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Infrared and microwave absorption in amorphous Ge

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The magnitude of the far-infrared ($\lesssim 150\ \mathrm{cm}^{-1}$) and microwave absorption in evaporated films of amorphous Ge depends on the deposition rate. The intrinsic absorption not attributable to voids or dangling bonds indicates a large decrease at the lowest frequency in the matrix elements which couple the radiation to the phonons. A low-frequency absorption tail, similar to that observed in other amorphous materials, is observed in amorphous Ge. This absorption is temperature independent and proportional to the square of the frequency. A thermally activated conductivity is observed at the higher temperatures in the microwave region. This conductivity has the same activation energy as the dc conductivity but is of greater magnitude.

I. INTRODUCTION

In amorphous Ge and Si infrared absorption and Raman scattering are observed at frequencies at which they are forbidden by selection rules in the crystalline modifications. These phenomena are presumably induced by the long-range disorder in the amorphous materials. Both the Raman[1] and the infrared[2,3] spectra of amorphous Ge and Si have been interpreted as fundamental properties of the amorphous forms which reflect primarily the densities of phonon states. Although this interpretation is generally consistent with the existing Raman and infrared data, the data presented in this article indicate that the infrared spectra (below $\sim 150\ \mathrm{cm}^{-1}$) of evaporated films of amorphous Ge are neither independent of sample preparation conditions (evaporation rate) nor exclusively a function of the phonon density of states. There is also evidence that the presence of voids strongly affects the magnitude of the infrared absorption at the lower frequencies ($\sim 100\ \mathrm{cm}^{-1}$).

Data of the present work in the microwave region indicate that several conductivity mechanisms are present, and that different mechanisms dominate at different temperatures. At high temperatures the dominant contribution is a thermally activated electronic conductivity, which can be greater in magnitude than the dc conductivity, but appears to have the same thermal activation energy. At low temperatures, a temperature-independent term approximately proportional to ν^2 remains. This term is attributed to vibrational and not to electronic processes. The frequency and temperature dependences of this contribution are identical to those observed in other amorphous materials at these frequencies.[4-6] However, unlike most bulk amorphous materials, in amorphous Ge this temperature-independent term is a strong function of sample preparation conditions. In this paper we present a detailed investigation of the infrared, far-infrared, and microwave conductivity spectra for evaporated films of amorphous Ge as functions of frequency, temperature, and sample evaporation rate. These data largely fill in the gap between the existing infrared[2,3,7,8] and ac conductivity[9-12] ($< 10^6$ Hz) measurements. In the frequency ranges where data are available, comparisons are made with Raman and neutron scattering results.[1,13] Although the general features of the conductivity spectrum in amorphous Ge are now well determined, dependences of the conductivity σ on sample preparation procedures make detailed statements impossible below 10^9 Hz. In particular, the precise behavior of the conductivity spectrum between the region where $\sigma \propto \nu$ ($\lesssim 10^7$ Hz) and the region where $\sigma \propto \nu^2$ ($\gtrsim 10^9$ Hz) remains unclear.

Section II describes the experimental procedures employed. The infrared and the microwave measurements are presented in Secs. III and IV, respectively. Section V contains a discussion of the results, and Sec. VI presents concluding remarks.

II. EXPERIMENTAL

Amorphous Ge films were prepared by thermal evaporation of high-purity Ge from a tungsten basket in a vacuum of $\sim 10^{-6}$ Torr. Films were deposited at normal incidence on clean glass substrates at three deposition rates 30, 8, and 2 Å/sec. The sample to substrate distance was 15 cm, and the substrate temperature was maintained at 300 ± 20 K. All films were determined to be amorphous by x-ray diffraction techniques, and no differences in the x-ray patterns were detected for films deposited at different rates.

For the infrared and far-infrared transmission measurements, free-standing samples of ~1 mm diam were used. These samples were flaked off the glass substrates by lightly flexing alternate corners of the substrate and lifting partially loose portions of the film with a fine-bristle brush. Samples were chosen which did not curl appreciably when removed from the substrate. This procedure constituted an attempt to minimize the effect of internal strains on the measurements. Two free-standing amorphous Ge samples were measured for each of the three film deposition rates.

Transmission samples were mounted over one hole of a matched pair of holes on a thin brass plate, which could be accurately positioned in the infrared beam using two orthogonal micrometer screws. Room-temperature far-infrared transmission measurements were performed at discrete frequencies in the range 30–130 cm^{-1} using either a pulsed water-vapor laser[14] or a pulsed molecular-gas laser[15] as the source and a cold (4.2 K) highly-doped and compensated InSb detector.[16] The molecular gas laser beam was focused on the sample holder using a quartz or polyethylene lens of sufficient focal length to ensure near normal incidence. In the frequency range from ~100 to 400 cm^{-1} room-temperature infrared transmission measurements were performed on an automated Research and Industrial Instruments Corporation (R*IIC*) interferometer (Model ES-720) system[17] and a grating monochromator was employed for measurements from 1000 to 4000 cm^{-1}.

