together. Therefore, it may not be necessary to include the effects of multiple scattering when making a calculation.

In principle, the surface-induced infrared absorption by acoustical modes will have infinities at frequencies where the appropriate one-dimensional dispersion curves have zero slope. A computer calculation using a simple surface model showed no peaks at these critical points, nor were there any peaks that might suggest a resonance phenomenon in the acoustical-mode region.

Small rectangular solids of NaCl showed strong absorption at acoustical-mode frequencies. The surface-induced absorption had no structure, was insensitive to the particle size, and was independent of temperature. Therefore, we have not observed either surface-induced absorption by acoustical modes or an anharmonic broadening of the fundamental absorption. The effect is probably due to polariton scattering.

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Raman Spectra of GeO_2

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Raman spectra of small single crystals of both the trigonal and tetragonal forms of germanium dioxide have been obtained. Frequencies and symmetries of the Raman-active optical phonons are given, and comparison is made with isomorphic α quartz and rutile. The temperature dependences of the spectra have been examined over the range 6–1100°K. The static dielectric constant and infrared reflectivity of the trigonal form have been calculated from the Raman data.

INTRODUCTION

GERMANIUM dioxide occurs in three stable forms at ambient temperatures.[1] The first form has the cassiterite (or rutile) tetragonal D_{4h}^{14} structure ($P4/mnm$) with octahedral coordination.[2] The second form has the trigonal D_3^4 (32) structure of α quartz,[3] with tetrahedral coordination. The third form is glassy, having the same short-range order of GeO_4 tetrahedra as the trigonal form, but lacking any long-range correlation.[4] The tetragonal and trigonal crystalline forms differ substantially in their chemical properties, especially solubility, in their densities and indices of refraction. The glassy form resembles the trigonal in all these respects.

While a substantial amount of study of the optical properties of glassy GeO_2 has been made in the past,[5] very little has been known about the crystalline varieties, since single crystals do not occur naturally. The recent growth of small single crystals of both trigonal and tetragonal forms of GeO_2 has made the present Raman investigation possible. The motivation for the present study is several fold. Both crystalline varieties of GeO_2 have interesting device possibilities. The rutile form is hard, colorless, and transparent; it is highly inert and of consequent interest as an encapsulating material[6] for germanium semiconductors. The quartz form is interesting from a device standpoint for all the reasons quartz is interesting: It is a hard, transparent, colorless piezoelectric with an index of refraction greater than that of quartz and a large enough birefringence (four times that of quartz) to make phase-matched nonlinear optical experiments possible. Both forms of GeO_2 have theoretical interest also: the rutile lattice has been the subject of several dynamical calculations recently[7]; quartz exhibits a well-studied phase transition[8] and a unique hybrid-phonon excitation,[9] as well as two modes (one infrared-active) with enough gain to produce stimulated Raman scattering,[10] and it is of special interest to see which of the preceding attributes are also

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[1] J. H. Muller and H. R. Blank, J. Am. Chem. Soc. **46**, 2338 (1924).

[2] X-ray studies first reported by A. W. Laubengauer and D. S. Morton, J. Am. Chem. Soc. **54**, 2303 (1932).

[3] W. H. Zachariasen, Z. Krist. **67**, 226 (1928).

[4] See, for example, T. G. Kujumzelis, Z. Phys. **100**, 221 (1935).

[5] V. V. Obukhov-Denisov, N. N. Sobolev, and V. P. Cheremisinov, Izv. Akad. Nauk SSSR **22**, 1083 (1958) [English transl.: Bull. Acad. Sci. USSR **22**, 1073 (1958)]; P. Flubacher, A. J. Leadbetter, J. A. Morrison, and B. P. Stoicheff, J. Phys. Chem. Solids **12**, 53 (1959). References to earlier work are given in the latter. V. P. Cheremisinov, Proc. (Trudy) Lebedev Inst. **25**, 127 (1965). The most complete optical study of GeO_2 is given here. See also E. R. Lippincott, J. Res. Natl. Bur. Std. **61**, 61 (1958), for a conflicting IR spectrum.

[6] See, for example, J. F. O'Hanlon, Appl. Phys. Letters **14**, 127 (1969).

[7] See, for example, F. Matossi, J. Chem. Phys. **19**, 1543 (1951).

