Raman spectra of SiF_4 and GeF_4 crystals

E. R. Bernstein and G. R. Meredith

Citation: The Journal of Chemical Physics **67**, 4132 (1977); doi: 10.1063/1.435390
View online: http://dx.doi.org/10.1063/1.435390
View Table of Contents: http://aip.scitation.org/toc/jcp/67/9
Published by the American Institute of Physics

Raman spectra of SiF_4 and GeF_4 crystals[a]

E. R. Bernstein and G. R. Meredith[b]

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

(Received 28 December 1976)

The Raman scattering spectra of large single crystals of SiF_4 and GeF_4 at 77 K are reported. These data have been reinterpreted based on the absence of any observable changes in the spectra for scattering angles between 0° and 90°. The previous assignment of the dipole allowed ν_3 and ν_4 modes based on a TO/LO splitting model is thereby shown to be incorrect. In the absence of an apparently correct crystal structure, an exact interpretation of the data in terms of a factor group-exciton analysis is not possible; nonetheless all observations appear to be consistent with a centrosymmetric space group having a multimolecular primitive unit cell. Mixed SiF_4/GeF_4 crystal spectra have also been obtained which demonstrate that GeF_4 does not substitute into the SiF_4 lattice but that SiF_4 does enter the GeF_4 crystal substitutionally.

I. INTRODUCTION

Inorganic volatile fluorides are excellent systems for study of the finer details of molecular crystal phenomena; their molecular spectra are typically simple due to the high symmetry and small number of atoms, and there is generally more than one member of a chemical series. In this paper the (internal) vibrational properties of SiF_4 and GeF_4 crystals will be discussed.

There have been numerous previous studies of the vibrational spectra of polycrystalline SiF_4,[1-9] but no reports of the crystal vibrational spectra of GeF_4 have appeared. Our interest in the Raman scattering of single crystal GeF_4 and SiF_4 was attracted by the reported large transverse optical (TO)-longitudinal optical (LO) splitting for the dipole allowed ν_3 and ν_4 modes of $SiF_4[\delta(\nu_3)\sim 70\ cm^{-1}$ and $\delta(\nu_4)\sim 30\ cm^{-1}]$. Such large TO/LO splittings in cubic crystals should give rise to substantial coupling between dipole active vibrations and the radiation field. This coupling leads to the mixing of mechanical unit cell modes and the electric field of the light wave propagating in the crystal. The combined modes have been called a polariton.[10-19]

Since the SiF_4 ν_3/ν_4 splittings did not seem excessive in comparison with other dipole active ground state vibrational exciton bands of molecular solids (i.e., C_6H_6 and MF_6)[16,20,21] for which the observed structures were not polariton related, we decided it would be appropriate to reinvestigate the mechanism for the SiF_4 ν_3/ν_4 crystal splittings. Indeed, the new data presented here for 0° and 90° Raman scattering do not support these assignments, as the scattering mode intensity and energy are scattering angle independent. The spectra are consequently reinterpreted in the more usual molecular crystal fashion in terms of exciton splittings of molecular levels arising from a centrosymmetric crystal with more than one molecule per primitive unit cell. The major stumbling block to a complete crystal spectra assignment is an incorrectly determined crystal structure.

In Sec. II. A we present a review of the previous vibrational spectroscopy on crystalline SiF_4 and a summary of the crystal structure data. The general concepts of polaritons as phonon-photon coupled polarization modes in noncentrosymmetric crystals[10-19] are reviewed in Sec. II. B. In Secs. III and IV our experimental techniques and results are presented. The details of crystal structure and mechanism for crystal splitting of ν_3 and ν_4 of both SiF_4 and GeF_4 are discussed in Sec. V.

II. REVIEW OF PREVIOUS STUDIES

A. Experimental

Both SiF_4 and GeF_4 are gases at room temperature and their infrared and Raman spectra have been studied and interpreted.[1] The four vibrations of an XY_4 T_d molecule, ν_1 through ν_4, transform as a_1, e, t_2, and t_2, respectively.

The crystal structure of SiF_4 was determined[2] at $-145\,^\circ C$ via x-ray diffraction to belong to the space group T_d^3. This is a body centered cubic structure and was reported to have one molecule per primitive unit cell at a T_d site. The only solid–solid phase transition known[3] is a first order transition observed at 8.2×10^3 kg/cm^2 and 175 K. Heat capacity measurements down to 15 K have revealed no transitions at normal pressures.[4]

The vibrational spectra of SiF_4 crystals first appeared in connection with a discussion of dipole summations.[5] Based on the cubic crystal structure, the expected $k=0$ Raman spectrum should contain four single lines corresponding to $\nu_1 \ldots \nu_4$. However, for the dipole allowed vibrations (t_2), a TO/LO splitting should exist for the $k\sim 0$ observed levels due to the occurrence of the accompanying longitudinal coulombic field. The low resolution spectra show just this: single features for ν_1 and ν_2 and apparent doublets for ν_3 and ν_4. The early infrared absorption spectra were consistent with this interpretation in that only ν_3 and ν_4 TO (lower energy branches) were found with appreciable intensity. In addition to large TO/LO splittings, a further splitting was noted for the low energy ν_3 component. If the polariton assignment is then still accepted, the TO mode degeneracy is removed. An alternative crystal structure was proposed[5] O_h^9 with eight molecules per primitive unit cell, which is entirely too complex to fit

---

[a] Supported in part by ARO-D and ONR.