For the microwave measurements, free-standing filaments of up to 0.5 mm width and 1 cm length were obtained using the same flexing procedure employed for the infrared samples. In some cases individual filaments or sets of filaments were inserted directly in the microwave cavities. In other cases, the amorphous Ge samples were placed in quartz tubes, and corrections were made for the dielectric loss of the quartz. Both procedures yielded identical results.

The microwave dielectric loss measurements were performed at 9, 22, 70, and 140 GHz using a cavity perturbation technique.[18,19] The dependence of the microwave absorption on temperature, incident power, and sample deposition rate were investigated at selected frequencies. Samples were introduced through a hole in the microwave cavities along the maximum electric field direction. Rectangular cavities were employed at all frequencies, except at 140 GHz where a cylindrical cavity was used. Variable temperatures (4.2–450 K) were obtained by enclosing the cavities in evacuated stainless-steel cans.

III. INFRARED MEASUREMENTS

The normalized transmission (T) through a thin disk or film of thickness d with plane parallel faces can be expressed in terms of the complex index of refraction $N=n-ik$, and the wavelength of the incident radiation λ by the usual multiple reflection formula.[20] At normal incidence the expression is

$$T=\frac{(1-R)^2(1+k^2/n^2)^2}{(e^{\beta}-Re^{-\beta})^2+4R\sin^2(\delta+\chi)}, \tag{1}$$

where R is the normalized single-surface reflectance at normal incidence given by

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2}, \tag{2}$$

and where $\tan\chi=2k/(n^2+k^2-1)$, $\beta=2\pi kd/\lambda$, and $\delta=2\pi nd/\lambda$.

When there is essentially no absorption in the film ($k\approx 0$), the transmission as given by Eq. (1) oscillates between unity and some minimum value, which depends on the reflectivity, with a period in λ^{-1} of $(2nd)^{-1}$. Thus the thickness of a film d can be determined from the period of this fringe pattern provided that n is known. The amorphous Ge samples are essentially free of absorption in the near infrared ($2000 \lesssim \lambda^{-1} \lesssim 4000$ cm^{-1}), and sample thicknesses were determined from measurements in this region assuming $n=4.25$.[2,3,3a]

The far-infrared transmission at selected frequencies for a representative film of amorphous Ge ($d=10.4$ μm, deposited at 2 Å/sec) is shown in Fig. 1 by the triangles. The solid line represents the expected transmission for an absorption free film. Similar spectra for films de-

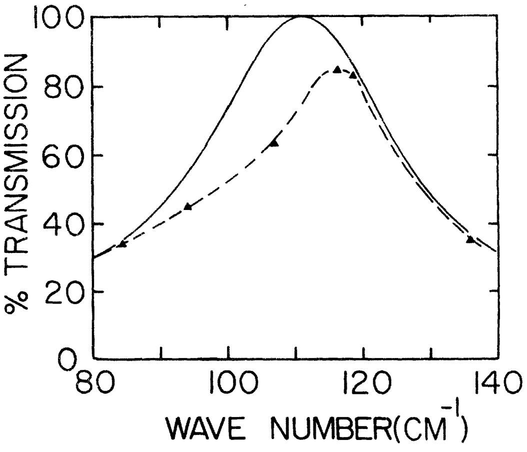

FIG. 1. Transmission as a function of frequency through a 10.4-μm-thick film of amorphous Ge evaporated at 2 Å/sec. Triangles are measured values. The solid curve represents the absorption-free transmission which was calculated as described in the text.

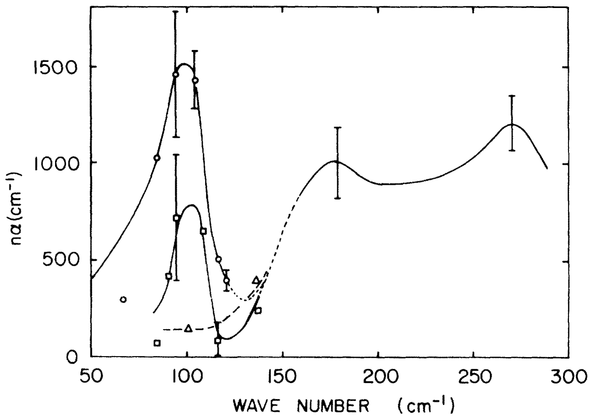

FIG. 2. Product of the index of refraction n and the absorption coefficient α as a function of frequency for amorphous Ge films evaporated at 30 Å/sec (circles), 8 Å/sec (squares), and 2 Å/sec (triangles). The data are independent of sample evaporation rate above approximately 150 cm^{-1} within the designated experimental error.

posited at 30 Å/sec were published previously.[6] The frequency dependence of the far-infrared absorption coefficient $\alpha = 2\beta/d$ can be obtained from the transmission data using Eq. (1) and the fact that n does not change appreciably with frequency. (Previous infrared absorption measurements on sputtered amorphous Ge films indicate that the total increase in n in the far infrared is less than 1% of its value in the near infrared.[2]) Two sample thicknesses were measured at each deposition rate, and the dependence of α on d was used as an internal check on the results.

