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Fine structure of the asymmetric stretching vibration of dispersed oxygen in monoisotopic germanium

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Dispersed oxygen in Ge leads to the formation of Ge_2O "quasimolecules" whose asymmetric stretching mode (ν_3), exhibits a remarkable, temperature-dependent fine structure when examined under the ultrahigh resolution of a Fourier-transform spectrometer. The large number of sharp lines observed arises from the coupling of ν_3 with the low-energy symmetric bending ν_2 mode; the thermal population of the ν_2 levels, together with the shifts associated with the isotopes of Ge in their natural abundances, underlie its fine structure and temperature dependence. By incorporating oxygen in monoisotopic ^{70}Ge, ^{73}Ge, ^{74}Ge, or ^{76}Ge, the excitation spectrum of the $\nu_2+\nu_3$ coupling is *selectively* simplified. From the temperature dependence of the intensities of the lines in the fine structure, the energies of the ν_2 levels are deduced. The ^{18}O counterpart of the $\nu_2+\nu_3$ coupling excitation has been observed and a consistent interpretation of the ν_2 levels as well as the shifts of the $\nu_2+\nu_3$ coupling excitations associated with any isotopic combination of oxygen and Ge is obtained by using an interaction mass $m'=23.1$ amu and a Ge-O-Ge bond angle $2\alpha=111°$.

I. INTRODUCTION

In silicon (Si) and germanium (Ge) grown by the Czochralski method, oxygen from the silica (quartz) crucible enters the crystal interstitially. Kaiser, Keck, and Lange[1] discovered that oxygen is introduced into Si and Ge in this manner on the basis of the infrared absorption bands around 9 μm in Si and ~ 11.7 μm in Ge, with strengths linear in the dispersed oxygen concentration deduced from vacuum fusion analysis. Consistent with the lower melting point and lower oxygen affinity of Ge and hence a lower extraction of oxygen from the quartz crucible, the intensity of the 11.7-μm band in crucible-grown Ge is two orders of magnitude smaller than that of the corresponding 9-μm band in crucible-grown Si. The 11.7-μm band in Ge is seen with sufficient intensity for quantitative study only in crystals deliberately doped with oxygen. The 9-μm band in Si is absent in crystals grown by the floating-zone technique. The 9-μm band in Si and the 11.7-μm band in Ge are ascribed to stretching vibrations of the Si-O (Ge-O) bonds of Si_2O (Ge_2O) "quasimolecules." Kaiser[2] reported dramatic changes in the electrical and optical properties of heat-treated Si samples. It has been established that heat treatment well below the melting point results in the formation of donors involving four oxygens (referred to as "thermal" donors) which affect the electrical behavior of Si (Ref. 2) and Ge.[3] Heat treatment at a still higher temperature produces colloidal clusters of oxygen and, finally, close to the melting point, a redispersion of oxygen as isolated centers. Thus the heat treatment can cycle dispersed oxygen to thermal donors to colloidal clusters and back to dispersed oxygen.[2]

When oxygen enters Si or Ge lattices interstitially, the bond between two adjacent Si or Ge atoms is broken and reconstituted with two Si-O or Ge-O bonds, respectively. The resulting Si_2O or Ge_2O "quasimolecule" has three normal modes of vibration: (1) the symmetric stretching mode ν_1, (2) the symmetric bending mode ν_2, and (3) the asymmetric stretching mode ν_3. In Si, infrared-absorption bands at 30, 515, and 1136 cm^{-1} (~ 9 μm) have been observed and assigned to the ν_2, ν_1, and ν_3 modes of the Si_2O quasimolecule, respectively.[4-11] In Ge, absorption bands have been observed[3,12,13] at ~ 855 (11.7-μm band) and 1270 cm^{-1}, with the 11.7-μm band being assigned to the ν_3 mode of the Ge_2O quasimolecule; while the intensity of the 1260-cm^{-1} band is proportional to that of the one at 855 cm^{-1}, the precise vibrational mode associated with the former has yet to be established.[3] Both the 9-μm band in Si and the 11.7-μm band in Ge display an extraordinary temperature-dependent fine structure as a consequence of two effects: (1) coupling of the ν_3 and ν_2 modes, first proposed by Bosomworth *et al.*[9] in connection with dispersed oxygen in Si and more recently analyzed in detail by Yamada-Kaneta, Kaneta, and Ogawa;[14,15] and (2) the shifts of the ν_3 mode associated with the different isotopic combinations of the two Si (Ge) atoms in the Si_2O (Ge_2O) quasimolecules, as first identified by Pajot and co-workers.[7,13]

Si has three stable isotopes whose natural abundances are listed in Table I;[16] hence for a given oxygen isotope, there are five *distinct* ways of constructing the Si_2O quasimolecule, $^{29}Si_2O$ and ^{28}Si-O-^{30}Si being considered equivalent in this counting. In contrast, Ge has five naturally abundant isotopes (Table I) and hence there are 11 *distinct* choices for the two Ge isotopes in a Ge_2O quasimolecule. Also, unlike Si, where ^{28}Si is much more abundant than ^{29}Si and ^{30}Si, the Ge isotopes occur with com-

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TABLE I. Natural isotopic abundances of oxygen, silicon, and germanium (representative isotopic compositions in Ref. 16).