[b] Present address: Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19174.

the relatively simple infrared and Raman spectra. Fox and Hexter[6] later suggested that the low energy ν_3 component splitting is a consequence of crystal size and shape (boundary conditions on the slowly converging dipole summations). Subsequently, Bessette *et al.*[7] showed that the ν_3 splitting was present even for "large" melt grown crystals. They also observed a similar but smaller splitting in ν_4 and observed ν_1 in the infrared. Coupling these facts with constancy of spectra as temperature was varied, they concluded that the crystal structure was indeed in error. They suggested C_3^4 or C_{3v}^5 space groups (with one molecule per unit cell) to describe structures differing from T_d^3 only slightly. These authors also maintain that the large splitting of the ν_3 and ν_4 modes should be assigned to TO/LO structure. They base their conclusion on the following observations: (1) the higher energy component of ν_3 and ν_4 bands is relatively much more intense in the Raman spectra than in the infrared spectra (the LO peak is forbidden in cubic crystals' infrared absorption spectra but observed due to beam convergence); (2) strong ν_3/ν_4 infrared reflection bands are bracketed by their high and low energy components; (3) approximate agreement of calculated TO/LO splittings for the ν_3 and ν_4 bands (based on vapor phase oscillator strengths) with the observed splittings; and (4) line shapes for ν_3 and ν_4 in liquid Raman spectra are asymmetric with widths comparable to the TO/LO splittings observed in crystals.

The remaining crystal investigations deal with the observation of two-particle bands (which have only been reported for infrared absorption). The marked similarity of $\nu_1+\nu_3$, $\nu_1+\nu_4$, and $\nu_2+\nu_3$ bands is considered strong support for TO/LO band structures.[8] Calculated $2\nu_3$ two-phonon band structure is in reasonable agreement with experiment.[9] In these studies the T_d^3 crystal structure was assumed.

Many of these points will be discussed further, in light of our new data and revised interpretations, in Sec. V.

B. Polariton theory

The theory of energy levels and first order Raman processes in crystals has been discussed extensively.[10,11] Briefly, we will review those pertinent qualitative features of the theory upon which our basic reasoning and conclusions are founded.

For crystals with inversion centers, factor group analysis ($k=0$ exciton predictions) will explain the first order Raman spectra since the dispersion (dE/dk) is very small over the range of optically accessible wavevectors. On the other hand, for crystals without inversion centers, Raman allowed states which are also dipole allowed may interact with electromagnetic radiation such that very rapid dispersion obtains near $k=0$. This assures that dispersion surfaces are continuous and meet degeneracy predictions of the factor group, since coulombic dipole sums which determine phonon energies for $k>0$ are nonanalytic around $k=0$. In the presence of spatial dispersion or when crystal symmetry is low, energies may depend on wavevector direction as well as magnitude. These rapid variations of energy with crystal wavevector are, under certain geometric or phase matching scattering conditions, accessible to Raman spectroscopy.[11-19] This description holds even when weak to moderate phonon damping complicates the character of the crystal response.

The theoretical conclusions for Raman scattering by polariton modes are roughly the same in all crystal structures. Since, however, the specifics of light propagation are different for cubic, uniaxial, and biaxial crystals, the particular details for polariton Raman scattering in each crystal system warrant separate consideration. Below, we present comments on just those aspects of polariton modes and Raman processes which pertain to the present discussion. More complete details and specific examples can be found in Refs. 10 through 19.

1. Cubic crystals.[10-15]

In isotropic crystals 90° Raman scattering spectra show TO/LO (coulombic dipole summation) mode splittings for dipole active vibrations. Small angle scattering experiments generate appropriate phase matching conditions to observe regions of large phonon–photon coupling and hence strong polariton dispersion. Such effects have been identified in both oriented single crystal and polycrystalline samples. Since, however, there may be a number of causes for mode splittings in a real crystal, scattering angle dependent spectra are the conclusive evidence for polaritons.