[8] References to recent work are given in S. M. Shapiro, D. C. O'Shea, and H. Z. Cummins, Phys. Rev. Letters **19**, 361 (1967) and in Ref. 9.

[9] J. F. Scott, Phys. Rev. Letters **21**, 907 (1968).

[10] P. E. Tannerwald and D. L. Weinberg, J. Quant. Electron. **3**, 334 (1967); J. F. Scott, *ibid.* **3**, 693 (1967).

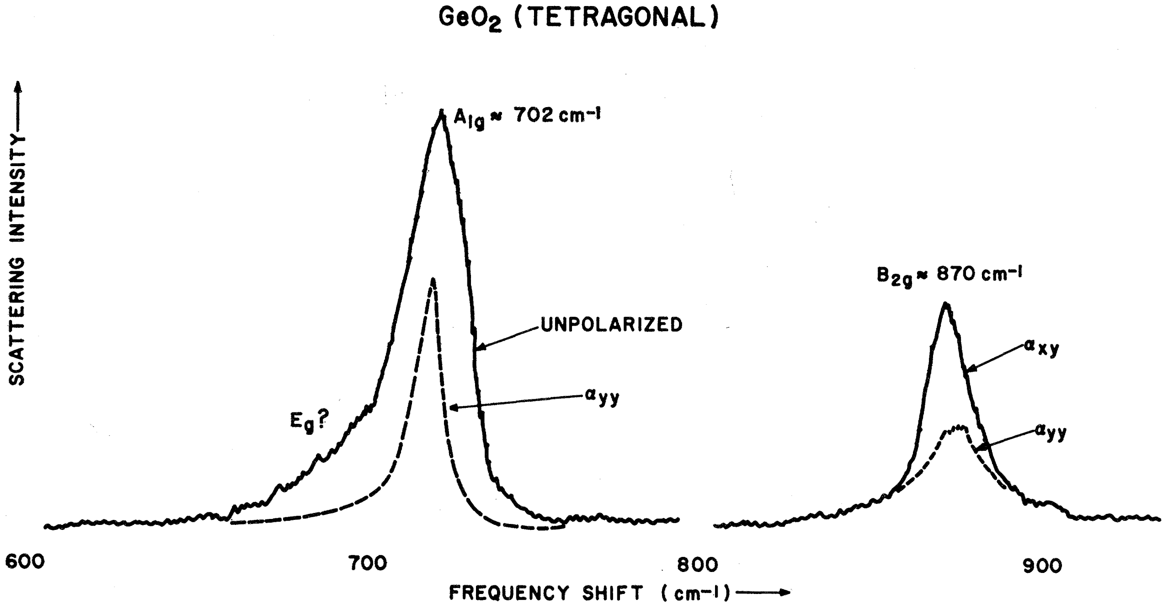

FIG. 1. High-frequency spectrum of tetragonal GeO_2, illustrating B_{2g}, A_{1g}, and E_g modes.