Oxygen		Silicon		Germanium	
isotope	abundance (%)	isotope	abundance (%)	isotope	abundance (%)
^{16}O	99.762	^{28}Si	92.23	^{70}Ge	21.23
^{17}O	0.038	^{29}Si	4.67	^{72}Ge	27.66
^{18}O	0.2	^{30}Si	3.10	^{73}Ge	7.73
				^{74}Ge	35.94
				^{76}Ge	7.44

parable abundances. As a result, at very low temperatures, the ν_3 mode of the Ge_2O quasimolecule exhibits a complex spectrum (with as many as 44 sharp lines within a 5-cm^{-1} range) associated with the 11 distinct isotopic combinations of the two Ge atoms; indeed, a considerable simplification occurs when oxygen is dispersed in monoisotopic ^{74}Ge as demonstrated by Khirunenko *et al.*[17]

We have successfully grown monoisotopic ^{70}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge in which oxygen was deliberately incorporated. This has enabled us to address the fascinating problem of the fine structure of the ν_3 mode of Ge_2O quasimolecules with the very high resolution of a Fourier-transform spectrometer. In the present paper we report the results of the ultrahigh resolution measurements over a series of temperatures, and discuss the results in terms of the coupling of the ν_2 and ν_3 modes. The case of Si_2O quasimolecules is compared and contrasted.

II. EXPERIMENTAL PROCEDURE

Infrared-absorption measurements were performed on a BOMEM DA.3 Fourier-transform spectrometer[18] capable of an unapodized maximum resolution of 0.0026 cm^{-1}. An unapodized resolution of 0.015 cm^{-1} was employed in all our measurements, and the signal-to-noise ratio was improved by coadding each spectrum 15 times. A HgCdTe (Ref. 19) photoconducting detector ($D^* > 2\times10^{10}$ cm Hz$^{1/2}$/W) operating at liquid-nitrogen temperature was used as the detector. A variable-temperature stainless-steel optical cryostat was used for measurements over the desired temperature range.[20] The temperature of the sample was monitored with a calibrated thermometer installed at the sample mount and controlled by an automatic temperature controller, allowing the sample to be maintained at any desired temperature between 1.8 K and room temperature with an accuracy of 0.1 K. Optical access into the cryostat was provided by a pair of *o*-ring sealed outer, room-temperature, CsI windows and a pair of epoxy-sealed inner, low-temperature, *cleartran* (ZnS) windows.

The isotopically enriched oxygen-doped Ge crystals were grown using the specially developed vertical Bridgman technique described in Ref. 21. All samples were grown in carbon-smoke-coated split graphite crucibles with a long, thin seeding section. A continuous flow of N_2 gas, saturated with water vapor at room temperature, was maintained throughout the growth process in order to incorporate oxygen into the crystals. For the absorption measurements, the optical surfaces of the samples were prepared by grinding with carborundum of successively finer grit, followed by a polish with 3-μm diamond paste and a suspension of 0.05-μm alumina in distilled water. The excitation spectra were recorded in the temperature range from 1.8 K to room temperature.

III. THEORY

A nonlinear symmetrical triatomic molecule X_2Y has three normal modes of vibration[22] labeled ν_1, ν_2, and ν_3, as shown in Fig. 1(a). The theoretical formulation of the problem of the normal modes of the Si_2O (Ge_2O) quasi-