2. Uniaxial crystals.[11-13,17,18]

The above conclusions are basically the same for uniaxial crystals except that both 90° and 0° Raman scattering are wavevector direction dependent in the crystal. The "TO" modes will depend on polariton wavevector inclination to the uniaxis c. For $k \parallel c$, the perpendicular (perpendicularly polarized) modes couple to the electromagnetic field as ordinary polaritons and the LO modes are the parallel phonons. For $k \perp c$, half of the perpendicular modes and the parallel modes couple to the field to become, respectively, ordinary and extraordinary polaritons while the LO modes are now perpendicular phonons. For arbitrary wavevector inclination, half of the perpendicular modes couple to the field to become ordinary TO polaritons, but general mixing occurs among the other modes. The ordinary dispersion curves are independent of wavevector direction (no spatial dispersion of the phonon component) while the other curves are not. The overall dispersion relations and final Raman spectra depend on the relative strengths of the anisotropy in crystal properties and mechanical mode–radiation field coupling. There are four Raman phase matching curves, only one of which is independent of crystal orientation, since both incident and scattered beams may be ordinary or extraordinary. Polycrystalline samples will generate spectra simultaneously evidencing many or all of these characteristics.

3. Biaxial crystals.[11]

For this crystal optical class, any direction of propagation results in nondegenerate "TO modes" or polariton branches. Only if the phonon modes are polarized along the principal axes and k is perpendicular or parallel to one of these, does a polariton branch possess simple, pure transverse or longitudinal polarization. All dispersion curves are functions of wavevector direction. Here also, four phase matching curves for each scattering geometry and crystal orientation exist, and both 90° and 0° spectra demonstrate polariton effects. Such spectra are in general quite complex and do not lend themselves to simple generalizations. Barker and Loudon review some of these features.[11]

Intensities, polarizations, and selection rules are discussed in the literature for all three systems.[10-19] The important points here are that not only do polaritons evidence different spectra in low angle and 90° scattering, but for the lower symmetry crystals, the spectra change with crystal orientation as well.

III. EXPERIMENTAL

A. 90° scattering geometry

Since 90° scattering experiments are the typical Raman configuration, little need be said about the experimental arrangement. The laser radiation (Ar^+ 5145 Å ~ 1 to 2 W) entered the sample at the bottom through a polished Pyrex cell wall. The beam was parallel to the double monochromator's vertical slits, focused with an $f/20$ lens to give a beam waist of $< 20\ \mu$ over a slit height of about 1 cm. Scattered radiation was focused into the monochromator using magnifying (a factor of 2) collection optics and was detected with photon counting techniques. All reported data were collected on samples at 77 K. More details are available in Ref. 16.

B. 0° or low angle scattering geometry

Experimental configuration for low angle Raman scattering was similar to the 90° geometry with the exception that the beam entered the sample in the horizontal plane and was not focused in the crystal. Beam quality did not appear to be substantially altered by the clear sample. Angles through the sample were varied by a system of two mirrors which directed the laser beam over a 2 m length on an optical table. A low power He–Ne laser was used to define the scattering direction and to test (with back reflections) for perpendicularity of surfaces. Additionally, to obtain accurate 0° scattering data, collection optics were limited in aperture to roughly $f/100$; this gave an angular acceptance of about 0.5° for the unfocused TEM_{00} laser beam. More details can be found in Ref. 16.

It was necessary to determine wavelength accurately in separate experiments to compare line positions obtained at different scattering angles. Over 600 Fe–Ne hollow cathode lamp lines were fitted to a calibration curve which included a term to correct for the small cam action of the monochromator drive screw. Each measurement had a standard deviation of less than 0.05 Å. Since spectra were obtained in second order of a 1200 g/mm grating mounted in a 0.5 m double monochromator, the absolute energy uncertainties (three standard deviations) are expected not to exceed $\pm 0.3\ cm^{-1}$. Reproducibility was seen to be better than $\pm 0.1\ cm^{-1}$.

C. Sample preparation, crystal growth, and crystal handling

Both SiF_4 and GeF_4 were prepared by burning the pure elements in prepurified fluorine.[16] Since these materials are gases at STP, crystals were grown from large (~ 2 l) volumes into small polished square cross section Pyrex ($6\times 6\times 20$ mm) or disc shaped (25×3 mm) cells at 77 K. The large volume was later removed by glass blowing.

These techniques produced high purity and optical quality samples. The samples extinguished uniformly though not completely when rotated inside a glass dewar between crossed polarizers. SiF_4 data were obtained on four separate crystals. It was not possible to study or orient samples conoscopically because they needed to be maintained at 77 K in sealed cells.

IV. RESULTS

Results of the 90° scattering experiments for GeF_4 and SiF_4 are presented in Table I and Figs. 1 and 2 depict the spectra for ν_3 and ν_4 of both samples. The previous TO/LO designations are included in the table and figures for comparison and discussion purposes only. There are three points to be noted about these data: (1) the new GeF_4 data are similar in most respects to the SiF_4 data; (2) the lower energy components of ν_3 and ν_4 are split in SiF_4 [by roughly 3.4 and 0.5 cm^{-1}, respectively] but not in GeF_4; and (3) the SiF_4/GeF_4 ratios of ν_3 and ν_4 total band splittings are about what would be expected based on transition dipole derivatives[22,23,24] for these modes in the different molecules.

