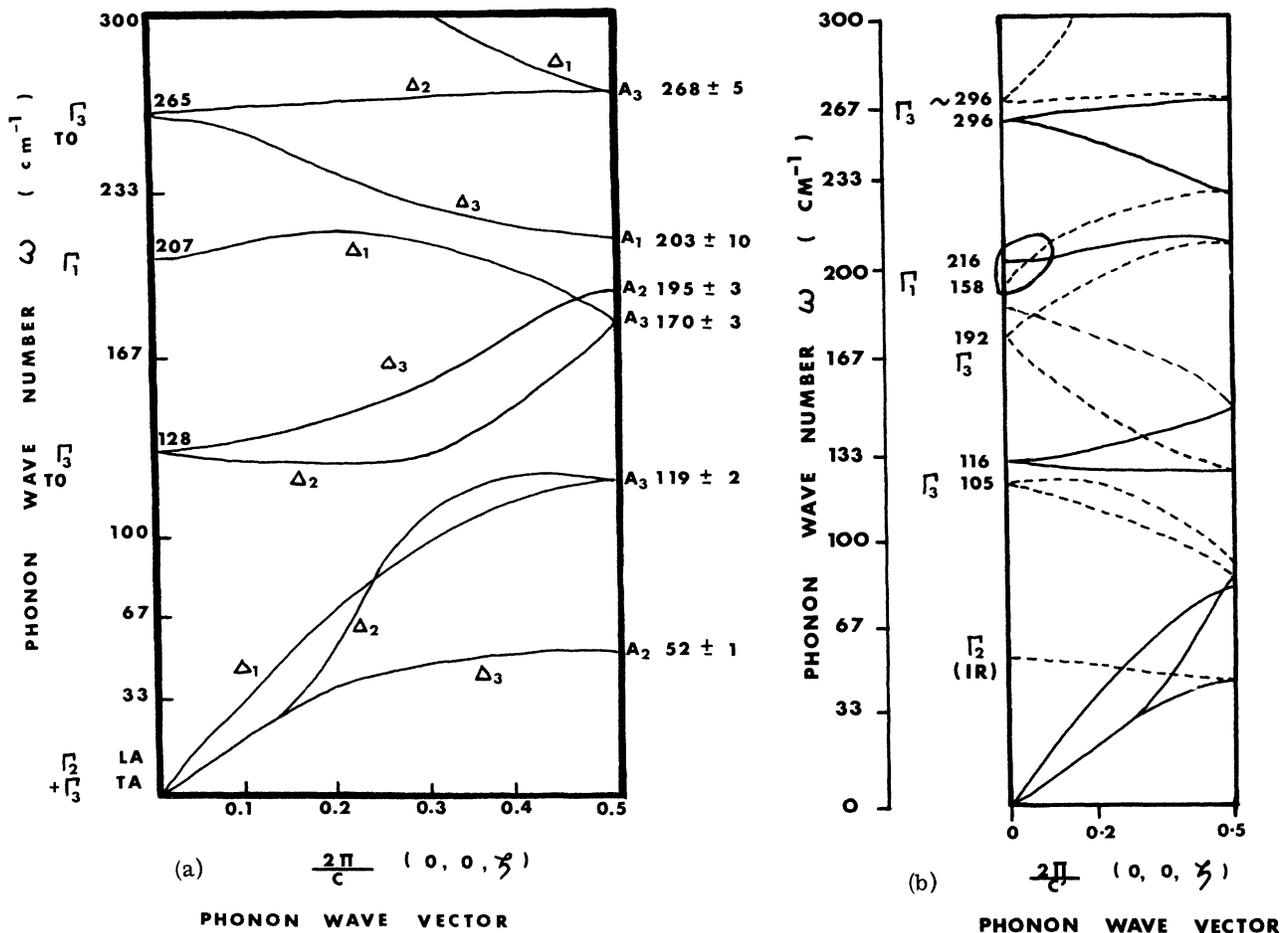


FIG. 1. (a) Phonon dispersion in α -quartz with frequencies and symmetries of branches at $\Gamma = (0, 0, 0)$ and $A = (0, 0, \pi/c)$ (from Elcombe). (b) Phonon dispersion in α -AlPO₄ obtained by folding over the dispersion curves in (a). The frequencies and symmetries at Γ are taken from the present Raman study.