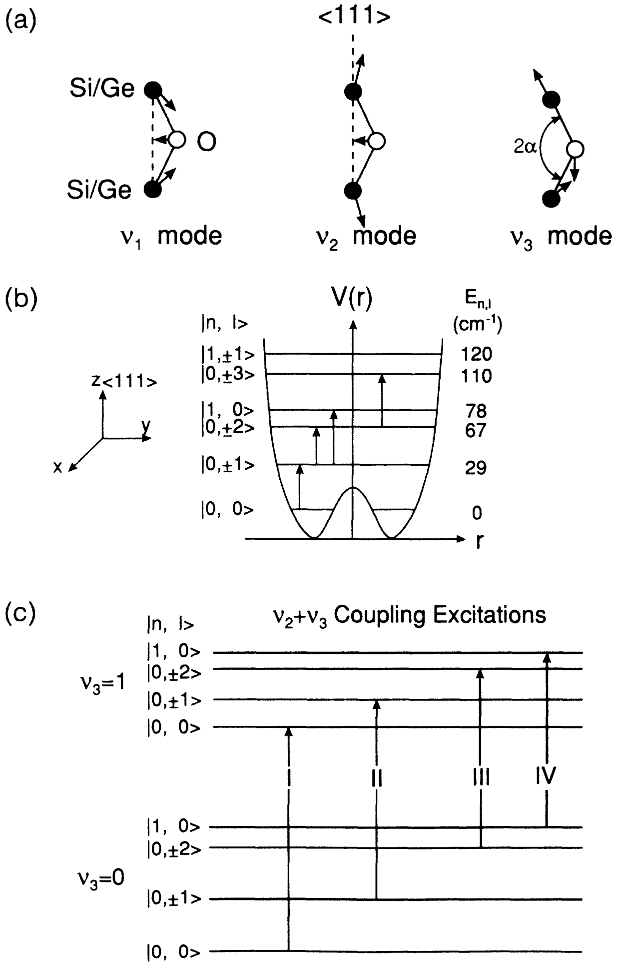

FIG. 1. (a) The configuration of interstitial oxygen in Si(Ge) showing the three normal modes of the Si_2O(Ge_2O) quasimolecules. (b) The phenomenological potential of Bosomworth *et al.* (Ref. 9) for the ν_2 mode. The states $|n,l\rangle$ are given by the central force labeling of Bosomworth *et al.* where $n(=0,1,2,\ldots)$ is the principal quantum number describing the radial dependence of the wave function, and l $(=0,\pm1,\pm2,\ldots$ for each $n)$ describes its angular dependence. The sequence of ν_2 levels $|n,l\rangle$ shown here is that determined experimentally for Si_2O. (c) $\nu_2+\nu_3$ coupling excitations responsible for the fine structure of the ν_3 mode in Si.

molecule and their coupling interactions which lead to the unusual temperature-dependent fine structure of the ν_3 mode has been developed by Bosomworth *et al.*[9] in the context of dispersed oxygen in Si. They reported the ν_2 levels of the Si_2O quasimolecule in the far-infrared $\sim 30\ cm^{-1}$ and were able to account for the observed spectrum by considering only the *x*-*y* motion of the oxygen atom [Fig. 1(b)] in a phenomenological potential

$$V=\tfrac{1}{2}m\omega^2r^2+A\exp\left[-\frac{qm\omega}{\hbar}r^2\right] \tag{1}$$

where r is the distance of the oxygen from the $\langle 111\rangle$ Si-Si axis, m is the mass of the oxygen atom, and the parameters A (representing the height of the potential barrier on the Si-Si axis restricting the *x*-*y* motion of oxygen), ω, and q are determined by comparison with experiment.[23] They proposed that the temperature-dependent fine structure of the ν_3 mode of the Si_2O quasimolecule at 9 μm is the result of a coupling interaction between the one-dimensional simple harmonic ν_3 mode and the two-dimensional perturbed low-energy ν_2 mode.[24] Due to this coupling, the spacings between the energy levels of ν_2 in the first excited state of ν_3 are smaller than the corresponding spacings in the ground state of ν_3, as shown schematically in Fig. 1(c), the sequence of ν_2 levels being consistent with that determined experimentally for Si_2O quasimolecules. As a result, the coupling excitations labeled I, II, III, and IV (in decreasing order of energy) for each isotopic combination of Si_2O cause the fine structure of the 9-μm band. The temperature dependence of this fine structure is a consequence of the thermalization of the low-energy ν_2 levels from which the $\nu_2+\nu_3$ coupling excitations originate.

More recently, Yamada-Kaneta, Kaneta, and Ogawa[14,15] have quantified the coupling interaction by formulating the Hamiltonian for the problem as the sum of the low-energy ν_2 mode with a phenomenological potential $\alpha r^2+\beta r^4$, the one-dimensional (1D) simple harmonic ν_3 mode, and an anharmonic coupling between them as given in Eq. (5) of Ref. 14. In this scheme, the energy levels of ν_2 and ν_3 can be determined fully in terms of four independent parameters which, in the notation of Ref. 14, are α and β, characterizing the renormalized potential for the ν_2 mode; $\omega_{A_{2u}}$, the bare frequency of the ν_3 vibration; and $g_{A_{2u}}$, the coupling interaction strength. In this model, the parameter $A_{\rm non}=\alpha(2m/\beta^2\hbar^2)^{1/3}\rightarrow+\infty$ or $-\infty$ describes the ν_2 mode as 2D simple harmonic oscillation or rigid rotation, respectively; for $A_{\rm non}<0$, the normalized height of the potential barrier on the $\langle 111\rangle$ axis is $A_{\rm non}^2/4$.