Figure 2 shows the far-infrared conductivity (spectral dependence of $n\alpha$, absorption coefficient α times index of refraction n) calculated from the transmission spectra of amorphous Ge deposited at different rates. The data from 65 to 140 cm^{-1} which were taken using the molecular-gas laser, are indicated by circles, squares, and triangles for sample evaporation rates of 30, 8, and 2 Å/sec, respectively. Between 150 and 300 cm^{-1} (data taken using an interferometer with 2-cm^{-1} resolution) the data were independent of sample deposition rate within the experimental error indicated in the figure.

The error bars in Fig. 2 reflect mainly the experimental uncertainties in the measured transmission. The frequency of the first transmission maximum is well determined. Provided there is no change in the index n between 2000 and 100 cm^{-1}, the position of the first transmission maximum is given precisely by the *separation* between transmission maxima in the near infrared regardless of the value of n. Since the maximum change in n from 2000 to 100 cm^{-1} is $\lesssim 0.04$, the uncertainty in the position of the first transmission maximum is less than 1% and can be neglected. Errors attributable to the effects of diffraction were encountered below 40 cm^{-1} ($\lambda > 0.25$ mm), but are negligible at the wavelengths for which data are reported in this paper. The magnitude of the absorption-free transmission could be less than that predicted by Eq. (1), especially near the transmission maximum (for example, near 110 cm^{-1} in Fig. 1), if the surfaces of the film are not plane parallel (i.e., surface roughness). One may approximate the effects of surface roughness by measuring the absolute magnitude of the fringes in the near infrared (2000–4000 cm^{-1}) and by calculating the transmission through a slightly wedged sample provided that scattering is negligible and that the departure from planarity is small in the spectral region of interest. The average transmission through a semi-infinite wedge of minimum thickness d_0 and maximum thickness $d_0 + \Delta$ is given by (provided that $\Delta \ll \lambda/n$)

$$\bar{T} = \frac{1}{\Delta}\int_{d_0}^{d_0+\Delta} T(x)\,dx, \tag{3}$$

where $T(x)$ is given by Eq. (1). Since the absorption in the range 2000–4000 cm^{-1} is very small ($\beta < 0.01$), one may calculate the integral of (3) in the limit of zero absorption ($k = 0$ or $\beta = 0$):

$$T = (1/\kappa\delta')\{\tan^{-1}[\kappa\tan(\delta+\delta')] - \tan^{-1}(\kappa\tan\delta)\}, \tag{4}$$

where

$$\delta' = 2\pi n\Delta/\lambda < 1$$

and

$$\kappa = 4R/(1-R)^2.$$

Since the average thicknesses d_0 of all samples are >10 microns and the values of Δ estimated using Eq. (4) in the 2000–4000-cm^{-1} region are all less than 0.2 μ, then the first absorption-free transmission maximum in the far infrared (near 100 cm^{-1}) is predicted to be greater than 99%. This situation may be contrasted with the behavior observed in amorphous Ge films sputtered on silicon wedges where the far-infrared fringe maxima deviate appreciably from 100%.[2]

IV. MICROWAVE MEASUREMENTS

In the cavity-perturbation technique, the field distribution inside the microwave cavity must remain substantially unaltered when the sample is introduced along a maximum electric field direction. This condition is satisfied provided that $(\nu - \nu_0)/\nu \ll 1$ and $Q^{-1} \ll 1$, where ν_0 and ν are the unperturbed and perturbed cavity resonant frequencies, respectively, and where Q (the maximum energy stored over the average energy loss per radian) refers to the perturbed or loaded

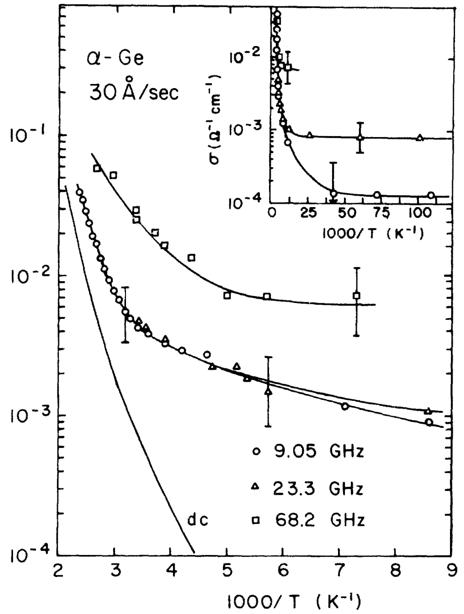

FIG. 3. Temperature dependence of the microwave conductivity in amorphous Ge films evaporated at 30 Å/sec. The solid line is the dc conductivity after Ref. 21 for films evaporated under similar conditions (50 Å/sec).