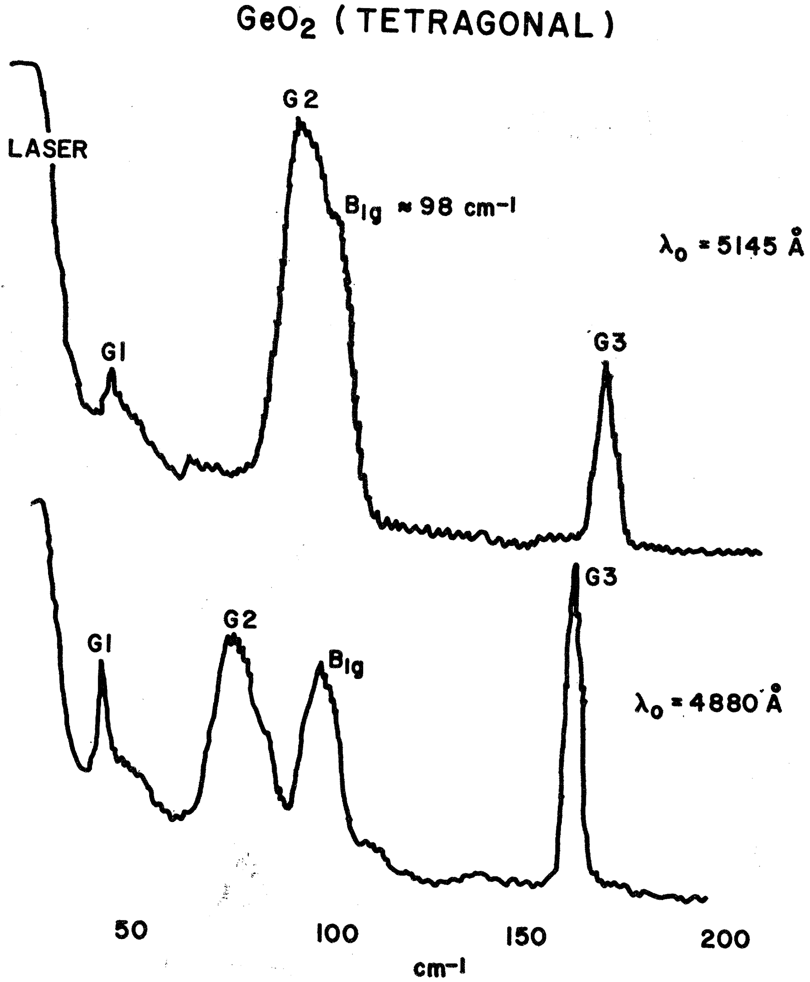

FIG. 2. Low-frequency spectrum of tetragonal GeO_2, illustrating B_{1g} mode.

TABLE I. Phonon frequencies at Γ (cm^{-1}).

	TiO$_2$[a]	GeO$_2$ (tetragonal)
B_{1g}	143	97
E_g	447	~680
A_{1g}	612	702
B_{2g}	826	870

[a] See Ref. 13.

to be found in GeO$_2$. Lastly, the geophysical interest in these materials should be mentioned: tetragonal GeO$_2$ is chemically the closest known kin of isomorphic Stishovite, a form of silicon dioxide thought to form much of the earth's mantle, and about which little is known, although it has been synthesized in the Soviet Union.

EXPERIMENTAL

The rutile form GeO$_2$ samples were grown by Donald Swets of General Motors Research Laboratories, Warren, Michigan, and obtained through the courtesy of Dr. W. A. Albers, Jr. They were thin rods, measuring approximately 1×0.2×0.1 mm with developed (110) faces. Raman data were collected from a clear, colorless sample and are shown in Figs. 1 and 2. The sample received no polishing or other treatment prior to the recording of the Raman data.

The trigonal GeO$_2$ samples were grown by Cable Finch of Oak Ridge National Laboratory and were kindly provided by Dr. Robert A. Weeks. They were also clear and colorless, but of irregular shape with typical dimension $\lesssim 1$ mm. The size and shape of these samples precluded the cutting and polishing operations normally employed to obtain polarized spectra. Consequently, data were obtained from a [112] rod mounted on a goniometer head so that the beam polarization was along [001]. It was found that the spectra are markedly similar to those of α quartz, which has been analyzed in great detail,[11] and assignment has been made with that as a guide, as discussed further in this paper.

Data were recorded from 6–1100°K using a conventional helium Dewar and alumina furnace. Excitation and detection were by means of a 1-W argon ion laser operating at 4880 Å, a Spex 1400 double monochromator, a cooled EMI 6256 phototube, and a Keithley 610B electrometer.

ANALYSIS

Tetragonal GeO$_2$ has two formula groups per primitive cell. The resulting fifteen vibrational degrees of freedom occur[12] as eleven optical modes of symmetries $A_{1g}+A_{2g}+B_{1g}+B_{2g}+A_{2u}+2B_{1u}+E_g+3E_u$. Of these, $A_{1g}+B_{1g}+B_{2g}+E_g$ are Raman-active. The symmetry assignments were made by means of polarization measurements and are listed in Table I. Figure 1 illustrates the high-frequency portion of the spectrum. While surface scattering from small samples always precludes complete polarization discrimination, it can easily be seen that the mode at 870 cm^{-1} is essentially an α_{xy}-scatterer, and hence of B_{2g} symmetry. The strong mode at 702 cm^{-1} is the A_{1g} vibration and exhibits $\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$ scattering. When this line is recorded without an analyzing polarizer, it manifests an asymmetry caused by a shoulder on the low-frequency side. We assign the shoulder as the E_g mode, which should exhibit $\alpha_{xz}+\alpha_{yz}$ scattering, on the basis of high-temperature data. These data show no change in the degree of asymmetry of the feature at ~700 cm^{-1} as a function of temperature, demonstrating that the shoulder cannot be due to second-order scattering. The remaining feature exhibits only trace scattering and is shown in Fig. 2. This B_{1g} mode is assigned from among the grating ghosts by changing the excitation frequency; it remains at a frequency shift of 97 cm^{-1}, while the ghosts are at shifts proportional to the excitation frequency. Grating ghosts are a problem here only because of the surface scattering from the tiny sample *and* because the B_{1g} scattering is α_{xx} and is not depolarized.

