

Phonon spectra of quartz isomorphs*

W. Dultz,[†] M. Quilichini,[‡] and J. F. Scott

Department of Physics and Astrophysics, University of Colorado, Boulder, Colorado 80302

G. Lehmann

Institut für Physikalische Chemie, Westfälische Wilhelms Universität, Münster, Germany

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Inelastic light scattering has been used to probe the phonon behavior in AlAsO_4 , GaAsO_4 , GaPO_4 , and BPO_4 . The results are compared with earlier studies of isomorphous AlPO_4 , SiO_2 , and GeO_2 . A previous ambiguity regarding symmetry assignments for phonons in GeO_2 is resolved. Linewidths and frequencies are measured up to 1300 °K.

I. INTRODUCTION

Raman spectroscopy has been employed successfully in the past for analyses of the long-wavelength phonons in quartz structures, including SiO_2 , GeO_2 , and AlPO_4 .¹⁻³ These experiments have given rise to several recent lattice-dynamical calculations for quartz structures.^{4,5} Such experiments and theoretical modeling are especially important in the case of GeO_2 , since they form the basis of our understanding of bonding in a large class of tetrahedrally coordinated GeO_4 germanates. Also of special interest has been the presence of nearly-second-order phase transitions from trigonal to hexagonal modifications in SiO_2 ,⁶ AlPO_4 ,⁷ and GeO_2 .⁸ The lattice dynamics of these α - β phase transitions are known from the inelastic-neutron-scattering studies of Axe and Shirane.⁹

The present study was undertaken to compare phonon spectra in several quartz isomorphs. (Although BPO_4 is nonisomorphous, it has been included as closely related.) It was hoped that such a study would resolve an ambiguous symmetry assignment for two phonon modes⁴ in GeO_2 , and that anharmonic effects observed at elevated temperatures in SiO_2 and AlPO_4 , such as anomalous phonon broadening and renormalization,¹⁰ and harmonic¹¹ and anharmonic¹² mode coupling, might be manifest in the other isomorphs.

II. EXPERIMENTAL

Data on small single crystals were obtained from 293 to 1283 °K. The samples were prepared via hydrothermal growth. Details are given in Ref. 13. The samples were placed in a tubular alumina furnace and illuminated with approximately 400 mW of argon-laser light at 5145 or 4880 Å, or about 200 mW of krypton-laser light at 5682 Å. Detection was via a 0.85-m double spectrometer, cooled phototube, and ratemeter. Because the samples were small and irregular in shape (typically 1 mm on a side), they were not oriented, cut, and polished. This would have re-

duced their volumes below usable size. Consequently, as-grown faces were used as laser entrance and exit surfaces. Except for GaAsO_4 this precluded phonon polarization measurements.

III. DISCUSSION

Table I summarizes frequencies observed for totally symmetric vibrations. Note that there are only four modes of this symmetry at $q=0$ in SiO_2 and GeO_2 , but eight in the isomorphous AlPO_4 , GaPO_4 , AlAsO_4 , and GaAsO_4 . (Spectra of AlAsO_4 are shown in Fig. 1.) In the latter crystals alternate Si (or Ge) ions are replaced by column-III or column-V ions; these lattices are perfectly ordered, and hence their primitive unit cells are twice as

TABLE I. Frequencies of Γ_1 -symmetry phonons in quartz and quartz isomorphs (cm^{-1}).^a

SiO_2	AlPO_4	AlAsO_4	GaPO_4	GeO_2	GaAsO_4
207	216	226	295	261 ^b	265
356	336	347	430	326	330
464	456	420	459	440	430
1085	1112	985	1070	880	888
(203)	158	136	145	(...)	...
(399*)	(...)	...
(764*)	729	(...)	...
(1100*)	1105	1000	1050	(...)	942 ^c

^aFrequencies in parentheses are zone-boundary values (Ref. 5). An asterisk denotes a frequency calculated from a lattice-dynamical model (Elcombe, Ref. 5) but not measured experimentally.

^bIt is interesting to note that weak ir features in GeO_2 are reported in Ref. 4 at about 261 and 326 cm^{-1} . We assign these modes as ir-inactive Γ_1 symmetry. Their weak ir activity in polycrystalline GeO_2 could be due to lattice vacancies or defects in the samples used in Ref. 4.