($q \sim 10^5$ cm⁻¹) by Coulombic forces. However, within 10^5 cm⁻¹ of $(0, 0, \pi/c)$, the A_3 splittings will be negligible. The Raman spectrum of AlPO₄ may therefore be interpreted as $4\Gamma_1 + 8\Gamma_3$ (TO) + $8\Gamma_3$ (LO) modes equivalent to those in the quartz spectrum, plus $4\Gamma_1 + 9\Gamma_3$ modes equivalent to the $4A_1 + 9A_3$ modes at $(0, 0, \pi/c)$ in quartz. These $9\Gamma_3$ modes will have vanishingly small TO/LO splittings if Al and P ions have equal charge, i. e., if the doubled unit cell has no effect on the lattice Coulomb field.

Although phonon frequencies have been published for only one direction in the quartz Brillouin zone⁸ (from inelastic neutron scattering experiments), it is just that direction $[00\xi]$ appropriate for the AlPO₄/SiO₂ extended zone analysis. The results of Elcombe's measurements on SiO₂ in the 0–275-cm⁻¹ region are shown in Fig. 1(a). The smooth curves approximate a fit given by Elcombe from a rigid-ion model, while the frequencies at Γ and A listed

are experimental. Figure 1(b) shows the predictions made for AlPO₄ by simply folding the zone in half (i. e., assuming equal Al and P effective charges). The symmetry and experimental frequencies given for AlPO₄ in Fig. 1(b) are those determined from the present work.

II. LOW-FREQUENCY PHONONS

It can be noted from Figs. 1(a) and 1(b) that the 0–300-cm⁻¹ region of the AlPO₄ Raman spectrum is in very good agreement with predictions based on Elcombe's $(0, 0, \pi/c)$ quartz frequencies: Γ_3 (TO + LO) unresolved doublets are found at 105, 116, and 192 cm⁻¹, compared with the quartz Γ_3/A_3 values of 119, 128, and 170 cm⁻¹; Γ_1 modes are found at 216 and 158 cm⁻¹, compared with the quartz Γ_1/A_1 values of 207 and 203 cm⁻¹. The large difference in frequency between the 158-cm⁻¹ Γ_1 mode in AlPO₄ and the 203-cm⁻¹ A_1 mode in SiO₂ is be-

lied to be due to strong coupling between the two Γ_1 modes in AlPO_4 at 216 and 158 cm^{-1} ; this coupling is also manifest in the Raman line shapes of the two modes^{9,10} and is discussed in Sec. IV.

We note that while undetected in Raman-scattering experiments, two modes IR active for $\mathcal{E} \parallel c$ are predicted at ~ 52 and 195 cm^{-1} in AlPO_4 . These Γ_2 branches would be described as TA^A and TO^A , respectively, in α -quartz.

III. HIGH-FREQUENCY PHONONS

The high-frequency portion of the AlPO_4 spectrum is more difficult to compare with $(0, 0, \pi/c)$ quartz frequencies, since there is insufficient flux from thermal neutron sources to perform inelastic neutron scattering much above 300 cm^{-1} (~ 400 °K). Hence, in the high-energy region we make comparison with Elcombe's model calculations, which in turn are based on phonon frequencies in the low-energy region.