In addition to the coupling interaction, the isotopic shift of the ν_3 mode with the appropriate Si or Ge isotopes has to be included in order to fully account for its observed fine structure. For a nonlinear symmetric triatomic molecule X_2Y with an *X*-*Y*-*X* bond angle of 2α, the isotopic shift of ν_3 when both end atoms X of mass M_x are replaced by the same isotope of mass $M_{x'}$ and atom Y of mass M_y is replaced by its isotope of mass $M_{y'}$ is given by[25]

$$\left[\frac{\nu_3'}{\nu_3}\right]^2=\frac{M_xM_y(M_{y'}+2M_{x'}\sin^2\alpha)}{M_{x'}M_{y'}(M_y+2M_x\sin^2\alpha)}\ . \tag{2}$$

For inequivalent isotopic substitutions of the two end atoms, Pajot and co-workers[6,13] have demonstrated that the asymmetric quasimolecule ${}^{M_1}X\text{-}Y\text{-}{}^{M_2}X$ is equivalent to ${}^{M_3}X_2Y$, where M_3 is the arithmetic mean of M_1 and M_2, the approximation being valid as long as $|M_1-M_2|/M_3\ll 1$. Pajot and Clauws[13] have also reported that Eq. (2) yields a better fit to experimental results if an interaction mass m' is added to the Si (Ge) mass to *empirically* account for the interaction between the Si_2O (Ge_2O) quasimolecules and the host crystal.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the infrared-absorption spectrum of dispersed oxygen in natural Ge at 297 and 13.5 K. At 297 K only a broad absorption band is seen, whose peak position corresponds to the energy of a $\nu_2+\nu_3$ coupling transition originating from the thermally averaged ν_2 level in the ground state of ν_3, and terminating at the thermally averaged ν_2 level in the first excited state of ν_3. As the temperature is lowered, the absorption band sharpens, shifts to higher energy, and displays an extraordinary fine structure. Unlike the case of Si_2O quasimolecules where the excited ν_2 levels have negligible thermal population below ~ 15 K, the ν_2 levels of the Ge_2O quasimolecules are much more closely spaced, thus requiring very low temperatures to significantly depopulate them. Figure 3(a) shows the spectral range 860.8–864.2 cm^{-1} for natural Ge at 2.03 K. Even at this low temperature as many as 22 sharp lines are resolved, and by 6 K 38 lines appear due to the increased population of excited ν_2 levels from which more coupling transitions originate. In comparison, Fig. 3(b) shows the enormous simplification which occurs when oxygen is

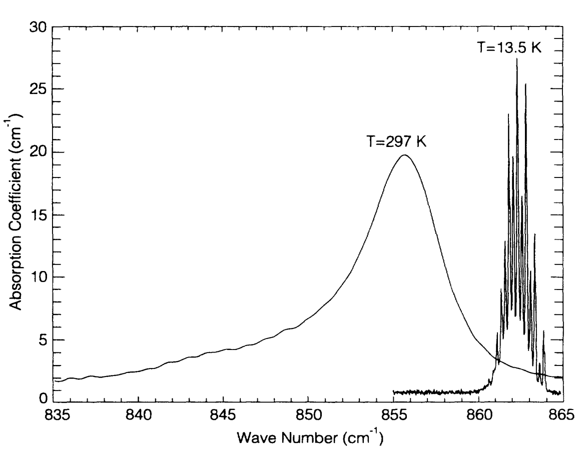

FIG. 2. Absorption spectrum of dispersed oxygen in natural Ge showing the shift of the 11.7-μm band to higher energy, and the development of a fine structure associated with the $\nu_2+\nu_3$ coupling excitations of the Ge_2O quasimolecules at lower temperatures.

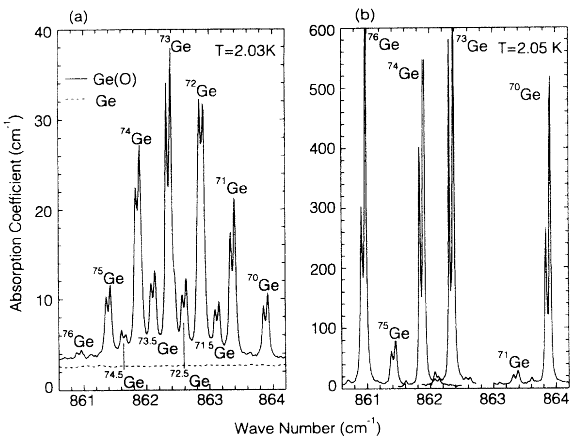

FIG. 3. (a) Spectrum of the Ge_2O quasimolecules in natural Ge at 2.03 K showing the complex fine structure arising from a pair of $\nu_2+\nu_3$ coupling excitations (I and II) associated with each of the 11 distinct isotopic combinations of the two Ge atoms in the Ge_2O quasimolecule as identified by the average Ge isotopic mass for each pair of lines. Shown by the dashed line for comparison is the spectrum of oxygen free Ge in this spectral range. (b) The superposition of the corresponding excitations in monoisotopic ^{70}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge in which oxygen was deliberately incorporated. The pairs labeled ^{71}Ge and ^{75}Ge are due to traces of ^{72}Ge in ^{70}Ge and ^{74}Ge in ^{76}Ge, respectively.