^cNote that the intensity of the 942- cm^{-1} mode is greater than that of the "allowed" mode at 888 cm^{-1} . This suggests a strong admixing of eigenfunctions for the two modes and shows the limitations of our "pseudo-zone-center" model.

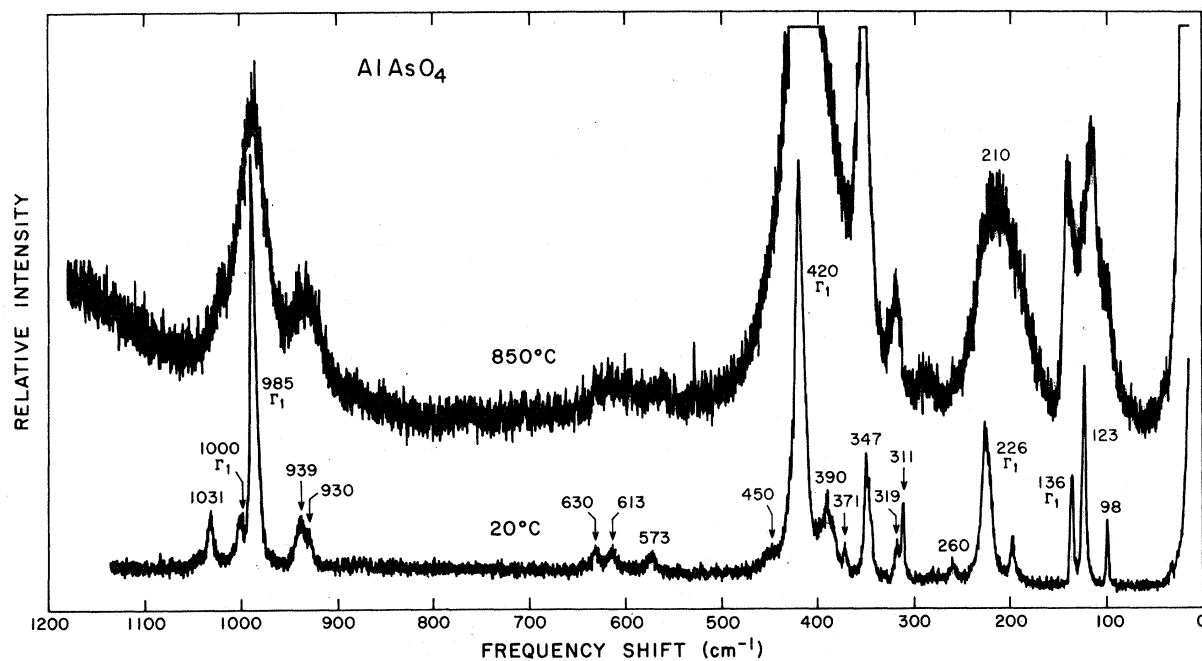


FIG. 1. Raman spectra of AlAsO_4 at various temperatures. Unoriented sample. 400 mW of 5145-Å excitation.

long in the c direction as are those of SiO_2 or GeO_2 . The Brillouin zones are consequently half as long in the c direction, and modes which would be described as zone-boundary and Raman-forbidden in quartz or GeO_2 are at $q=0$ and Raman-

allowed in the other isomorphs. This is discussed in some detail in Ref. 3. It is found empirically for all of the ternary ABO_4 compounds studied that the intensities of the modes which would be described as lying at the zone boundary in SiO_2 are