cavity. In the perturbation limit the real and imaginary parts of the dielectric constant ($\epsilon = \epsilon' - i\epsilon''$) are given by[19]

$$\epsilon' = 1 + [(\nu - \nu_0)/2\nu]\,(V/v), \tag{5}$$

$$\epsilon'' = \tfrac{1}{4}[(Q - Q_0)/QQ_0]\,(V/v), \tag{6}$$

where V and v are the volume of the cavity and the volume of the sample, respectively. These equations assume that the sample is homogeneous and isotropic.

Figure 3 shows the temperature dependence of the microwave conductivity in the temperature range from about 100 to 430 K. Data are presented at 9.05, 23.3, and 68.2 GHz for amorphous Ge deposited at the fastest rate (30 Å/sec). The inset to Fig. 3 displays the temperature dependence over an extended range (8–430 K). At the lowest temperature (below ~20 K) the conductivity is temperature independent. The dc conductivity data of Beyer and Stuke[21] for films evaporated under similar conditions (~50 Å/sec) are presented for comparison. The conductivity scale in Fig. 3 is related to the scale of $n\alpha$ in Fig. 2 by $n\alpha\,(\mathrm{cm}^{-1}) = 120\,\pi\sigma(\Omega^{-1}\,\mathrm{cm}^{-1})$.

The microwave conductivity can be written approximately in the following form:

$$\sigma(\omega, T) = \gamma\,\sigma_{\mathrm{dc}}(T) + \sigma(\omega), \tag{7}$$

where

$$\sigma_{\mathrm{dc}} = \sigma_0 e^{-\Delta E/kT},$$

$$\sigma(\omega) = \sigma_1 \omega^m, \quad m \approx 1.7.$$

At temperatures greater than 330 K, this conductivity is thermally activated with an activation energy, $\Delta E \cong 0.3$ eV, which is essentially identical to the activation energy for dc conductivity.[21] However, the magnitude of this thermally activated microwave conductivity is greater than that of the dc conductivity by a factor γ. The values of γ are not well determined because the same samples were not employed for both the dc and microwave conductivity measurements, but γ is approximately 10 at 70 GHz.

The temperature-independent term, which is the dominant contribution to the conductivity at low temperatures, scales roughly as the frequency squared, as shown in Fig. 4. These data connect smoothly with the far-infrared data previously described. Room-temperature data are also shown in Fig. 4 for comparison (circles).

For temperatures between the high and low extremes, the microwave conductivity contains an additional contribution which is not accounted for

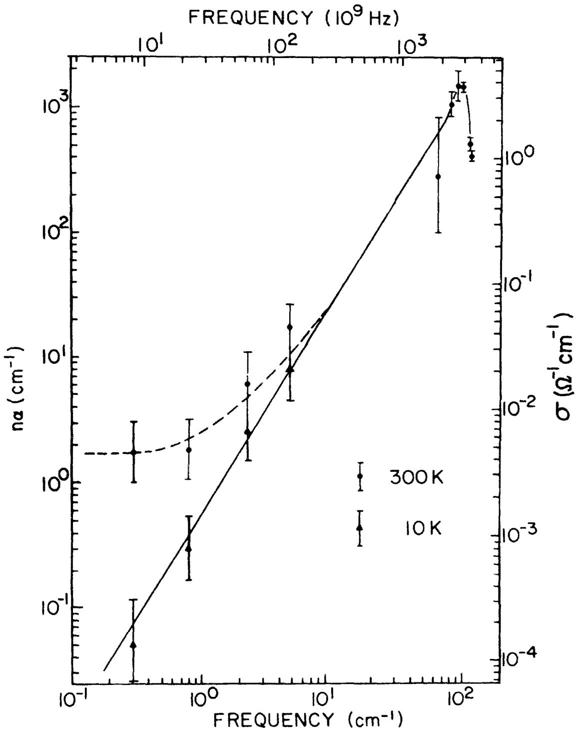

FIG. 4. Frequency dependence of the far-infrared and microwave conductivity in amorphous Ge films evaporated at 30 Å/sec. Data are presented for 300 K (circles) and 10 K (triangles). The 10-K point at 140 GHz has been extrapolated from the 300-K value by subtracting the temperature-dependent component observed at 70 GHz (see Fig. 3).