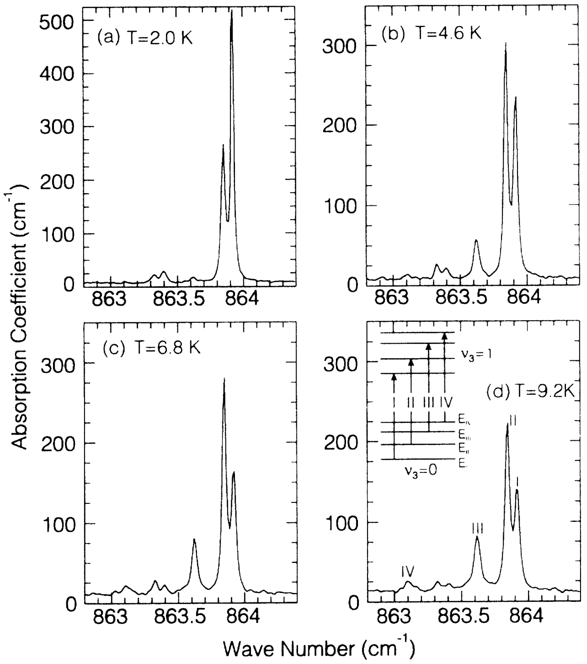

FIG. 4. Temperature dependence of the $\nu_2+\nu_3$ coupling excitations in ^{70}Ge. The coupling excitations are identified in the inset in (d) and the quantum numbers n and l describing the ν_2 levels from which these excitations originate are given in Table II. The temperatures are accurate to ±0.1 K.

dispersed in monoisotopic Ge. Due to the asymmetric combinations possible in natural Ge, e.g., ^{73}Ge-O-^{76}Ge with average mass number $M_{\rm avg}=74.5$, its spectrum has many more features than that expected from a mere superposition of the spectra of the monoisotopic samples. Note that labels such as $^{73.5}$Ge indicate only the averaged Ge mass number, not that of a stable isotope. Thus an analysis of the fine structure of the ν_3 mode of the Ge_2O quasimolecule is more straightforward in monoisotopic Ge. Even in the highly enriched specimens, traces of residual isotopes lead to features such as those labeled ^{71}Ge and ^{75}Ge.

Figure 4 shows the temperature dependence of the $\nu_2+\nu_3$ coupling excitations of the Ge_2O quasimolecule in ^{70}Ge. The lines labeled I, II, III, and IV in Fig. 4(d) are attributed to the coupling transitions from the ν_2 levels in the ground state of ν_3, as shown in the inset. The intensities of the transitions labeled II, III, and IV increase with temperature due to the increasing thermal population of the excited ν_2 levels from which these transitions originate; thus the temperature dependence of the intensities can be used to determine E_i, $i=$II, III, and IV, the energies of the excited ν_2 levels in the ground state of ν_3. More specifically, the intensity A_i of a $\nu_2+\nu_3$ coupling excitation originating from a ν_2 sublevel of energy E_i is proportional to its population n_i when in thermal equilibrium, viz.,

$$A_i=C_i n_i=C_i\frac{e^{-E_i/kT}}{\sum_j g_j e^{-E_j/kT}}\ , \tag{3}$$

where g_j is the degeneracy of level j, and C_i is a constant of proportionality incorporating the degeneracy of level i. Taking the ground state E_I of ν_2 as the zero of energy, we obtain

$$\ln\left[\frac{A_i}{A_I}\right]=\text{const}-\frac{E_i}{kT}\ ; \tag{4}$$

thus the slope of $\ln(A_i/A_I)$ vs $1/T$ yields E_i, $i=$II, III, and IV. The intensities of the coupling excitations in the different monoisotopic samples at each temperature was obtained by fitting Lorentzians to the excitation lines and integrating the area under the fitting curves. The data from all the Ge isotopes were used to compute a common slope (E_i) for each ν_2 level, because within the accuracy of the measurements any small isotopic shift of the ν_2 levels could not be detected. Figure 5 shows such a plot for $E_{\rm III}$; the values for $E_{\rm II}$, $E_{\rm III}$, and $E_{\rm IV}$ obtained in this manner are listed in Table II. As can be seen, $E_{\rm I}$, $E_{\rm II}$, and $E_{\rm III}$ are proportional to l^2, $l=0$, 1, and 2, as in the rotational levels of a rigid rotator with

$$E_l=\frac{\hbar^2}{2\mu r_0^2}l^2\ , \tag{5}$$

where $\mu=2(M_{\rm Ge}+m')M_{\rm O}/[2(M_{\rm Ge}+m')+M_{\rm O}]$ is the reduced mass of the Ge_2O quasimolecule incorporating the Ge interaction mass m', and r_0 is the distance of O from the Ge-Ge axis. This picture is indicative of a very high potential barrier, centered on the Ge-Ge axis, re-