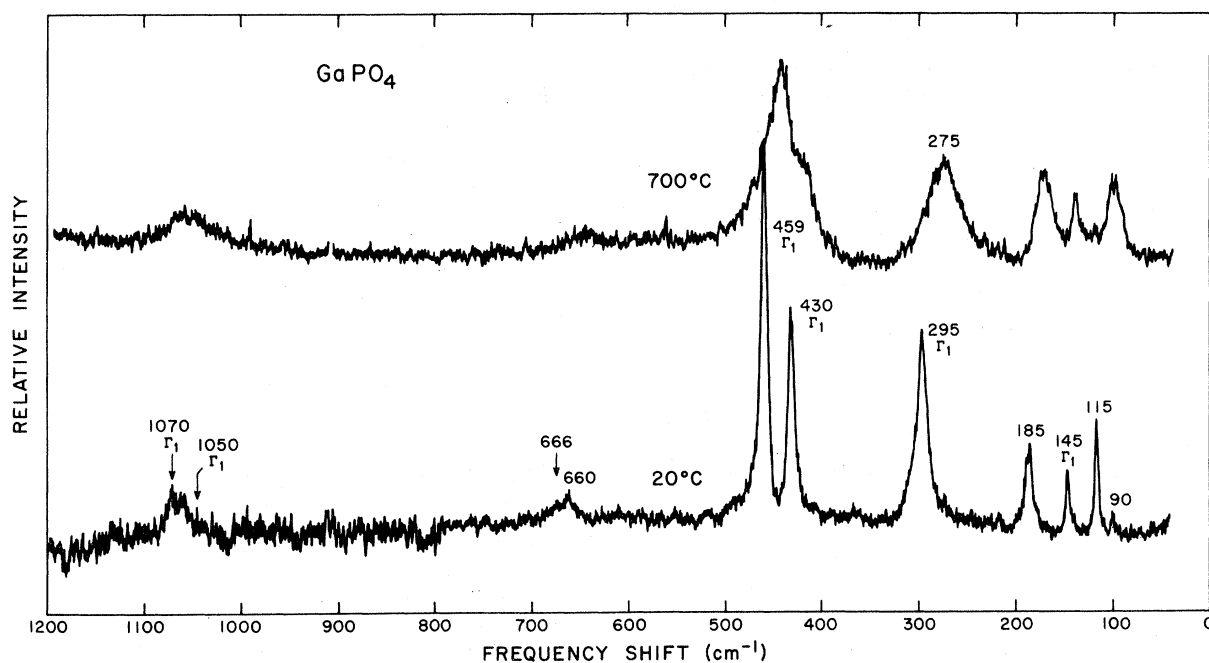


FIG. 2. Raman spectra of GaPO_4 at various temperatures. 200 mW of 5682-Å excitation.