To test the hypothesis that the large ν_3/ν_4 splittings are in fact due to dipolar TO/LO splittings, low scattering angle experiments were performed on a thin disc-shaped single crystal of SiF_4. *No peaks were observed at energies differing by more than* 0.3 cm^{-1} *from the* 90° *scattering spectra*. It was necessary to enhance these spectra on a signal averager due to the requisite small scattering solid angle. After ten to twenty scans, the spectra were integrated and intensities of the various peaks tabulated and normalized to ν_1 peak intensities. The "TO" to "LO" branch intensity ratio remained constant to within roughly 20%. The absence of any angle-dependent intensity (or in general, an increase in the baseline) at lower energy than the 90° ν_3 peaks is at variance with the polariton model.[11-15]

Relative peak to peak intensity variations for the different SiF_4 and GeF_4 samples studied were less than 20% for both 0° and 90° spectra. Unfortunately, due to the lack of orientational information on each crystal, little can be said concerning crystal optical properties based on this observation.

Motivated by the uncertainty over crystal structure, mixed crystal experiments were attempted to obtain information about the crystal site symmetries. These experiments were not entirely successful. GeF_4 oc-

TABLE I. Summary of crystal spectra.

	Frequencies (cm^{-1})					Assignment[a]	
	Infrared		Raman				
	Bessette *et al.*[b]	Schettino[c]	Bessette *et al.*	Schettino	This work[d]		
A. $\mathrm{SiF_4}$			258.3	261	259.0 (0.4)	ν_2	
	370.3	374	370.6	374	373.5 (1.2)	ν_4	(Transverse)
	373.7		373.3		374.0		
		409	407.5	410	408.3 (0.8)		(Longitudinal)
	795		795.3	797	796.2 (0.9)	ν_1	
	987.7	988	987.8		988.2 (2.2)	ν_3	(Transverse)
	991.2	992	991.3	991	991.6 (1.8)		
		1059	1057.3	1058	1058.3 (1.1)		(Longitudinal)
B. $\mathrm{GeF_4}$					194.8 (1.0)	ν_2	
					253.2 (0.9)	ν_4	(Transverse)
					301.8 (1.0)		(Longitudinal)
					729.5 (<0.3)	ν_1	
					774.4 (0.8)	ν_3	(Transverse)
					817.9 (0.6)		(Longitudinal)

[a] Old ($\mathrm{SiF_4}$) TO/LO $\nu_3-\nu_4$ assignments and parallel ones in $\mathrm{GeF_4}$ are indicated in parentheses for discussion purposes only (see text).

[b] Reference 7.

[c] Reference 8.

[d] Measured FWHH are listed in parentheses.

cupies several sites in $\mathrm{SiF_4}$ and, at higher concentrations, a portion is excluded (deduced from variation of spectra along the length of the crystal and occurrence of neat crystal peaks). On the contrary, $\mathrm{SiF_4}$ appears to occupy unique sites in $\mathrm{GeF_4}$. (See Figs. 3-5.) This behavior can be correlated with the fact that the Si–F bond length (1.56 Å)[2] is less than the Ge–F bond length[1] (1.67 Å) for the gas phase molecules. However, the situation is not so straightforward since the densities of $\mathrm{SiF_4^4}$ at -170°C (2.18 g/cc) and $\mathrm{GeF_4^{25}}$ at -195°C (3.148 g/cc) yield nearly equal packing densities (1.23×10^{22} and 1.25×10^{22} molecules/cc). Apparently the larger number of electrons in Ge increases the Ge–Ge and Ge–F attraction requiring shorter F–F contacts to create balancing repulsive interactions. Unfortunately, however, even for $\mathrm{SiF_4/GeF_4}$ crystals, weak signals necessitated the use of slit widths too large to yield useful ν_3 and ν_4 site information. These spectra, however, indicate that reevaluation of the structure would be quite useful.

V. DISCUSSION OF ν_3/ν_4 CRYSTAL SPECTRA

The implications of the $\mathrm{SiF_4}$ ($\mathrm{GeF_4}$) ν_3 and ν_4 data, reported in the previous section, require further discussion. We believe the major conclusions to be drawn from these results deal with the crystal structure of $\mathrm{SiF_4}$ and $\mathrm{GeF_4}$ and the question of the mechanism for ν_3 and ν_4 splitting. Clearly these are not independent problems. The possibilities for the structure are: (1) T_d^3 as reported originally; (2) either C_3^4 or C_{3v}^5 (uniaxial with one molecule/unit cell) as proposed in Ref. 7; (3) any other noncentrosymmetric structure; or (4) a centrosymmetric structure (required to have a multimolecular unit cell) with inversion not a site operation. Below, each of these four cases will be specifically considered.