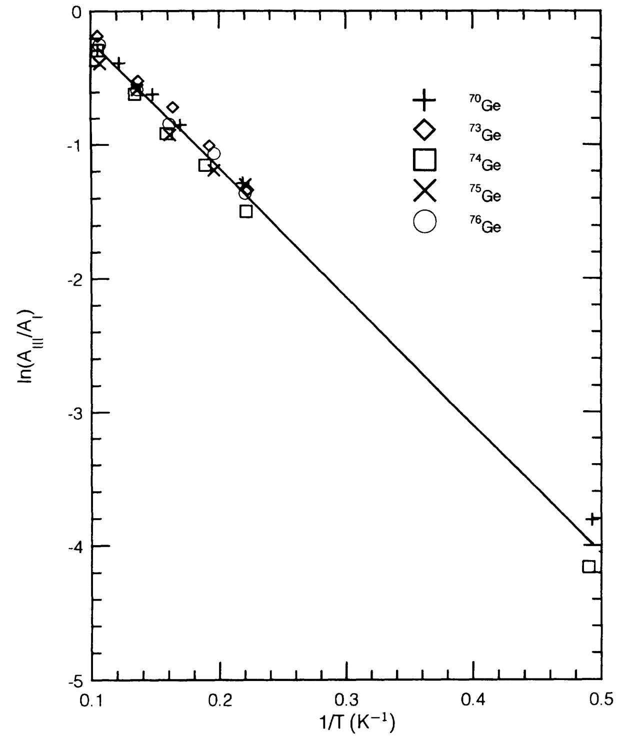

FIG. 5. Plot of ln($A_{\rm III}/A_{\rm I}$) vs $1/T$ [Eq. (4)] with data from the different Ge isotopes. A linear least-squares fit yields $E_{\rm III}=0.82\pm0.03$ meV.

stricting the radial motion of oxygen perpendicular to the Ge-Ge axis, and corresponds to the case $A_{\rm non}\rightarrow-\infty$ in the model of Yamada-Kaneta, Kaneta, and Ogawa.[14] However, $E_{\rm IV}$ departs from 1.8 meV ($=3^2\times0.2$ meV); this departure can be attributed to the $l=\pm3$ degeneracy being lifted by the sixfold crystal potential due to the six second-nearest Ge atoms.

The positions of the $\nu_2+\nu_3$ coupling excitations are listed in Table III. Equations (2) and (5) can now be used to simultaneously solve for m' and α, a best fit for both the ν_2 levels and the $\nu_2+\nu_3$ coupling excitations being obtained with $m'=23.1$ amu and $\alpha=55.5°$. It is assumed that the Ge-Ge distance in the Ge$_2$O quasimolecule is unchanged from its value of 2.449 Å in the Ge lattice. With these estimates for α and m' the deviation of theory from experiment is not more than 0.03 cm^{-1} in the worst case. The calculated positions of those lines either obscured by a strong line or too weak to be observed are given in brackets in Table III.

TABLE II. Energy levels of ν_2 in the coupled $\nu_2+\nu_3$ ground state. The quantum numbers for $|n,l\rangle$ are obtained from the model of Yamada-Kaneta, Kaneta, and Ogawa (Ref. 14) in the limit $A_{\rm non}\rightarrow-\infty$ corresponding to the case of a rigid rotator.

$\|n,l\rangle$	Energy (meV)
$\|0,0\rangle$	$E_{\rm I}=0$
$\|0,\pm1\rangle$	$E_{\rm II}=0.20\pm0.01$
$\|0,\pm2\rangle$	$E_{\rm III}=0.82\pm0.03$
$\|0,\pm3\rangle$	$E_{\rm IV}=1.49\pm0.16$

TABLE III. Observed $\nu_2+\nu_3$ coupling excitation energies (in cm^{-1}) of the different Ge$_2$O quasimolecules at 4.5 K. $M_{\rm avg}$ represents the average isotopic mass number of the two Ge atoms in the Ge$_2$O quasimolecule. The frequencies are accurate to ±0.003 cm^{-1}, and the numbers in brackets represent values calculated from Eq. (2) with $m'=23.1$ amu, $\alpha=55.5°$, and the positions of the lines of ^{70}Ge, but not identified experimentally.