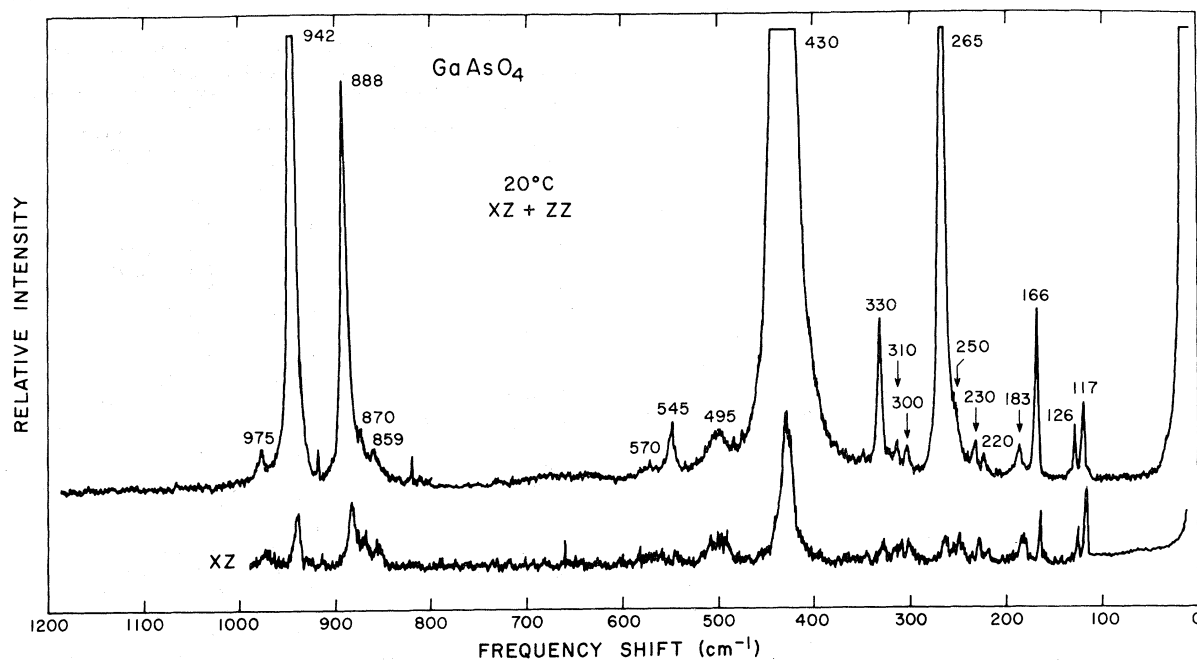


FIG. 3. Raman spectra of GaAsO_4 . Oriented sample. 200 mW of $5682\text{-}\text{\AA}$ excitation. The upper trace is $xz + zz$ polarizability-tensor components and illustrates Γ_1 plus Γ_3 modes. The lower trace is xz polarizability-tensor component only and illustrates Γ_3 modes; the Γ_1 modes are present due to crystal imperfections and imperfect orientation, but their intensities are very greatly reduced, making symmetry assignment unambiguous.

much weaker than the intensities of modes corresponding to $q=0$ modes in quartz. This may be understood in a qualitative way as follows: In an ABO_4 structure such as AlPO_4 , the fact that there are eight Raman-active totally symmetric modes (and not four, as in quartz) is due to the fact that Al and P ions are not equivalent. But in what way are they not equivalent? They have almost the same mass, and it is known³ from Coulombic splittings for the vibrations in AlPO_4 that the effective charges for Al and P in this lattice are nearly identical—i. e., nominally +4, instead of +3 and +5. Thus, four of the eight totally symmetric vibrations in AlPO_4 should have very small Raman intensities, since the fact that these intensities are nonzero depends upon the chemical difference between Al and P, which is small. This same line of argument has been used in an entirely different context by Shay,¹⁴ who has discussed the weak intensities of certain direct-gap transitions in ternary I-III-VI₂ semiconductors having doubled unit cells; in the simpler diatomic II-VI semiconductor these transitions would be indirect, and very weak; their intensities thus depend upon the chemical difference between the A and B ions. Shay refers to these electronic transitions as "pseudodirect." This concept is valid and equally applicable to phonon spectra; the analogous termi-

nology for the weak modes in our ABO_4 compounds would be "pseudo-zone-center," or "quasi-Raman-allowed."

Spectra of GaPO_4 are shown in Fig. 2. The compound of greatest importance in the present study is GaAsO_4 . Its spectra are shown in Fig. 3. It has exactly the same atomic weight as does GeO_2 , since Ga and As straddle Ge in the Periodic Table. Thus it behaves like GeO_2 with a doubled unit cell and no mass change. As can be seen from Tables I and II, its phonon frequencies are nearly identical with those in GeO_2 . This has greatly helped to resolve the symmetry assignments for several of the phonons. In earlier work² an extremely small unoriented single crystal of GeO_2 was employed which did not permit complete polarizability measurements. In the present study an oriented single crystal was employed, so that symmetry assignments are unambiguous. It is found that the mode at 212 cm^{-1} in GeO_2 is of Γ_3 symmetry, and that at 326 cm^{-1} is of Γ_1 symmetry; the opposite assignment was originally made. The equivalent of the 212-cm^{-1} mode is a resolvable TO/LO doublet in GaAsO_4 at $220/230\text{ cm}^{-1}$, which makes its assignment absolutely certain. These assignments do not agree with those of Ref. 4. In GeO_2 a weak shoulder at about 456 cm^{-1} was originally assigned² as an $E(\text{LO})$ mode; it is apparent

TABLE II. Frequencies of Γ_3 -symmetry phonons in quartz and quartz isomorphs (cm^{-1}).^a

	SiO ₂	AlPO ₄	AlAsO ₄	GaPO ₄	GeO ₂	GaAsO ₄
TO	128	116	123	115	121	126
LO	128	116	123	115	121	126
TO	265	...	260	...	165	166
LO	265	...	260	...	165	166
TO	394	371	371	...	212	220
LO	401	378	390	...	212	230
TO	450	460	450	...	372	300
LO	509	568	573	...	385	310
TO	697	697	613	660	492	495
LO	697	697	630	666	512	545
TO	795	583	570
LO	807	595	...
TO	1072	1100	857	859
LO	1163	...	930	...	949	...
TO	1163	...	939	...	961	...
LO	1235	1239	1031	...	972	975
TO+LO ^b	(119)	105	98	90	(...)	117
TO+LO	(170)	192	198	185	(...)	183
TO+LO	(268)	296	311-319	...	(...)	250
TO+LO	(413*)	417-436	(...)	...
TO+LO	(483*)	(...)	...
TO+LO	(546*)	(...)	...
TO+LO	(723*)	713	(...)	...
TO+LO	(1125*)	1125-1130	(...)	870
TO+LO	(1132*)	1231	(...)	...