In general, phonon frequencies in the very-high-frequency region (> 1000 cm^{-1}) of a crystal are expected to be rather independent of long-range forces. They are therefore considered *a priori* to be relatively dispersionless. However, the Si-O stretching modes from 1070–1240 cm^{-1} in quartz exhibit some interesting wave-vector dependences along $[00\xi]$. This is primarily due to the compatibility relations between the degenerate representations at Γ and A and the nondegenerate branches $\Delta_1, \Delta_2, \Delta_3$ between Γ and A , as shown for the 1000–1250- cm^{-1} region in Fig. 2. Whereas Γ_3 divides into $\Delta_2 + \Delta_3$ branches at finite wave vector ξ for $[00\xi]$, it is $\Delta_1 + \Delta_2$ which combine at $(0, 0, \pi/c)$ to form A_3 .

IV. EXPERIMENTAL

The AlPO_4 data presented in the present work were obtained from a single crystal hydrothermally grown by Lang at McMaster University and provided through the courtesy of Calvo. It was of irregular shape and mean dimension 1.5 mm. The C axis was determined optically. Data were recorded using a 300-mW argon-ion laser at 4880 or 5145 Å, a double monochromator, cooled S-20 phototube, and strip chart. α_{xx} spectra observed at 295 °K are shown in Fig. 3(a), and α_{xx} spectra under the same conditions are shown in Fig. 3(b). The observed frequencies and symmetry representations are given in Table I and compared with α -quartz modes.¹¹

The TO or LO character of the modes in AlPO_4 were in most cases verifiable from intensity measurements made by back scattering along the C axis; for this geometry the Γ_3 LO modes are forbidden. However, due to the small size of the sample, some light scattered from the crystal surface also entered the collection optics, so that none of

the LO modes assigned had vanishing cross sections for this $Z(XY)Z$ geometry. Despite the sample size the anisotropy measurements made seem sufficiently reliable to establish the LO and TO assignments, which have been aided by a comparison with quartz. Larger samples would eliminate the uncertainty due to "leak through."

Γ_1 Modes

For the α_{xx} spectrum the agreement between observed features in AlPO_4 and those predicted from SiO_2 Γ_1/A_1 modes is virtually complete, lacking only a clear indication of a Γ_1 doublet at ~ 450 cm^{-1} for perfect agreement. We note that the Γ_1 modes in AlPO_4 at 216, 336, 456, and 1112 cm^{-1} correspond to Γ_1 in quartz at 207, 356, 464, and 1085 cm^{-1} ; while Γ_1 in AlPO_4 at 158, 729, and 1105 cm^{-1} correspond to A_1 in quartz calculated from Elcombe's Born-von Karman model as 187, 764, and 1100 cm^{-1} . The fourth calculated A_1 mode is at 399 cm^{-1} and is probably obscured by the E -mode leak through in the α_{xx} spectrum; a shoulder at