	Transition			
$M_{\rm avg}$	I	II	III	IV
70	863.918	863.846	863.620	863.105
71	863.401	863.334	863.095	(862.590)
71.5	863.153	863.089	(862.850)	(862.335)
72	862.910	862.846	862.623	(862.085)
72.5	862.629	862.564	(862.350)	(861.836)
73	862.384	862.315	862.091	861.600
73.5	862.137	862.073	(861.860)	(861.346)
74	861.903	861.835	861.611	861.118
74.5	861.672	861.605	(861.379)	(860.865)
75	861.428	861.365	861.137	(860.629)
76	860.976	860.910	860.689	860.199

It is of interest to note that oxygen has three stable isotopes: ^{16}O, ^{17}O, and ^{18}O, occurring with natural abundances of 99.762%, 0.038%, and 0.2%, respectively. Thus the $\nu_2+\nu_3$ coupling excitations associated with ^{18}O at 818 cm^{-1} will be ~500 times weaker than its ^{16}O counterpart at 862 cm^{-1}. In fact, by incorporating oxy-

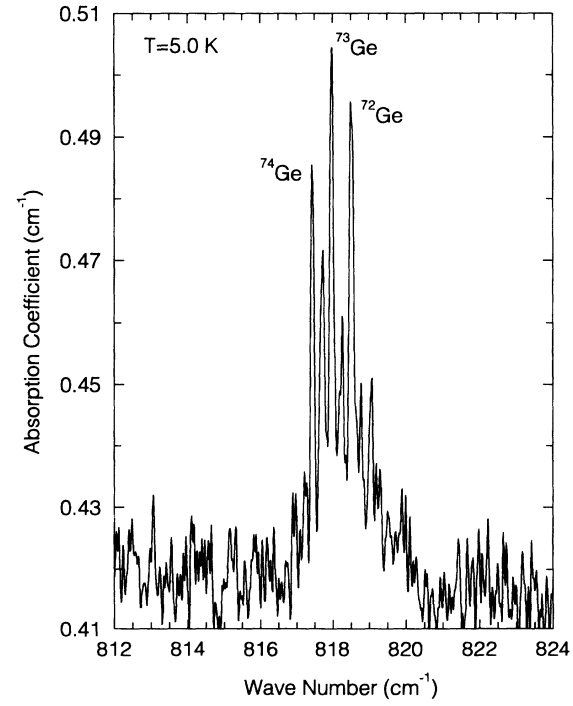

FIG. 6. The $\nu_2+\nu_3$ coupling excitation due to ^{18}O in natural Ge. A 5-mm-thick sample was used and the resolution was 0.03 cm^{-1}.

TABLE IV. Observed and calculated $\nu_2+\nu_3$ coupling excitation energies (in cm^{-1}) associated with ^{18}O in natural Ge. The observed energies are accurate to $\pm 0.01\ \mathrm{cm}^{-1}$. The calculated values were obtained using Eq. (2) with $m'=23.1$ amu and $\alpha=55.5°$.

	I		II	
M_{avg}	Obs.	Calc.	Obs.	Calc.
70	819.63	819.60		819.54
71	819.09	819.06	819.03	819.00
71.5	818.79	818.79	818.74	818.73
72	818.55	818.52	818.48	818.46
72.5	818.26	818.26	818.19	818.20
73	818.00	origin	817.94	origin
73.5	817.72	817.74	817.67	817.68
74	817.46	817.49	817.41	817.43
74.5		817.24		817.18
75	816.97	816.99	816.90	816.93
76		816.50		816.44

gen enriched with 65% ^{18}O in Ge, Whan[26] reported corresponding significant increase in the intensity of the 818-cm^{-1} band; the low resolution of the measurement and the sample temperature of 10 K prevented the observation of a fine structure. We have observed the fine structure of the $\nu_2+\nu_3$ coupling excitations associated with ^{18}O in a 5-mm-thick sample of natural Ge. Due to the extremely small natural abundance of ^{18}O, these lines are very weak as can be seen in Fig. 6, the spectrum being coadded 150 times with a resolution of $0.03\ \mathrm{cm}^{-1}$. The positions of these transitions are listed in Table IV. Using the above estimates of m' and α in Eq. (2) with the lines of $^{73}Ge_2{}^{18}O$ as the origin, the calculated isotopic shifts are again within $0.03\ \mathrm{cm}^{-1}$ of those observed. The $\nu_2+\nu_3$ excitation I of $^{73}Ge_2{}^{18}O$, calculated from that of $^{73}Ge_2{}^{16}O$, is at $818.5\ \mathrm{cm}^{-1}$, i.e., within $0.5\ \mathrm{cm}^{-1}$ of the observed value of $818\ \mathrm{cm}^{-1}$. In all these cases, however, the error in the predicted isotopic shift is less than 1% of the experimentally measured shift.