^aFrequencies in parentheses are zone-boundary values (Ref. 5). An asterisk denotes a frequency calculated from a lattice-dynamical model (Elcombe, Ref. 5) but not measured experimentally.

^bModes which would be described as at the zone boundary in quartz should have very small TO/LO splittings in the ternaries, since the presence of any splitting depends on the nonequivalence of *A* and *B* ions.

from the present work that this feature is not one of the fundamental modes of vibration, but may be due to impurities or second-order scattering. The assignments in Table II allow us to calculate the low-frequency dielectric constant of GeO₂ for po-

TABLE III. Phonon frequencies in BPO₄ and in α -cristobalite (cm^{-1}) for Raman-active modes.

BPO ₄ Experiment (symmetries uncertain)	Theory ^a	SiO ₂ Experiment ^b
...	79 B ₁	...
...	94 B ₁	...
...	128 E	121 E
230 A ₁	229 A ₁	233 A ₁
...	276 E	286 E(TO+LO)
...	296 B ₂	275 B ₁ or B ₂
...	365 B ₁	368 B ₁
...	370 E	380 E(TO)
450 A ₁	381 A ₁	...
...	416 B ₂	...
475 A ₁	416 A ₁	426 A ₁
534-595 E(TO)+E(LO)?	494 E	485 E(LO+TO)
612-650 E(TO)+E(LO)?
832?	628 E	...
920?
970?	755 E	785-796 E(LO)+E(TO)
1116 A ₁	759 B ₂	...
1048 E?	762 B ₁	...
1066 B ₁ ?	1081 A ₁	1076 A ₁
1262 E(LO)?	1087 E	1086 E(LO+TO)
...	1092 B ₁	...
...	1142 E	1188 E(LO)?
...	1195 B ₂	...

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larization in the *xy* plane: we find $\epsilon_0^{\perp} = 4.12$. This value, previously unknown, compares with 4.32 in quartz.¹⁵

We should point out that BPO₄ does not have the α -quartz structure. It has the D_4^1 α -cristobalite structure¹⁶ at ambient temperatures. Its spectra are listed in Table III and shown in Fig. 4.

IV. HIGH-TEMPERATURE EFFECTS

We have obtained the spectra of all of the ABO₄ ternaries at high temperatures, typically up to be-

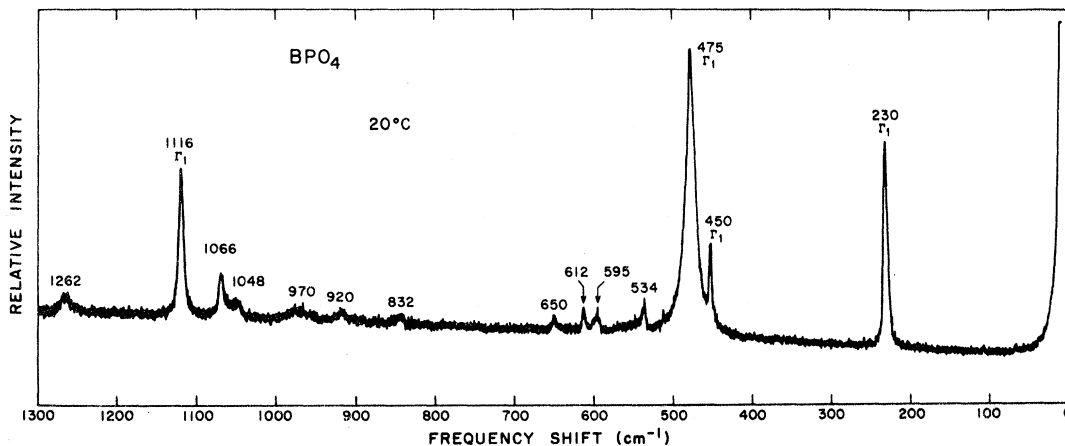


FIG. 4. Raman spectra of BPO₄ at ambient temperatures. 400 mW of 5145-Å excitation. Although this sample was unoriented, the observed spectral lines are predominantly Γ_1 symmetry vibrations.