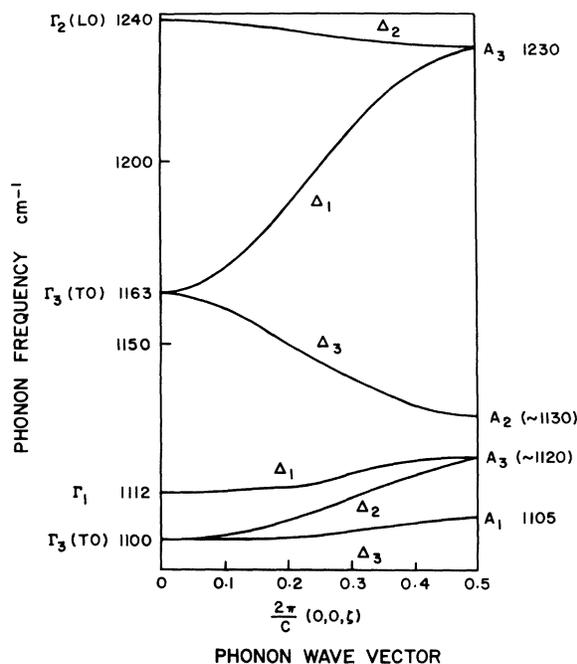


FIG. 2. Schematic dispersion relations for quartz and/or AlPO_4 obtained from the present Raman study. The frequencies 1100, 1105, 1112, 1230, and 1240 cm^{-1} are experimentally determined from Raman measurements in the present work; the values ~ 1120 , 1130, and 1163 cm^{-1} are taken from quartz data and Elcombe's Born-von Karman calculation. Note that the $\Gamma_2(\text{TO})$ mode at ~ 1100 cm^{-1} is not an eigenvector for the propagation direction shown; neither $\Gamma_2(\text{TO})$ nor $\Gamma_3(\text{LO})$ exist for $[0, 0, \xi]$ propagation. We have neglected anisotropy in equating $\Gamma_2(\text{LO}) = 1240$ $\text{cm}^{-1} = \Gamma_3(\text{LO})$ since these values differ by only ~ 3 cm^{-1} in quartz.

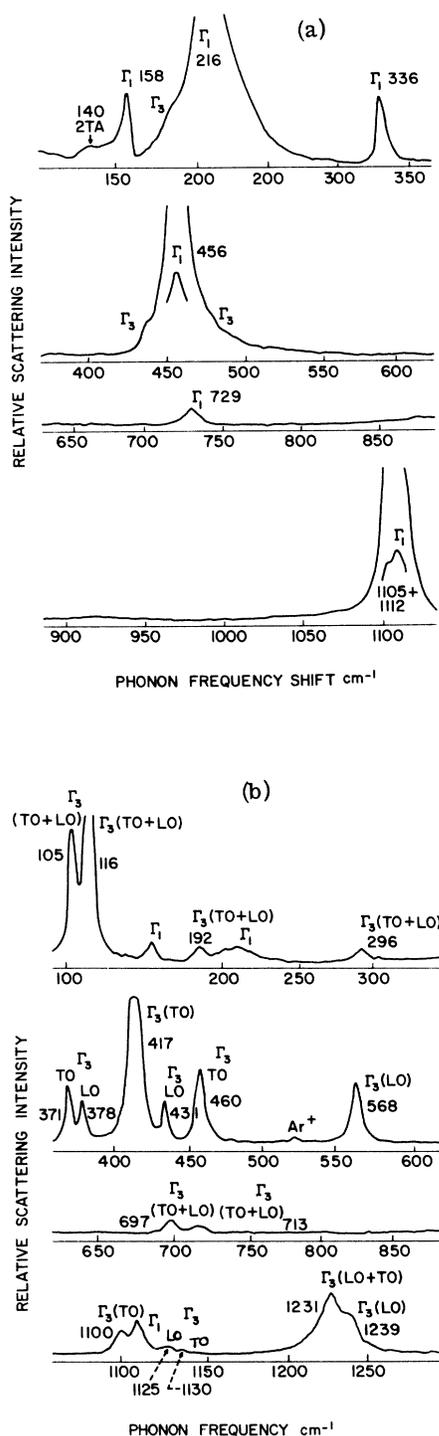


FIG. 3. (a) α_{zz} spectrum of α - AlPO_4 at $\sim 295^\circ\text{K}$. Slit width $100 \mu\text{m}$ (or $\sim 3 \text{ cm}^{-1}$); time constant 2 sec. (b) α_{xz} spectrum of α - AlPO_4 , as in (a). A value for the static dielectric constant for $\mathcal{E}_{\perp c}$ of $\epsilon_0^{\perp} = 4.7$ may be obtained from these data and Bond's measurement of $n_0(\omega)$, using the relationship $\epsilon_0^{\perp} = n_0^2 \prod \omega_{LO}^2 / \omega_{TO}^2$ with $n(\omega)$ evaluated at $\sim 1 \mu$ [W. L. Bond, J. Appl. Phys. **36**, 1674 (1965)].

436 cm^{-1} is presumably due to a strong $E(\text{LO})$ at that frequency.