Case 1. This possibility for the crystal structure of $\mathrm{SiF_4}$, T_d^3 with one molecule per primitive unit cell, was originally suggested by Atoji and Lipscomb.[2] It has been rejected by most subsequent workers due to the splitting of the low energy components of $\mathrm{SiF_4}$ ν_3 and ν_4, as was pointed out in Sec. II. A. Such splittings do not occur for $\mathrm{GeF_4}$. However, splittings of the supposed $\mathrm{SiF_4}$ TO branches can be accounted for within the scope of a T_d^3 structure by spatial dispersion of the phonon modes.[26] An effect of spatial dispersion is to lift the degeneracy of transverse polariton modes for nonzero wave vectors which do not fall on one of the cubic symmetry axes. Typically, for the small band widths found in molecular solids, such spatial dispersion effects would be vanishingly small. However, it is possible that this dispersion might be enhanced in $\mathrm{SiF_4}$ by interaction of the two dipolar modes. Disregarding spatial dispersion effects for the moment, ω vs k cubic dispersion curves can be calculated for reasonable values (unmeasured) of ϵ_∞ and the observed 90° spectrum. These, together with the phase matching requirements for various angles, have been plotted and can be found in Ref. 16. Raman scattering at a particular angle is allowed at the intersection of a dispersion curve and the appropriate phase matching curve.[11] Scattering angles (in the crystal) between 0 and $4.5\,(\epsilon_\infty)^{-1/2}$ degrees were investigated. While observation of polariton dispersion in the ν_4 branch might be beyond the experimental capacity, the behavior of the largely ν_3 polariton (TO) branch should have been quite dramatic. The ν_3 curves predict a deviation of *at least* 40 cm^{-1} for angles less than 4° (in vacuum exterior to the crystal). Even if there were destructive interference between the three-wave mixing and true Raman mechanisms, a complete cancellation could occur only at one angle; that is, only for one ratio of photon to phonon admixture coefficients. However, at the "knees" of the dispersion curves, both the *energies and the ad-*

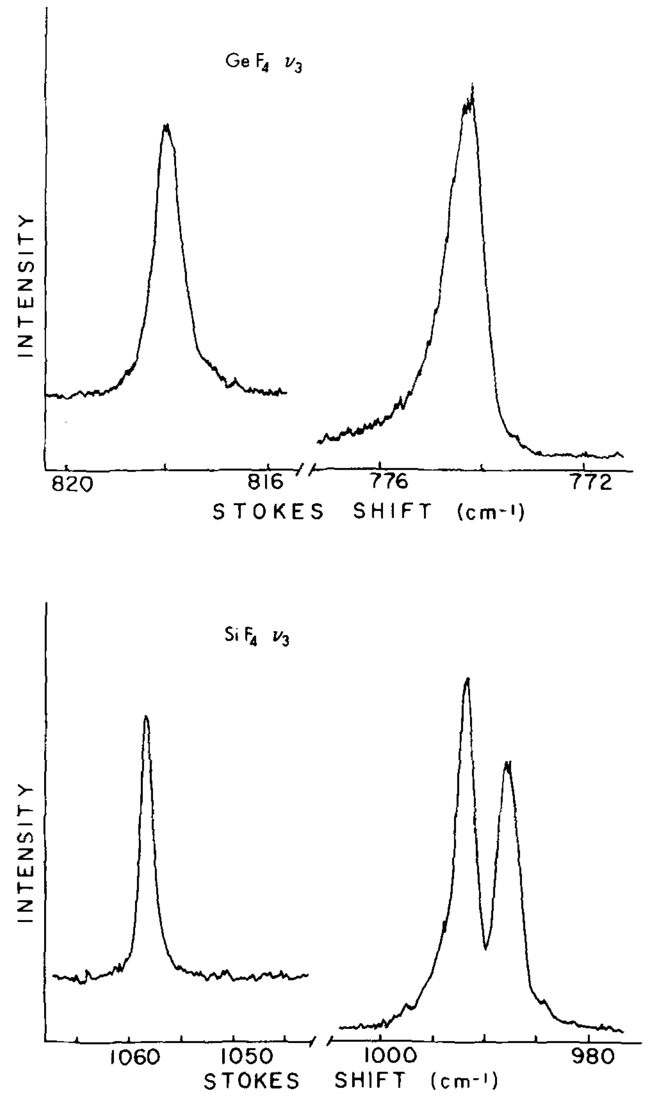

FIG. 1. 90° Raman spectra of the SiF$_4$ and GeF$_4$ ν_3 region at 77 K. The low energy feature for SiF$_4$ has previously been assigned as a transverse optical (TO) mode branch for this dipole allowed vibration. Note that this low energy feature is split in SiF$_4$ but not in GeF$_4$. The higher energy mode would then correspond to a longitudinal optical (LO) branch and has been previously so designated.

mixture are changing rapidly. This fact, coupled with the earlier discussion of scattering geometry and approximate polarization rules,[11,16] suggests that the magnitude of the scattering matrix element is not responsible for failure to observe any intensity to lower energy than ν_3 in small scattering angle experiments. On this basis, one must reject the T_d^3 space group for SiF$_4$ (GeF$_4$); the cubic structure can only be maintained if the small scattering angle data are to be attributed to large angle Raman scattering caused by back reflections from nonindexed matched surfaces and optical imperfections. Since scattered beam intensity was estimated at less than a factor of ten of the main laser beam, we consider this possibility unlikely. The anticipated polariton scattering is therefore not present.