From Table I we can see that GeO$_2$ closely resembles rutile in regard to the frequencies of its Raman-allowed modes.[13] A striking difference is to be noted, however: Second-order Raman scattering in rutile[13] is even more intense than one-phonon scattering, while in GeO$_2$ no

TABLE II. Phonon frequencies at Γ (cm^{-1}).

Osc. strength	GeO$_2$ (trigonal)		α-quartz[a]		Osc. strength
0.01	121	E(TO+LO)	128	E(TO+LO)	0.001
0.01	166	E(TO+LO)	265	E(TO+LO)	0.05
	212	A_1	207	A_1	
	261	A_1	356	A_1	
3.32	326	E(TO)	450	E(TO)	0.82
	372	E(LO)	401	E(LO)	
0.47	385	E(TO)	394	E(TO)	0.33
	440	A_1	464	A_1	
	~456	E(LO)	509	E(LO)	
0.10	492	E(TO)	697	E(TO)	0.02
	512	E(LO)	697	E(LO)	
0.08	583	E(TO)	795	E(TO)	0.11
	595	E(LO)	807	E(LO)	
0.57	857	E(TO)	1072	E(TO)	0.67
	880	A_1	1085	A_1	
	949	E(LO)	1163	E(LO)	
0.01	961	E(TO)	1163	E(TO)	0.01
	972	E(LO)	1235	E(LO)	
	GeO$_2$: $\epsilon_0^\perp=7.44$		SiO$_2$: $\epsilon_0^\perp=4.32$		

[a] Reference 11.

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[11] J. F. Scott and S. P. S. Porto, Phys. Rev. **161**, 903 (1967); J. F. Scott, L. E. Cheesman, and S. P. S. Porto, *ibid.* **162**, 834 (1967); J. F. Scott and S. Ushioda, in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer Verlag, New York, 1969), p. 57.

[12] P. S. Narayanan, Proc. Indian Acad. Sci. **32A**, 279 (1950).

[13] TiO$_2$ assignments in Table I are taken from S. P. S. Porto, P. A. Fleury, and T. C. Damen, Phys. Rev. **154**, 522 (1967).