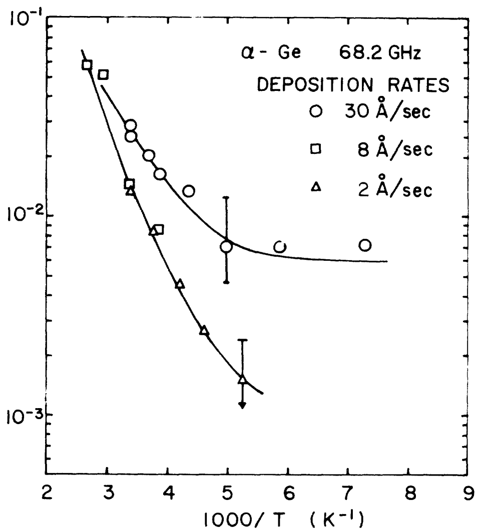

FIG. 5. Dependence of the microwave conductivity in amorphous Ge at 68.2 GHz on sample evaporation rate.

in Eq. (7). At 9 GHz where the data are most complete, this additional term can be estimated by subtracting the high-temperature thermally-activated conductivity ($\gamma\sigma_{dc}$) and the low-temperature remnant. Within experimental error, the remaining conductivity in the temperature range from ~150 to ~300 K at 9.05 GHz is thermally activated with an activation energy $\Delta\epsilon \approx 0.1$ eV which is less than that of σ_{dc}. The magnitude of this conductivity is comparable to the constant low-temperature term near 150 K. This behavior has been observed in some other amorphous materials at these frequencies,[5] and similar behavior occurs in many amorphous materials at frequencies below 10^6 Hz, where the most common explanation of the data involves a generalization of Eq. (7) that allows m to vary with temperature.[22]

As in the far infrared, the microwave conductivity depends on sample deposition rate. Figure 5 shows the temperature dependence of the conductivity at 68 GHz for films deposited at the three different rates. At high temperatures the conductivity is relatively insensitive to deposition rate. This behavior is similar to that observed in the dc measurements.[21] However, there is a strong dependence of the magnitude of the conductivity at low temperatures on deposition rate. The films with faster deposition rates show greater residual conductivity. Although the low-temperature conductivity at 70 GHz for films deposited at 2 Å/sec is below the level of detectability for the amount of sample available, an extrapolation of the data of Fig. 5 imply that this conductivity is approximately a factor of ten less than the value for films deposited at 30 Å/sec. The same factor also relates the two temperature-independent conductivities in the far infrared (see Fig. 2).

V. DISCUSSION

Differences in the infrared absorption among sputtered, evaporated, and electrodeposited amorphous Ge films were first noted by Tauc *et al.*[8] from measurements performed mainly at higher frequencies (up to 5650 cm^{-1}). These authors also first observed the disorder-induced optical-phonon peak near 270 cm^{-1} in amorphous Ge. Recent infrared measurements on sputtered films in the far infrared (50–300 cm^{-1}) also show distinct differences[2,3,7] from sample to sample as evidenced by the data in Fig. 6. This figure presents the existing data from three different laboratories on sputtered films in comparison with the data from the present experiments on films evaporated at 30 Å/sec. With the exception of the results of Prettl *et al.*,[7] the remaining three spectra are quite similar in that they all consist of three fairly broad peaks of roughly similar intensities. However, for the films evaporated at the slowest rate (2 Å/sec) in the present work, the magnitude of the low-frequency peak near 100 cm^{-1} is about a factor of five to ten smaller than that obtained by either Stimets *et al.*[3] or Brodsky and Lurio[2] while the magnitudes of the other peaks remain roughly

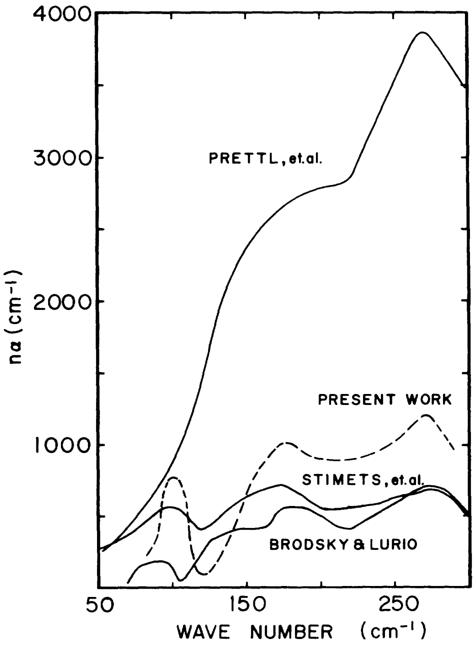

FIG. 6. Infrared absorption in amorphous Ge as measured by Prettl *et al.* (Ref. 7), Stimets *et al.* (Ref. 3), and Brodsky and Lurio (Ref. 2) on sputtered films. Data of the present work are also presented for films evaporated at 30 Å/sec.

the same. Thus, even though three of the curves (Refs. 2 and 3 and the 30-Å/sec films of the present work) of Fig. 6 have features of similar shapes and magnitudes, this agreement cannot be considered as evidence for sample-independent, intrinsic, disorder-induced absorption in amorphous Ge below 150 cm^{-1}.