Cases 2 *and* 3. Although similar dispersion curves obtain for Case 2,[11] the certainty of observation of low angle scattering dispersion is not easily arguable in the absence of detailed optical properties of the crystal. However, the polariton energies should vary not only with scattering angle, but with crystal orientation. We reiterate that no peaks were observed at energies differing by more than 0.3 cm^{-1} in any of our spectra of SiF$_4$ crystals. It might be suggested that the differences between "TO-mode" splittings reported in Ref. 7 and those reported here (see Table I) for SiF$_4$ could be attributed to such angular effects. However, the nature of these differences is not consistent with expectations for Case 2 if random orientation of crystals or powders is allowed.[11,16]

Case 4. Having observed no shifts in energies or changes in intensity with scattering angle, we must admit the possibility that no polariton effects are observed in Raman scattering and that the crystal is centrosymmetric. Since the molecules are noncentrosymmetric, inversion must be an interchange operator. Then, of course, every molecular vibration has both *g* and *u* factor group states and can be allowed, subject to tensorial selection rules, in both infrared and Raman spectra. Strong phonon–photon coupling can occur only for *u* states, however. In this regard, it should be noted

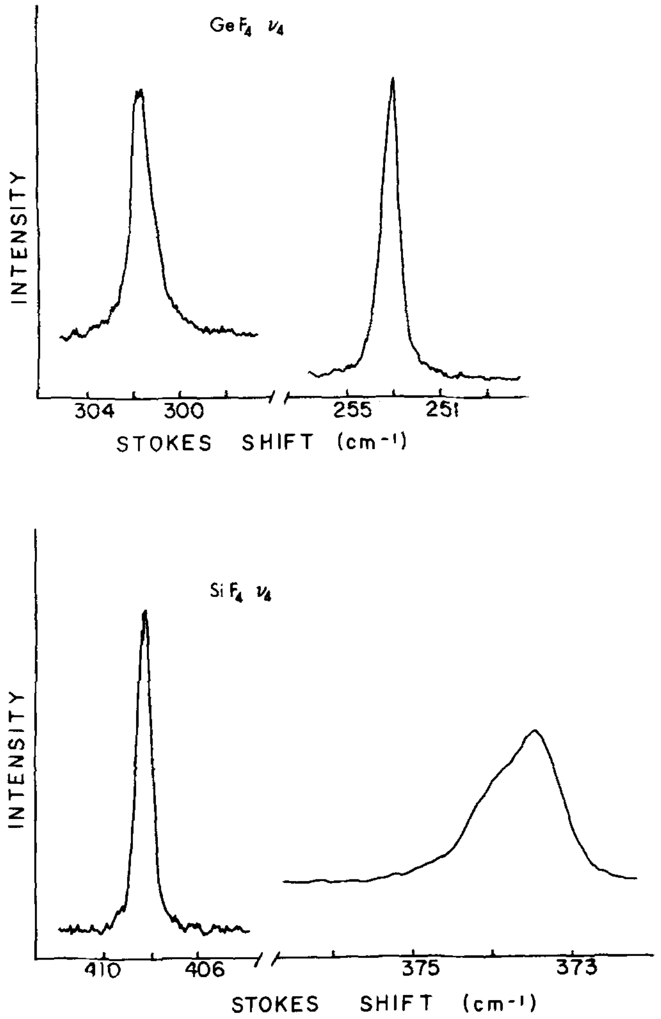

FIG. 2. 90° Raman spectra of the SiF$_4$ and GeF$_4$ ν_4 region at 77 K. See Fig. 1 for explanation.

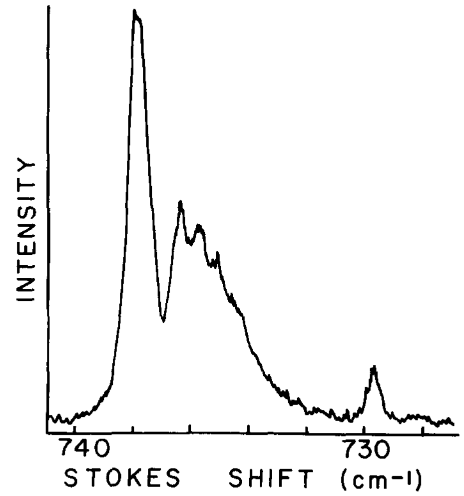

FIG. 3. 90° Raman spectrum of the ν_1 region of GeF_4 in a nominal 5% GeF_4 in SiF_4 crystal. The multiplicity of peaks indicates several sites. The peak near 730 cm^{-1} corresponds to the neat crystal vibrational transition. The relative intensities of these peaks were observed to vary depending on the particular portion of crystal examined.

that ν_1 has been observed in infrared[7] as well as Raman spectra. It would be interesting to examine ν_2 in the infrared to determine if it too has induced dipolar properties. In the ensuing paragraph we will show that this interpretation, which we favor, is consistent with observations previously considered to support assignment of the ν_3 and ν_4 structures to TO/LO splittings, under the assumption of either Case 1 or 2.