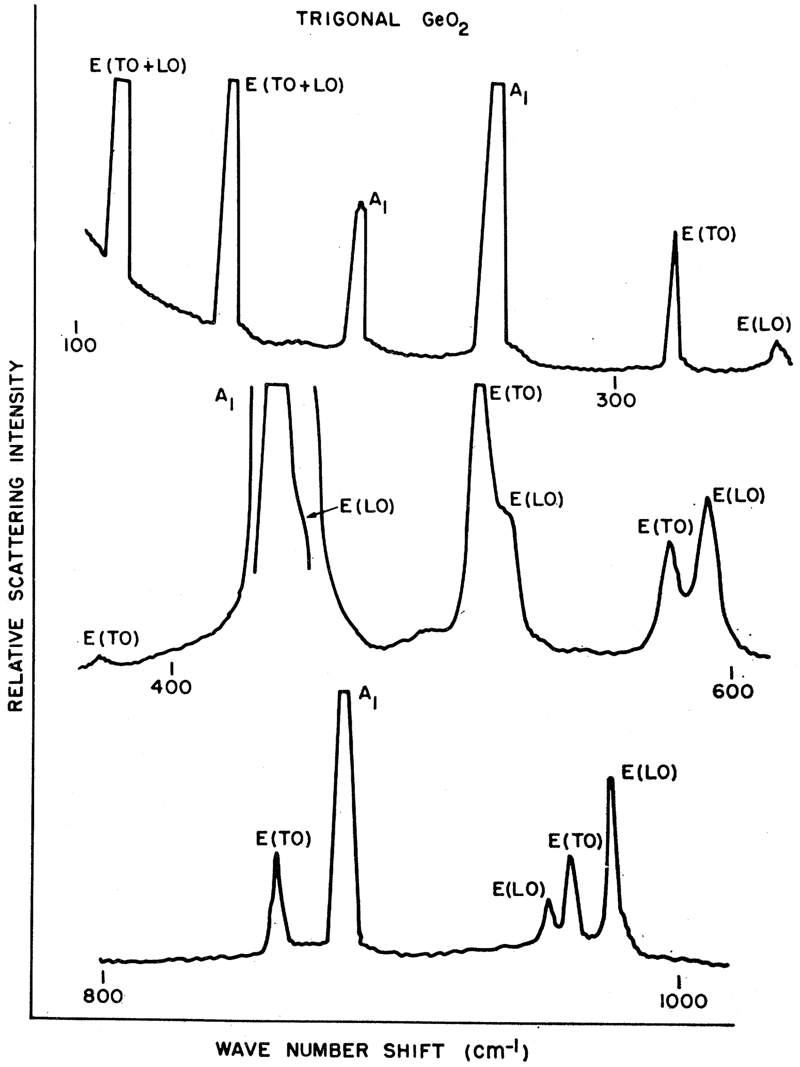

FIG. 3. Spectrum of trigonal GeO_2, illustrating the A_1, E(TO), and E(LO) modes. Note that the 880-cm^{-1} A_1 line is quite intense, unlike the corresponding line in quartz. The intensity of this line was discussed theoretically by D. A. Kleinman and W. G. Spitzer [Phys. Rev. **125**, 16 (1962)].

two-phonon scattering is observed. This is presumably due to the large anharmonicities present in TiO_6 bonding; in other octahedrally coordinated titanates, such as $SrTiO_3$ and $BaTiO_3$, the second-order Raman effect is very intense.[14] The d-electron bonding is certainly the most likely cause of this anharmonicity, as evidenced by the striking comparison with p-electron bonding in tetragonal GeO_2. (Hence, we would expect little anharmonicity in Stishovite.)

Since no Raman spectrum for tetragonal GeO_2 has previously been reported, no comparisons can be made. Cheremisinov[5] reported an unsuccessful attempt to obtain spectra from a polycrystalline sample. He attributed his lack of success to "very weak scattering evidencing considerable bond ionicity" in the compound. This is incorrect, of course. We obtained very intense scattering from a small crystal of tetragonal GeO_2 and attribute Cheremisinov's earlier difficulty to polycrystalline domain scattering.

Several force-constant models have been studied for the rutile lattice.[7] Since polarized infrared studies have not yet been made on GeO_2, these cannot be applied here in detail. One check is afforded by the Raman data alone, however, using Matossi's model. The frequency of the "silent" A_{2g} mode is given both by the equation

$$\omega(A_{2g}) = [\omega^2(B_{1g}) + \omega^2(B_{2g}) - \omega^2(A_{1g})]^{1/2}$$

and by

$$\omega(A_{2g}) = 4.8\omega(B_{1g}),$$

where 4.8 is a geometrical factor derived from ion positions in the lattice. For GeO_2, the A_{2g} frequency obtained from these two equations is 466 and 522 cm^{-1}. This ~10% disagreement is somewhat greater than that obtained for rutile, but less than that in the isomorphic fluorides.[13] Matossi's model seems to de-

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[14] See, for example, W. G. Nilsen and J. G. Skinner, J. Chem. Phys. **48**, 2240 (1968).