We note that in each case the Raman intensities of the Γ_1 modes in AlPO_4 , which are also Γ_1 in quartz, are somewhat greater than those which would be A_1 in quartz. This is to be expected. In the limit in which Al and P ions become truly equivalent, the cross sections of the "extra" modes must become vanishingly small.

We also note that the cross section for the Γ_1 mode at 1112 cm^{-1} is very large. This is to be expected for a symmetric oxygen stretching vibration, which normally involves a large polarizability derivative; it is observed in the isomorphic lattice GeO_2 , as well, where the mode lies at 880 cm^{-1} . Hence, the very weak intensity of this mode in α -quartz, discussed from a lattice-dynamical point of view by Kleinman and Spitzer,¹² must be regarded as anomalous even for this lattice structure, as well as for crystals in general and dependent upon parameters unique to α -quartz.

Γ_3 Modes

The correlation of Γ_3 frequencies in quartz and AlPO_4 as shown in Table I is generally good. All of the Γ_3 modes in quartz are found in AlPO_4 , except those at $795/807$ and $1163/1164 \text{ cm}^{-1}$. (These doublets were also very weak in the quartz α_{xz} Raman spectrum.) All of the observed Γ_3 modes in quartz have frequencies within 12% of those in AlPO_4 , and the TO/LO splittings agree reasonably well, where resolvable.

In addition, seven Γ_3 modes are found in AlPO_4 which correspond to $(0, 0, \pi/c) A_3$ vibrations in quartz. Of these, the three unresolved doublets observed at 105 , 192 , and 713 cm^{-1} agree quite well with Elcombe's measured and calculated values of 119 , 170 , and 723 cm^{-1} in quartz. The TO/LO doublet at 417 – 436 cm^{-1} is in good agreement with the calculated A_3 quartz doublet at 413 cm^{-1} ; the doublet at 1230 cm^{-1} is about 100 cm^{-1} higher than calculated.

Of the Γ_3 doublets, those which are weak in quartz (394 – 401 , 697 – 698 , 1072 – 1235 , and 1163 – 1164 cm^{-1}) also have small Raman cross sections in AlPO_4 (viz., those at 371 – 378 , 697 , and 1100 cm^{-1}). One discrepancy in intensity is the unresolved Γ_3 at 296 cm^{-1} in AlPO_4 , which is very weak, in contrast with the strong mode at 265 cm^{-1} in quartz. A second intensity anomaly is that the $\Gamma_3(\text{TO})$ at 417 cm^{-1} , which we assign as analogous to A_3 (quartz) at 413 cm^{-1} , is the most intense Γ_3 mode. Hence, unlike the Γ_1 AlPO_4 spectrum, in which modes corresponding to $(0, 0, \pi/c)$ quartz vibrations were consistently the weakest, the A_3 -like modes in the Γ_3 spectrum are quite strong. Because of the large number of Γ_3 branches in the 370 – 480-cm^{-1} region (four doublets), it is likely

TABLE I. Phonon frequencies and symmetries in α -AlPO₄ and α -quartz (all values are experimental except those with asterisks, which are calculated by Elcombe from a Born-von Karman model).

Γ_1 (quartz)		Γ_1 (AlPO ₄)	
207		216	
356		336	
464		456	
1085		1112	
A_1 (quartz)		Γ_1 (AlPO ₄)	
203		158	
399*		?	
764*		729	
1100*		1105	
Γ_3 (quartz)		Γ_3 (AlPO ₄)	
128	TO+LO	116	TO+LO
265	TO+LO	296	TO+LO
394-401	TO/LO	371-378	TO/LO
450-509	TO/LO	460-568	TO/LO
697	TO+LO	697	TO+LO
795-807	TO/LO	?	
1072	TO	1100	TO
1163	LO+TO	?	
1235	LO	1239	LO
A_3 (quartz)		Γ_3 (AlPO ₄)	
119	TO+LO	105	TO+LO
170	TO+LO	192	TO+LO
268	TO+LO	296	TO+LO
413*	TO+LO	417-436	TO/LO
483*	TO+LO	?	
546*	TO+LO	?	
723*	TO+LO	713	TO+LO
1125*	TO+LO	1125-1130	LO'/TO
1132*	TO+LO	1231	LO+TO