First, the approximate agreement of the large observed splittings with those calculated from the squares of ν_3/ν_4 dipole derivatives based on the T_d^3 polariton model[16] is not unique. Davydov splittings also depend on these parameters through crystal sums. Second, the agreement of transition dipole calculations with observed two-particle structure found in the infrared is also not unique. In this regard, similarities between SiF_4 $(\nu_1+\nu_3)$, $(\nu_2+\nu_3)$, and $(\nu_1+\nu_4)$ two-particle spectra[8] and UF_6 $(\nu_1+\nu_3)$ and $(\nu_2+\nu_3)$ two-particle spectra (ν_1, ν_2, ν_3 are a_{1g}, e_g, and t_{1u} in O_h) are particularly striking and revealing.[20,27] In general, UF_6 fundamental single particle spectra are characterized by site and large exciton splittings, which derive from four translationally inequivalent molecules in a centrosymmetric unit cell. Nonetheless, except for the sharp single particle combination peaks in SiF_4 (associated with large anharmonicity), the SiF_4 and UF_6 two-particle spectra are practically identical. This, of course, implies that the density of states for the dipolar levels are similar in these cases. Since, however, gerade $k=0$ components have been observed throughout the UF_6 ν_3 fundamental band region,[20] a simple identification of the bimodal distribution of states with unit cell transverse or longitudinal character is not correct. We would suggest that it is the approximate crystal packing (spacings and orientations of molecules) which determines the overall density of states and consequently the observed two-particle (combination and overtone) spectra. Apparently this type of data is related only to the dipolar property of the vibrational bands and not specifically to the nature of $k=0$ modes. Third, the observed reflection bands of the crystal are consistent with this interpretation as can be seen from qualitative oriented gas arguments. In the oriented gas approximation, the sums of the squared transition dipole moments over all factor group components is equal to the product of the number of molecules in the unit cell times the molecular dipole moment squared. Since the transverse/longitudinal shift (width of reflection band) is approximately proportional to the moment squared divided by the unit cell size, the sum of the reflection band widths over all factor group states is nearly constant and independent of crystal structure if (as in this case) the infrared intensity falls within a few transitions. And finally, the above arguments also predict that liquid state spectra will have band widths comparable to the crystal band widths as has been observed.

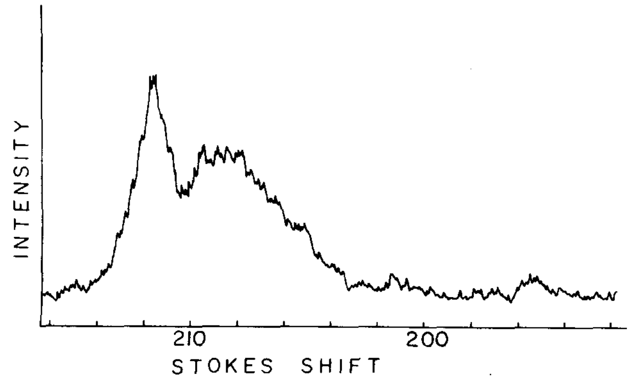

FIG. 4. 90° Raman spectrum of the ν_2 region of GeF_4 in a nominal 5% GeF_4 in SiF_4 crystal. Comments given in the caption of Fig. 3 are applicable here. The neat crystal transition is also observed near 195 cm^{-1}. The similarity of this structure to that of Fig. 3 should be noted.

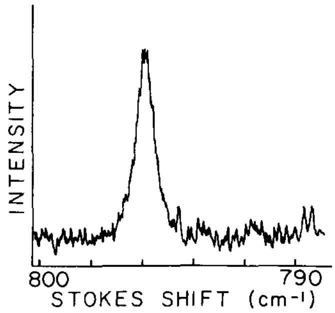

FIG. 5. 90° Raman spectrum of the ν_1 region of SiF_4 in a nominal 5% SiF_4 in GeF_4 crystal. The slight upward shift (~ 0.4 cm^{-1}) and single peak are indications that the SiF_4 occupies substitutional sites in the GeF_4 structure.

The major difficulty with the interpretation of vibrational spectra of SiF_4 and GeF_4 crystals based on Case 4, above, is that the less than ~ 2 cm^{-1} shifts between reported infrared and Raman transitions must now be associated with different factor group states and polaritons. Nonetheless, we believe this to be the most likely and most consistent approach to all the existent data on both crystals.