It has often been argued[2,3,7] that both the Raman and infrared spectra in amorphous Ge reflect primarily the shape of the vibrational density of states and that the effect of the matrix elements is of secondary importance. The density of vibrational states in amorphous Ge has been estimated by broadening the density of states of crystalline[2] Ge and by several model calculations.[23–26] All of these estimates yield spectra which look qualitatively like the infrared spectra of Fig. 2 (with the exception of the data of Prettl *et al.*). In particular, the lowest-frequency feature, which corresponds to the crystalline TA peak, is roughly the same intensity as the two higher-frequency features. Since the magnitude of this peak is down by an order of magnitude in our slowly evaporated films, while the other features do not change significantly, we conclude that there is a strong frequency dependence of the matrix elements in the slowly evaporated films. Recent calculations[26] of the infrared absorption in amorphous Ge, which apply the Keating model to several illustrative random networks, suggest that the matrix element at the lower frequencies scales as the mean-square compression of the bonds which is proportional to ω^2. Our data on the slowly evaporated films (Fig. 2) are not consistent with the infrared absorption spectra predicted using this simple approach. In these films the intensity of the peak near 180 cm^{-1} relative to that of the peak near 90 cm^{-1} is about 10, whereas a scaling of the density of states by ω^2 yields a factor of less than about 3 for several model calculations.[26]

Since the slowly evaporated films have fewer dangling bonds and voids,[27] we contend that the absorption in these films is more representative of the intrinsic level, which is induced by the disorder alone, and not greatly enhanced by the presence of dangling bonds and voids. The resemblance of the infrared absorption spectrum to the vibrational density of states over the entire spectral region in the earlier measurements[2,3] is thus somewhat fortuitous and the coupling to infrared radiation in amorphous Ge free of dangling bonds and voids is much weaker at the lower frequencies. It is interesting to note that the weaker coupling occurs in the frequency region where acoustic phonons dominate the corresponding crystalline density of states, and conversely, that the stronger coupling occurs in the optic-phonon region.[28]

We have argued that the enhanced infrared activity at the lower frequencies in the films evaporated at the faster rates is probably due to the presence of greater numbers of voids in the films. In the sputtered films voids represent (5–10)% of the volume with a distribution of radii that peaks around 16 Å.[29] Although there are fewer voids in the slowly evaporated films than in films evaporate at faster rates, there is evidence from valence force estimates of the heat of crystallization in amorphous Ge for the presence of voids, dangling bonds, and macroscopic strains even in well annealed films.[30]

A frequency dependence of both the infrared and Raman coupling coefficients at low frequencies has been considered by several authors,[7,31,32] but no consistent explanation exists which explains both the low-frequency infrared and Raman data. The Raman scattering intensity in amorphous materials can be approximated by[33]

$$I_R \propto \omega^{-1}\, C(\omega)\, \rho(\omega)\, (n+1), \tag{8}$$

where C is the coupling constant, ρ, is the density of phonon states, and n is the Bose population factor. At high temperatures ($\hbar\omega \ll kT$), the factor $(n+1)$ is proportional to ω^{-1} and

$$I_R \propto [\rho(\omega)/\omega^2]\, C(\omega). \tag{9}$$

In the low-frequency regime the density of states is well approximated by the Debye form $[\rho(\omega) \propto \omega^2]$, and the frequency dependence of the Raman scattering intensity merely reflects the frequency dependence of the coupling coefficient $C(\omega)$. Whalley and Bertie[34] first suggested that $C(\omega)$ is proportional to ω^2 at low frequencies, and this dependence has been confirmed for amorphous Si by Lannin.[31] Although the data are perhaps less convincing for amorphous Ge,[32] the general frequency dependence of the Raman intensity is seen from Fig. 7 to be slightly less than ω^2.

Figure 7 also shows the density of states as inferred from neutron scattering measurements[13] and the infrared and microwave absorption measurements of the present work. One will note from this figure that the neutron scattering data do indicate a density of phonon states which tends toward ω^2 at low frequencies.