that a significant mixing of eigenvectors occurs between the Γ_3 modes in this energy range. Hence the intensity of a mode described as "A₃ like" may be larger than one listed in Table I as analogous to Γ_3 in quartz. In general, however, the frequency distribution, the TO/LO splittings, and the Raman intensities of Γ_3 and Γ_1 modes in AlPO₄ are in remarkably close agreement with those in quartz.

V. EFFECTIVE-CHARGE CALCULATION

The effective charges of Al, P, and O ions in the lattice can be determined from the measured LO and TO frequencies, through Eq. (1) below¹³:

$$4\pi^2 \sum_{j=1}^{17} (\omega_{\text{LO},j}^2 - \omega_{\text{TO},j}^2)_{\alpha} = \frac{4\pi}{V} \sum_{k=1}^{18} \frac{Z_k^2}{m_k}, \quad (1a)$$

where the j sum is over the 17 Γ_3 modes having polarization in direction α ; V is the unit-cell volume (231×10^{-24} cm³ in AlPO₄)¹⁴; Z_k is the effective charge of the k th ion, with mass m_k ; the k sum is over all 18 atoms in the AlPO₄ primitive cell. This expression follows directly from the equations derived by Cochran,^{13a} who shows that we may write

for the simple diatomic lattice

$$\mu \omega_{\text{TO}}^2 = R_0 - 4\pi Z^2/3V, \quad (1b)$$

$$\mu \omega_{\text{LO}}^2 = R_0 + 8\pi Z^2/3V, \quad (1c)$$

where R_0 is a short-range force and the Coulomb terms in Z^2 are the Lorentz field $\frac{4}{3}\pi P$ and Lorentz plus macroscopic field $\frac{4}{3}\pi P - 4\pi P$; μ is the reduced mass $M_1 M_2 / (M_1 + M_2)$. Subtracting (1c) from (1b) we obtain

$$\mu(\omega_{\text{LO}}^2 - \omega_{\text{TO}}^2) = (4\pi/V) Z^2, \quad (1d)$$

which may be rewritten in terms of M_1 , M_2 , and $Z_1 = -Z_2 = Z$ as

$$\sum_{j=1}^1 (\omega_{\text{LO},j}^2 - \omega_{\text{TO},j}^2) = \frac{4\pi}{V} \sum_{k=1}^2 \frac{Z_k^2}{m_k}, \quad (1e)$$

which is the form given in (1a). The general expression (1a) for the multimode case ($j > 1$) follows in a straightforward manner from the equations of motion written in matrix form, as is discussed in Ref. 13, pp. 387-388; note that the sum of the eigenvalues $\sum_j \omega_{\text{LO},j}^2$ or $\sum_j \omega_{\text{TO},j}^2$ is equal to the trace of the dynamical matrix, so that the form of (1e) is the same for single- or many-mode lattices.

For AlPO₄ there are two equations of the form given in (1a): one for modes of A_2 symmetry having polarization along the C axis ($\alpha = C$) and one for modes of E symmetry having polarization in the XY plane ($\alpha = a, b$). Therefore, there are two sets of Z_k for the ions; but in quartz or other crystals with small birefringence (i. e., little optical anisotropy) the difference is exceedingly small. We have therefore suppressed the subscript α on the right-hand side of (1a). Since A_2 modes are Raman inactive, we cannot experimentally assess the difference in AlPO₄.