VI. SUMMARY AND CONCLUSIONS

The Raman scattering spectrum of GeF_4 is somewhat simpler than that of SiF_4. Splitting of the low energy components of ν_3 and ν_4 has not been observed. Either the crystal structure of GeF_4 is closer to an ideal high symmetry space group than is that of SiF_4 or spatial dispersion in GeF_4 is smaller than that of SiF_4.

Failure of GeF_4 to occupy simple unique (substitutional) sites in SiF_4 is observed, as is the apparent exclusion of GeF_4 at moderate concentrations, even though the neat crystals have nearly equal molecular packing densities.

The polariton model for the ν_3 and ν_4 vibrations is not successful in explaining the observed 0° and 90° Raman spectra of SiF_4 or GeF_4. The main unique feature of this model is crystal orientation and/or scattering angle dependent spectra; neither of these effects has been observed. We would suggest that the observed splittings previously assigned as transverse and longitudinal components are gerade Davydov components of dipolar exciton bands. The polariton dispersion curves in this case would be drastically altered; the electromagnetic field vibrations must couple with ungerade *unit cell* mechanical vibrations. This would remove the expectations for angle and crystal orientation dependent Raman spectra.

A detailed study of the structure and interactions in these molecular crystals seems warranted. There are several ambiguities in the vibrational spectra which could thereby be resolved. Moreover, careful polarization studies on oriented single crystals would then be worthwhile.

[1] A. D. Caunt, L. N. Short, and L. A. Woodward, Trans. Faraday Soc. **48**, 873 (1952); O. Linnett and V. Heath, J. Chem. Phys. **19**, 801 (1951).

[2] M. Atoji and W. N. Lipscomb, Acta Crystallogr. **7**, 597 (1954).

[3] J. W. Stewart, J. Chem. Phys. **33**, 128 (1960).

[4] E. L. Pace and J. S. Mosser, J. Chem. Phys. **39**, 154 (1963).

[5] R. M. Hexter, J. Chem. Phys. **37**, 1347 (1962).

[6] D. Fox and R. M. Hexter, J. Chem. Phys. **41**, 1125 (1964).

[7] F. Bessette, A. Cabana, R. P. Fournier, and R. Savoie, Can. J. Chem. **48**, 410 (1970).

[8] V. Schettino, Chem. Phys. Lett. **18**, 535 (1973).

[9] D. P. Craig and V. Schettino Chem. Phys. Lett. **23**, 315 (1973).

[10] G. Turrell, *Infrared and Raman Spectra of Crystals* (Academic, New York, 1972); and M. M. Sushchinskii, *Raman Spectra of Molecules and Crystals* (Keter, New York, 1972).

[11] R. Loudon, Adv. Phys. **13**, 423 (1964); A. S. Barker and R. Loudon, Rev. Mod. Phys. **44**, 18 (1972); and C. Y. She, J. D. Masso, and D. F. Edwards, J. Phys. Chem. Solids **32**, 1887 (1971).

[12] R. Loudon, in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer–Verlag, New York, 1969), p. 25.

[13] E. Burstein, S. Ushioda, A. Pinczuk, and J. F. Scott, in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer–Verlag, New York, 1969), p. 4.

[14] W. Vedder and D. F. Hornig, Adv. Spectrosc., **2**, 189 (1961).

[15] C. H. Henry and J. J. Hopfield, Phys. Rev. Lett. **15**, 964 (1965).

[16] G. R. Meredith thesis, Princeton University, 1977.

[17] S. P. S. Porto, B. Tell, and T. C. Damen, Phys. Rev. Lett. **16**, 450 (1966).

[18] J. F. Scott and S. Ushioda, in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer–Verlag, New York, 1969), p. 57.

[19] G. G. Mitin, V. S. Gorelik, L. A. Kulenskii, Y. N. Polivanov, and M. M. Sushchinskii, Zh. Eksp. Teor. Fiz. **68**, 1757 (1975); [English translation: Sov. Phys. JETP **41**, 882 (1976)].

[20] E. R. Bernstein and G. R. Meredith, Chem. Phys. (to be published).

[21] E. R. Bernstein and G. W. Robinson, J. Chem. Phys. **48**, 5596 (1968); **49**, 4962 (1968).

[22] G. Herzberg, *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1945), p. 100.

[23] B. Beagley, D. P. Brown, and J. M. Freeman, J. Mol. Struct. **18**, 337 (1973).

[24] P. N. Schatz and D. F. Hornig, J. Chem. Phys. **21**, 1516 (1953).

[25] Research Inorganic Chemicals, Product Information.

[26] V. M. Agranovich, in *Optical Properties of Solids*, edited by Abeles, (North–Holland, Amsterdam, 1972) Chap. 6, and V. M. Agranovich and V. L. Ginzburg, *Spatial Dispersion in Crystal Optics and the Theory of Excitons* (Wiley–Interscience, New York, 1965).

[27] R. Bougon and P. Rigny, C. R. Acad. Sci. C **263**, 1321 (1966).