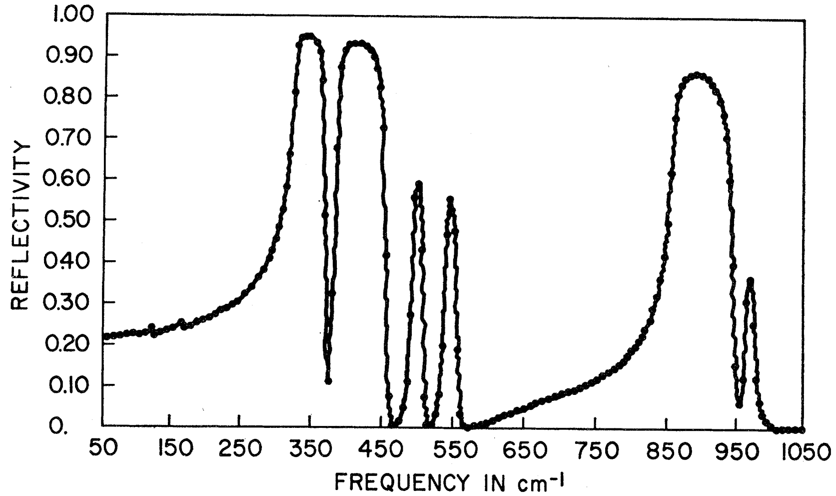

FIG. 4. Calculated infrared reflectivity spectrum for trigonal GeO_2 for $\mathcal{E}\perp c$. The oscillator strengths calculated for the eight E(TO) modes are, in order of ascending frequency: 0.01, 0.01, 3.32, 0.47, 0.10, 0.08, 0.57, and 0.01. These oscillator strengths yield a value of the static dielectric constant $\epsilon_0{}^{\perp}=7.44$ which is compatible with the generalized Lyddane-Sachs-Teller relation

$$\frac{\epsilon_0{}^{\perp}}{\epsilon_\infty{}^{\perp}}=\prod_{i=1}^{8}\left(\frac{\omega_{i,\,\mathrm{LO}}}{\omega_{i,\,\mathrm{TO}}}\right)^2.$$

The reflectivity is

$$R(\omega)=\frac{[n(\omega)-1]^2+K(\omega)^2}{[n(\omega)+1]^2+K^2(\omega)},$$

where $n(\omega)$ and $K(\omega)$ are given by

$$n(\omega)K(\omega)=\tfrac{1}{2}\sum_j S_j\omega_j{}^2\frac{\gamma_j\omega_j\omega}{(\omega_j{}^2-\omega^2)^2+\gamma_j{}^2\omega_j{}^2\omega^2},$$

$$n^2(\omega)-K^2(\omega)=(1.695)^2+\sum_j S_j\omega^2{}_j\frac{(\omega_j{}^2-\omega^2)}{(\omega_j{}^2-\omega^2)^2+\gamma_j{}^2\omega_j{}^2\omega^2},$$

with s_j, ω_j, and γ_j known from Raman measurements.

scribe the odd-parity modes less well in rutile than the Raman modes. These observations suggest ways in which similar force constant models can be improved: Matossi's model, which was basically a covalent model neglecting several next-nearest-neighbor interactions, fits even-parity modes of TiO_2 and GeO_2 fairly well, but both even and odd modes of MgF_2 and MnF_2 poorly.[13] Although the evidence is not substantial, this indicates a greater degree of ionicity in the fluorides, as expected.

TRIGONAL GeO_2

The first thing to be said about the spectrum of trigonal GeO_2 is that it in no way resembles that of the rutile phase. It is, however, strikingly analogous to that of its isomorph, α quartz. There are four totally symmetric modes of A_1 symmetry and eight doubly degenerate polar modes of E symmetry; each of the latter is split into transverse (TO) and longitudinal (LO) components by the electric dipole field accompanying the vibration. This splitting is not present at the exact zone center; the small but finite wave vector ($\sim 3\times 10^5$ cm^{-1}) of phonons sensed in Raman scattering is sufficient to lift the degeneracy of LO (Γ) and TO (Γ) states.

Figure 3 illustrates the spectrum of a small unoriented sample at 6°K. At room temperature several of the TO/LO doublets are more difficult to resolve. The four features labeled A_1 were the only features observed for α_{zz} scattering. Their assignment is also established by a comparison with α-quartz; see Table II. The assignment of E(TO) and E(LO) modes is made almost entirely on detailed comparisons with quartz. Not only are the frequencies the same, except for a reduced mass factor, but even relative intensities and linewidths are strikingly similar to quartz. In both materials, there are two narrow (<1 cm^{-1}) very intense E(TO+LO) doublets in the region 100–250 cm^{-1}; two A_1 modes in the region 200–350 cm^{-1}; a weak resolvable doublet E(TO) $+E$(LO) at about 400 cm^{-1}; a sharp moderately intense E(TO) in the same region (326 cm^{-1} in GeO_2 and 450 cm^{-1} in quartz); an enormous A_1 feature at ~ 460 cm^{-1} with an E(LO) shoulder at ~ 500 cm^{-1}; two closely spaced E(TO)+E(LO) doublets in the 500–800-cm^{-1} region; an E(TO)+A_1 pair (at ~ 860 cm^{-1} in GeO_2, 1080 cm^{-1} in quartz) in which the E(TO) exhibits large oscillator strength by virtue of its distance from all neighboring LO's; an "inverted" E(LO)+E(TO) pair at high frequencies; and finally the last E(LO).