A comment is in order concerning the rigid-ion charges. These charges are not the same as the "apparent" ionic charges,^{13b} nor the Szigeti charges, nor the nominal valence charges. A comparison of such charges is given by Cochran.^{13b}

The sum $\sum_j (\omega_{\text{LO},j}^2 - \omega_{\text{TO},j}^2)_{\alpha}$ is taken from frequencies listed in Table I. The unmeasured Γ_3 modes may safely be eliminated in computing the sum, since in each case they are anticipated to have negligibly small LO/TO splittings. The sum is numerically found to be 4.5×10^5 cm⁻² $\approx 40.5 \times 10^{25}$ sec⁻². We assume this sum to be accurate to about 5% in the numerical estimates which follow.

Equation (1) is then combined with the expression for lattice charge neutrality given in Eq. (2):

$$Z(\text{Al}) + Z(\text{P}) + 4Z(\text{O}) = 0. \quad (2)$$

This yields only two equations in three unknowns. To determine $Z(\text{Al})$ and $Z(\text{P})$ individually we infer that $Z(\text{O})$ has the same effective charge as in quartz. This inference can be made from the fact that Γ_3

LO/TO splittings in Table I are very nearly the same in AlPO_4 and quartz. Using Eqs. (1) and (2) we will first assume $Z(\text{Al}) = Z(\text{P})$ to estimate $Z(\text{O})$, and then use $Z(\text{O})$ to calculate $Z(\text{Al}) - Z(\text{P})$. With this $Z(\text{Al}) = Z(\text{P})$ assumption, we obtain

$$\frac{4\pi^2 \times 40.5 \times 10^{25} \times 1.66 \times 10^{-24} \times 231 \times 10^{-24}}{12\pi \times 23 \times 10^{-20}} = \frac{Z_A^2}{27} + \frac{Z_P^2}{31} + \frac{4Z_0^2}{16} \quad (3a)$$

or

$$Z_0 = 1.16e. \quad (3b)$$

This is almost exactly the same value $-1.15e$ obtained by Elcombe⁷ for α -quartz.

Now let us assume that $Z(\text{Al}) \neq Z(\text{P})$ but that the value $Z(\text{O}) = -1.15e$ found for quartz is unchanged in AlPO_4 . In this case, we find from Eqs. (1) and (2) that

$$Z(\text{P}) - Z(\text{Al}) \leq 0.2e,$$

i. e., if $Z(\text{O}) = -1.15e$, then (3a) becomes

$$0.38 = Z_A^2/27 + Z_P^2/31. \quad (4)$$

Equation (4) is satisfied to within ± 0.01 if $Z_A = Z_P$. If $Z(\text{P}) - Z(\text{Al})$ is increased to $0.2e$, then the right-hand side is too small by 0.02 . If the charge difference becomes larger, say 2.0 for $Z(\text{Al})$ and 2.6 for $Z(\text{P})$, then Eq. (5) fails by more than 12% . Hence, we believe $Z(\text{P}) - Z(\text{Al}) \leq 0.2e$ on the basis of an estimated error of 5% in the Coulomb sum $\sum(\omega_L^2 - \omega_T^2)$ for AlPO_4 .

We emphasize that this result would be exact, within the rigid-ion model approximation, if all Γ_3 -symmetry LO and TO frequencies had been determined. Since only 13 out of 17 Γ_3 have actually been determined in the present work, the values $Z(\text{Al})$ and $Z(\text{P})$ obtained should be regarded as only an estimate.

However, the assumption that the effective charges of oxygen ions in SiO_2 and AlPO_4 are the same, seems physically reasonable, and thus the Al and P ions of nominal valence $+3$ and $+5$ actually differ in effective charge by only $\approx 10\%$ of the nominal charge difference.

Γ_1 Mode Interaction

The seven Γ_1 modes measured in AlPO_4 all have frequencies which agree with those in quartz, to within 0.5 – 6% , except for the mode at 158 cm^{-1} , which lies 45 cm^{-1} (or 22% !) from the corresponding mode in α -quartz.