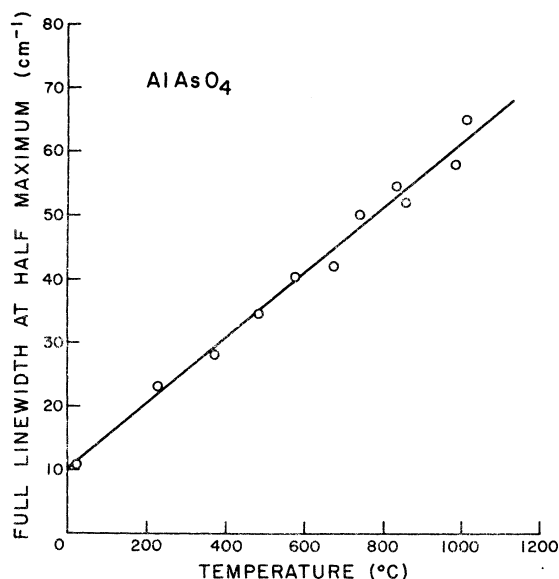


FIG. 5. Linewidth (full width at half-maximum) vs temperature for the "soft mode" in AlAsO_4 .

tween 1200 and 1300 °K. In each case it is found that the lowest-lying totally symmetric mode broadens anomalously and decreases in energy with increasing temperature. However, with the exceptions of SiO_2 and AlPO_4 , these decreases in energy do not exceed 15%, and no phase transition

from trigonal to hexagonal structure is observed. The largest increase in linewidth is exhibited by AlAsO_4 , whose low-energy Γ_1 mode broadens to 70 cm^{-1} (full width at half-maximum) at 1283 °K, as shown in Fig. 5. This crystal, and to a lesser extent the other ternaries, may be viewed as having an *incipient soft mode*.¹⁷ It seems likely that solid solutions of the form $\text{AlP}_x\text{As}_{1-x}\text{O}_4$ would exhibit transitions for $x \approx 1$ to hexagonal phases at temperatures near those in pure AlPO_4 (about 850 °K).

An attempt was made to observe coupling between one-phonon states and between one- and two-phonon states like those manifest in AlPO_4 and SiO_2 .^{11,12} However, at the higher temperatures required to produce significant mode softening in the new materials, such effects could not be distinguished clearly.

As in the case of quartz, where the lowest-energy Γ_3 mode renormalizes from 128 to 98 cm^{-1} as the β phase is approached, the low-energy Γ_3 modes decrease about 25% as temperature is increased from 293 to 1200 °K; this softening is not directly related to a phase transition, however.

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[†]Permanent address: Fachbereich Physik, Universität Regensburg, Regensburg, BRD; work at The University of Colorado supported by a grant from the Deutsche Forschungsgemeinschaft.

[‡]Permanent address: Université Paris VI, Paris, France.

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¹⁵ ϵ_0 is calculated as $\epsilon_\infty \prod_{j=1}^3 (\omega_{LO}^2 / \omega_{TO}^2)^2$, where ϵ_∞ is the square of the index of refraction and j sums over modes of Γ_3 symmetry. See W. Cochran and R. A. Cowley, *J. Phys. Chem. Solids* **23**, 447 (1962); T. Kurosawa, *J. Phys. Soc. Jpn.* **16**, 1298 (1961).

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¹⁷Such incipient soft modes are well known in KTaO_3 ,

SrTiO₃, and TiO₂, where absolute zero is reached (in principle) before the vibrational frequency decreases all the way to zero, and in BaZnF₄ and other BaM²⁺F₄ ferroelectrics, where the melting point is reached

slightly before the ferroelectric soft mode reaches zero. See M. Quilichini, J. F. Ryan, J. F. Scott, and H. J. Guggenheim, *Solid State Commun.* (to be published).