The absorption coefficient in disordered materials at far-infrared and microwave frequencies, $\alpha(\omega)$, can be expressed in general as a complicated average over some fluctuating disorder-induced charge of the product of a density of states times a generalized coupling coefficient.[4] To the extent that this average can be expressed as an average coupling coefficient $\langle M(\omega)\rangle$ times an average density of states $\langle \rho(\omega)\rangle$ the absorption coefficient can be approximated by

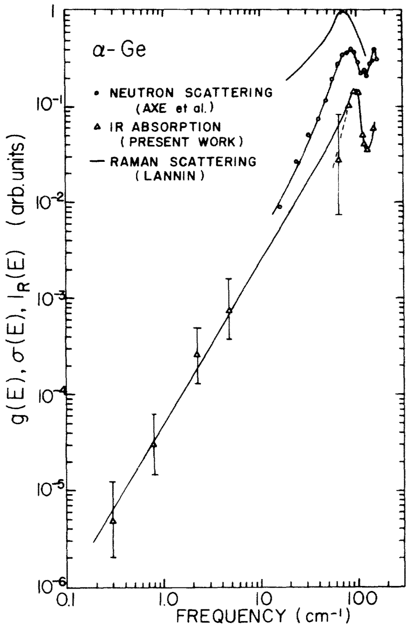

FIG. 7. Comparison of the density of states $g(E)$ as determined from neutron scattering (Ref. 13), the temperature-independent component of the far-infrared and microwave conductivity $\sigma(E)$ of the present work, and the high-temperature Raman scattering intensity (Ref. 32), $I_R(E)$ in amorphous Ge.

$$\alpha(\omega) \propto \langle \rho(\omega) \rangle \langle M(\omega) \rangle . \tag{10}$$

In the Debye regime, the frequency dependence of α is ω^2 times the frequency dependence of M. Several authors, using different model calculations, have suggested different frequency dependences for $M(\omega)$ at low frequencies.[7,34-36] Whalley[34,37] using a model of disorder induced charge fluctuations, predicts that $M(\omega)$ is proportional to ω^2 in glassy SiO_2. Bagdade and Stolen,[34] using a model of charged atoms or defects due to Schlömann[38] and Vinogradov,[39] suggest that $M(\omega)$ is constant in SiO_2 at the higher frequencies where there are no correlations between the charged defects, but that $M(\omega)$ goes as some power of ω at the lower frequencies where correlations become important. An interpretation similar to that of Bagdade and Stolen has been suggested by Amrhein and Müller[40] to explain the room-temperature microwave dielectric loss in glassy SiO_2. On the other hand, Prettl *et al.*[7] suggest that $M(\omega)$ is proportional to ω^4 at low frequencies from an expansion of M assuming plane waves in the quasicontinuous limit. All of these estimates for the frequency dependence of M are at variance with the data of Fig. 7 which suggest that in fact M is constant even at the lowest frequencies. Similar behavior has been observed in other amorphous materials.[4]

Connell[41] has suggested that over a limited frequency range 70–110 cm^{-1} near the peak at 80 cm^{-1} the infrared coupling coefficient is proportional to ω^4. Although it is difficult to refute this contention given the accuracy of the present data, such behavior is certainly not present over any extended frequency range.

Conflicting predictions for the relationship between the Raman and infrared coupling coefficients, $C(\omega)$ and $M(\omega)$, also exist.[7,34,42,43] Some model calculations suggest that $M(\omega) \propto \omega^2 C(\omega)$ at low frequencies[7,42,43] while another predicts the two coupling coefficients to have the same frequency dependence.[34] The experimental data imply that $\omega^2 M(\omega) \propto C(\omega)$. This empirical result is inconsistent with all of the above predictions, and clearly indicates the need for additional calculations.

In bulk amorphous materials, which are predominently covalent, there is a correlation between the magnitude of the ω^2 far-infrared and microwave absorption and the magnitude of the ω^2 density of vibrational states as obtained from specific-heat measurements.[4] If the density of states is given by an expression of the form $N(\omega) = b\omega^2$ and the absorption coefficient times the index of refraction is written $n\alpha(\omega) = K\omega^2 = (K/b)N(\omega)$, then the frequency-independent matrix element $M = K/b$ is found to be nearly constant for most covalent amorphous materials.[4] The value of M calculated from specific-heat data[44] and the far-infrared absorption observed in either the sputtered amorphous Ge films or the rapidly deposited films (30 Å/sec) is more than an order of magnitude greater than that observed in the other covalent amorphous materials. On the other hand, the magnitude of M calculated from the slowly deposited films (2 Å/sec) approaches the values observed in other materials. These facts lend additional support to the contention that the absorption in the slowly evaporated films is more representative of the "intrinsic" value.