We propose that the explanation for this anomaly is that a very strong interaction between the Γ_1 branch at 216 and that at 158 cm^{-1} occurs.^{9,10} (Such interaction is not present in quartz since the 207 –

cm^{-1} mode is Γ_1 and the 203-cm^{-1} mode is A_1 .)

While some interaction is always present between branches of the same symmetry and near in frequency, the one in AlPO_4 seems quite strong.

It is known on the basis of Raman line-shape measurements that the Γ_1 branches at 216 and 158 cm^{-1} do indeed couple anharmonically^{9,10} through their mutual decay into the same two-acoustic-phonon state. The Γ_1 mode at 216 cm^{-1} at $\sim 300^\circ \text{K}$ is the "soft mode" in AlPO_4 , and it decreases with temperature as the α - β phase transition is approached from below, becoming coincident with the 158-cm^{-1} mode at $\sim 800^\circ \text{K}$.

What Fig. 1 indicates is that this interaction between the two Γ_1 branches will exhibit the same dependence upon wave vector as on temperature. As q is increased along $[00\xi]$ the frequency of the 158-cm^{-1} Γ_1 mode will *increase* until it becomes coincident with the 216-cm^{-1} soft mode. The inelastic-neutron-scattering spectrum of AlPO_4 along $[00\xi]$ at 300°K should therefore exhibit striking interference effects at $\sim q = (\pi/c)$ ($0, 0, 0.2$) or so. Unfortunately, AlPO_4 samples of size suitable for neutron study do not presently exist. Inasmuch as AlPO_4 is grown in the same way as synthetic quartz, however, it seems possible that samples several centimeters on a side could be procured in the future.

We note that other isomorphous structures such as AlAsO_4 are also available in single crystals of size adequate for Raman studies. Such piezoelectric arsenates are good candidates for nonlinear optical experiments, in view of their characteristically high index of refraction.

VI. SUMMARY

The Raman spectra of α - AlPO_4 have been obtained and interpreted in terms of an extended Brillouin-zone scheme, using Elcombe's inelastic neutron data and lattice-dynamical models of quartz. All modes observed, except one, agree in symmetry and frequency with those at the zone center and $(0, 0, \pi/c)$ zone boundary in quartz. The one anomalous mode manifests evidence of anharmonic interaction which is correlated with Raman line shapes and which suggests new inelastic-neutron-scattering experiments. IR modes at ~ 52 and 195 cm^{-1} are predicted in AlPO_4 , in addition to those at frequencies found in quartz; the effective charges of Al and P ions are found to differ by only $\sim 0.2e$, compared to the nominal value $2.0e$, demonstrating extreme charge compensation.

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¹⁰A. Zawadowski and J. Ruvalds, *Phys. Rev. Letters*

24, 1111 (1970). Although this paper shows that the interaction between the modes at 158 and 216 cm^{-1} is anharmonic, the mere existence of a discrepancy of frequency for the 158- cm^{-1} mode in AlPO_4 (203 cm^{-1} in SiO_2) does not; such level repulsions more commonly arise from harmonic interaction. In the present case the line shape is the evidence that the interaction is strongly anharmonic.

¹¹Zone-center frequencies for the Raman-active modes in quartz are taken from J. F. Scott and S. P. S. Porto, *Phys. Rev.* 161, 903 (1967).

¹²D. A. Kleinman and W. G. Spitzer, *Phys. Rev.* 125, 16 (1962).

¹³(a) W. Cochran, *Advan. Phys.* 9, 387 (1960), especially Eqs. (1.12) and (1.13) and the related discussion; (b) W. Cochran, *Nature* 191, 60 (1961).

¹⁴Calculated as $a^2c \cos 30^\circ$ using a and c from Ref. 1, this value is approximately 2.7% larger than twice the quartz cell volume given by R. A. Young and B. Post [*Acta Cryst.* 15, 337 (1962)].