Qualitatively, the spectra of quartz and trigonal GeO_2 differ in only two respects, as indicated in Table II: the E(TO) mode in GeO_2 equivalent to the 450-cm^{-1}

line in quartz lies below the pair at ~400 cm^{-1} instead of above, so that the frequencies of the 400-cm^{-1} TO/LO doublet are reversed in GeO_2 (LO below TO); more of the doublets are resolvable than in quartz, demonstrating slightly larger oscillator strengths.

The oscillator strengths have in fact been calculated from the Raman data, using the above assignments. They were determined by a least-squares procedure and occur as solutions to the eight oscillator equations

$$0=(1.695)^2+\sum_{j=1}^{8}\left[\frac{\omega_j^2(\mathrm{TO})}{\omega_j^2(\mathrm{TO})-\omega_k^2(\mathrm{LO})}\right]S_j,\qquad K=1,2,\ldots,8$$

where 1.695 is the ordinary ray index of refraction.[3] Using these S_j we have calculated the static dielectric constant for fields perpendicular to the optic axis, $\epsilon_0^{1}=(1.695)^2+\sum_{j=1}^{8}S_j$, and have also determined a theoretical infrared spectrum for polarization perpendicular to the optic axis. The latter is shown in Fig. 4.

The intensity and linewidths of the scattering is worthy of note. The A_1 line at 440 cm^{-1} is more intense than the corresponding mode in quartz, which can easily be made to produce stimulated Raman scattering (SRS) (we achieved SRS in quartz at 300°K with only a 2-MW pump).[15] In addition, the sharp mode at 121 cm^{-1} in GeO_2 is of comparable intensity to the 128-cm^{-1} line in quartz, which goes stimulated at low temperatures[10] (these lines are infrared-active). Hence, there is every reason to believe that it would be easy to obtain SRS in GeO_2 if larger samples can be obtained. Hopefully, the considerable expertise acquired in growing synthetic quartz can be applied to the problem.

The high-temperature studies were disappointing. No mode in either form of GeO_2 varied frequency by more than 20 cm^{-1} over the range 6–600°K. The trigonal sample was heated to 1100°K, at which temperature considerable broadening of linewidths was observed, but no anomalies. It had been hoped that some evidence of lattice instability[16] would manifest itself at these elevated temperatures, but no "soft" modes were observed. The trigonal form of GeO_2 can be converted at high temperatures and pressures, in a nondestructive way, into the tetragonal form.[17,18] However, from a lattice dynamical viewpoint this is a violent first-order phase transition, with changes in density of 50% and change in unit cell of a factor of $\frac{3}{2}$. Therefore, it is not surprising that no soft modes are observed.

Quartz has been shown to exhibit a unique hybrid-phonon excitation consisting of coupled one- and two-phonon states.[9] Trigonal GeO_2 was closely scrutinized for evidence of such an interaction, but none was found. Like quartz (excluding the coupled mode), trigonal GeO_2 has no indication in either its infrared or Raman spectrum of two-phonon processes. This is indicative of extreme lattice harmonicity and again suggests the effect of *p*-electron bonding.

CONCLUSIONS

The Raman spectra of both known crystalline forms of GeO_2 have been obtained. All group-theoretically predicted modes have been found and assigned. The static dielectric constant and infrared spectrum of the trigonal form have been calculated. Comparisons have been made with force constant models and with isomorphic rutile and quartz.

Note added in proof. Private communication from Dr. S. M. Shapiro indicates that B_{1g} in tetragonal GeO_2 is at 170 cm^{-1} and not the 97 cm^{-1} indicated in Table I. This line is apparently obscured by grating ghosts G3 in Fig. 2.

ACKNOWLEDGMENTS

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