Since the ω^2 far-infrared and microwave absorption is present in all amorphous materials but is generally absent in crystalline solids,[4] it is tempting to suggest that this absorption might be connected with the appearance of highly anharmonic, localized tunneling modes[45] in the amorphous structures, such as those which are thought to contribute to the low-temperature specific heat. If these tunneling modes were partially responsible for the ω^2 absorption tail, then there should be evidence at low temperature of saturation in the absorption as a function of power.[46] Measurements on the amorphous Ge samples (30-Å/sec deposition rate) at 9.05 GHz and 4.2 K showed no

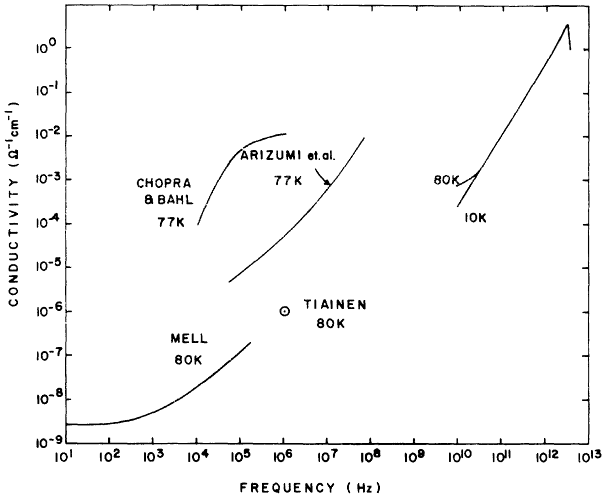

FIG. 8. Frequency dependence of the conductivity in amorphous Ge from 10 to 10^{13} Hz. The data presented are from Mell, (Ref. 11) Chopra and Bahl (Ref. 9), Arizumi *et al.* (Ref .10), Tianen, (Ref. 12) and the present work (above 10^{9} Hz).

evidence for saturation as the incident power was increased by more than 30 dB up to a maximum of 10 mW. Unfortunately, this measurement does not necessarily exclude the influence of the tunneling modes in the far-infrared and microwave absorption processes, because it is difficult to estimate the power at which saturation should occur.[47]

The agreement between conductivity data for amorphous Ge films from sample to sample and laboratory to laboratory below 10^{9} Hz is even less satisfactory than the agreement just discussed at frequencies greater than 10^{9} Hz. Figure 8 presents the available data on the conductivity of amorphous Ge films from 10 to 10^{12} Hz. Data on different samples near 10^{5} Hz differ by as much as five orders of magnitude. The data from 10^{10} to 10^{12} Hz are from the samples deposited at 30 Å/sec, and thus are about an order of magnitude greater than the smallest absorption observed. Of the existing results at lower frequencies, only those of Mell[11] and Tiainen[12] appear consistent with the present measurements.

It should be noted that the present measurements above 10^{10} Hz employ no contacts while those below 10^{9} Hz all employ contacting electrodes. The influence of contacts on the results at lower frequencies can be very serious.

The nature of the transition between the low-frequency ($\nu \lesssim 10^{6}$ Hz) region where $\sigma(\omega)$ is approximately proportional to ω and the high-frequency region ($\nu \gtrsim 10^{10}$ Hz), where $\sigma(\omega)$ rises approximately as ω^{2} remains unexplored. Since the existing low-frequency and high-frequency measurements were performed on different samples, extrapolation between the two regions is impossible. In particular, it is impossible to tell whether the conductivity proportional to ω rises smoothly into the ω^{2} contribution or whether it saturates at frequencies lower than those at which the ω^{2} term dominates. Careful contact-free measurements on one set of samples over this very extended, and somewhat inaccessable, frequency range are necessary to resolve this dilemma.

The nature of the thermally activated conductivity at microwave frequencies in amorphous Ge is not understood. In particular, the physical significance of the increased conductivity at 70 GHz over the dc value (Fig. 3) at a given temperature, which was denoted by the factor γ in Sec. IV, has not been determined, although similar increases have been observed in other amorphous materials[48,49] at infrared frequencies greater than the one-phonon frequencies and attributed either to a generalized Maxwell-Wagner effect or to strong polaronic effects.[48,49]

VI. SUMMARY

The magnitude of the infrared absorption in evaporated amorphous Ge films is dependent on the deposition rate in the spectral region below about 150 cm^{-1}. This region corresponds to the TA phonon peak in the density of states of crystalline Ge. In films deposited at the slowest rate, the infrared spectrum is strongly suppressed below 150 cm^{-1} and indicates a strong frequency dependence of the matrix element which couples the radiation to the phonons. Several arguments were presented which suggest that in the slowly evaporated amorphous Ge films the infrared spectra more closely approximate the intrinsic disorder-induced absorption in the absence of voids and dangling bonds.

There is a temperature-independent tail on the low-frequency far-infrared and microwave absorption in amorphous Ge which rises approximately as ω^{2} and is similar to the behavior observed in other amorphous materials. The most likely explanation for this absorption involves a disorder-induced coupling of the far infrared and microwave radiation to acoustic phonons, although no model presently exists which explains consistently both the Raman and infrared results.

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