V. CONCLUSION

The present investigation demonstrates the *selective* simplification in the fine structure of the $\nu_2+\nu_3$ coupling excitations of the Ge_2O quasimolecules when oxygen is dispersed in monoisotopic ^{70}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge. The simplification of the fine structure in the monoisotopic samples permits a detailed analysis of the temperature dependence of the coupling excitations. An ultrahigh resolution ($0.009\ \mathrm{cm}^{-1}$) measurement at 4.5 K yields a typical full width at half maximum (FWHM) of $\sim 0.02\ \mathrm{cm}^{-1}$ for the coupling excitations I and II, and $\sim 0.03\ \mathrm{cm}^{-1}$ for the coupling excitations III and IV. From the temperature dependence of the intensities of the coupling excitations we have deduced the low-energy ν_2 levels. These energies ($E_{\mathrm{II}}=0.2$ meV, $E_{\mathrm{III}}=0.82$ meV, and $E_{\mathrm{IV}}=1.49$ meV) are in reasonable agreement with the superconducting-tunneling measurements of Gienger, Glaser, and Laßmann[27] ($E_{\mathrm{II}}=0.18$ meV, $E_{\mathrm{III}}=0.67$ meV, and $E_{\mathrm{IV}}=1.37$ meV) and can be understood in terms of the levels of a rigid rotator. However, the value for $l=\pm 3$, i.e., E_{IV}, in both sets of measurements does not fit Eq. (5); the deviation can be explained on the basis of the splitting of the $l=\pm 3$ ($\Delta l=6$) levels by a sixfold crystal potential due to the six second-nearest Ge atoms as suggested by Gienger, Glaser, and Laßmann. An interaction mass $m'=23.1$ amu and a Ge-O-Ge bond angle $2\alpha=111^0$ consistently account for the low-energy ν_2 levels as well as the isotopic shifts of the $\nu_2+\nu_3$ coupling excitations associated with any isotopic combination of oxygen and Ge to within 1%. Had the ν_2 levels been measured directly in the very far-infrared, a much better theoretical fit could be obtained with the model of Yamada-Kaneta, Kaneta, and Ogawa which has worked well for the Si_2O quasimolecules. The limitations of our spectrometer did not permit us to make such measurements in the relevant spectral range, i.e., $1-10\ \mathrm{cm}^{-1}$.

It is interesting to contrast the coupling excitations of Si_2O quasimolecules shown in Fig. 7 with those of Ge_2O quasimolecules; striking differences are immediately apparent: (1) Much higher temperatures ~ 20 K are required to significantly populate the excited ν_2 levels of Si_2O, as compared to ~ 2 K for Ge_2O (Fig. 3), reflecting the much larger separation of the ν_2 levels of Si_2O. (2) At 6 K the coupling excitations of Si_2O quasimolecules typically have a FWHM of $0.5-2\ \mathrm{cm}^{-1}$, while those of Ge_2O range between 0.02 and $0.04\ \mathrm{cm}^{-1}$ i.e., the lines in Ge are 25–50 times sharper. (3) In both Si and Ge, for each coupling transition there are as many lines in the spectrum as there are distinct isotopic combinations of the two Si or Ge atoms. In Si, all the isotopic counterparts for each coupling excitation occur together, whereas in Ge the coupling excitations I and II associated with a given isotopic combination of Ge atoms occur together. This is simply a consequence of the much smaller spacings of the ν_2 levels of the Ge_2O quasimolecules. The ν_1 symmetric stretching vibration of the Si_2O quasimolecule has been reported at $515\ \mathrm{cm}^{-1}$, and the assignment confirmed by stress-induced dichroism measurements.[10] The proximi-

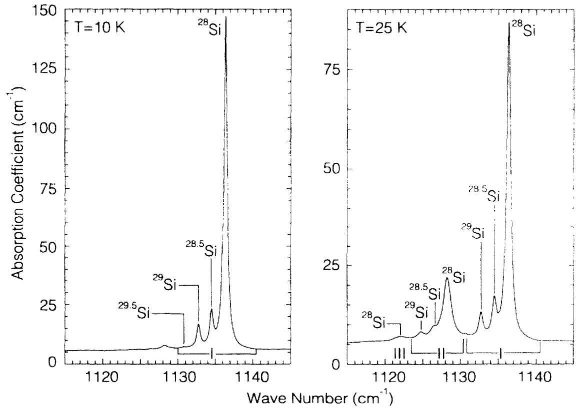

FIG. 7. The $\nu_2+\nu_3$ coupling excitations of Si_2O quasimolecules at 10 and 25 K showing the relatively higher temperatures required to populate excited ν_2 levels $|0,\pm 1\rangle$ and $|0,\pm 2\rangle$ from which II and III originate.

ty of this mode to the zone-center Raman line of Si (Ref. 28) is responsible for its asymmetric line shape,[8] a clear indication of the resonance of a localized vibration with the phonon continuum. A band associated with Ge_2O due to similar vibration is expected around 330 cm^{-1},[3] close to the zone-center Raman line of Ge ~ 304 cm^{-1}.[29] We have not been able to observe this band, presumably due to its small oscillator strength.

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