# Temperature and frequency dependences of the far-infrared and microwave optical absorption in amorphous materials

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Microwave and far-infrared absorption have been studied in several chalcogenide and oxide glasses $(As_2Se_3, Tl_2SeAs_2Te_3, 3SiO_2 \cdot Na_2O)$ at frequencies between 0.1 and 100 $cm^{-1}$ at 300 K and at 0.8 $cm^{-1}$ between 10 and 300 K. In addition, previously published data for $SiO_2$ and other amorphous materials are analyzed. The results exhibit comparable frequency- and temperature-dependent behavior for all amorphous materials. The magnitude of the absorption in the amorphous solids over the entire frequency range is strongly enhanced (by an order of magnitude) over the absorption in the corresponding crystalline solids. The enhanced absorption is interpreted in terms of disorder-induced optical coupling to Debye-like as well as to non-Debye-like modes. The non-Debye-like modes dominate the absorption at low frequencies $\omega/2\pi c < 10$ $cm^{-1}$ at temperatures $10 < T < 300$ K. It is shown that multiphonon difference processes as well as resonant optical excitations of two-level modes do not account for the experimental observations.

## I. INTRODUCTION

When a crystalline substance becomes disordered there is a concomitant increase of the optical absorption in the very-low-frequency region ($\lesssim 100$ $cm^{-1}$) of the infrared spectrum. Many different types of disorder lead to such an increase, including vitrification,[1] impurity doping (as, for example, in alkali halides),[2] partial decrystallization (as in polymers),[3] and disorder induced by evaporation or sputtering of thin films (as in Si or Ge).[4] In each case the disorder causes a relaxation of the selection rules which govern the optical excitation of the lattice-vibrational modes. This relaxation of the selection rules can create a coupling·to modes which are optically inactive in a periodic crystalline solid. The experimental optical spectrum represents a convolution of a density of states with an optical matrix element and neither of these factors can be determined independently just from the frequency dependence of the optical absorption. Since independent measurements of either the densities of states or the matrix elements do not generally exist, we attempt to discern more about these two quantities by exploring correlations in the frequency and temperature dependences of the far-infrared and microwave absorptions among a number of structurally and electronically different amorphous solids. In the absence of a microscopic theory of optical absorption in amorphous solids such an approach allows us to compare key experimental features with the predictions of simple phenomenological models.

Far-inrared absorption in glasses has been the subject of numerous studies. Among these Hadni *et al.*[5] first suggested that the far-infrared absorption in glassy $SiO_2$ was due to a disorder-induced optical coupling to Debye-like modes. Subsequently, Bagdade and Stolen[6] and Whalley[7] have interpreted similar observations in the 20–120-$cm^{-1}$ range in other oxide glasses, notably $GeO_2$ and $B_2O_3$, in terms of models which assume the existence of charged defects or disorder-induced local dipole moments.

In a previous communication[1] we established that a far-infrared absorption, which is temperature independent but depends quadratically on frequency, is a characteristic feature of many amorphous materials, at least for frequencies above 10 $cm^{-1}$. For most chalcogenide glasses the $\omega^2$ dependence is clearly established with no evidence for additional structure in the far-infrared spectra between 10 and 100 $cm^{-1}$. In oxide glasses, additional optical modes in this spectral range partially obscure an $\omega^2$-dependent absorption. Nevertheless a superposition of local optic modes and an absorption depending quadratically on frequency can account for the far-infrared spectra of glassy $SiO_2$, $GeO_2$, and $B_2O_3$. In addition, if the observed absorption is assumed to be proportional to the product of a matrix element $M$ and a Debye-like ($\propto \omega^2$) density of states,[1,5,6] then $M$ is found to be of comparable magnitude for a considerable number of amorphous materials.[1] This behavior indicated that the observed far-infrared absorption was due to an aspect of disorder which was shared by many structurally different amorphous materials and was therefore in some sense characteristic of the amorphous state.

In the present paper we provide more detailed data for the two chalcogenide glasses $As_2Se_3$ and $Tl_2SeAs_2Te_3$ in the microwave region (0.1–5 $cm^{-1}$) at $T = 300$ K. The temperature dependence (20 $< T < 300$ K) of the absorption at $\omega/2\pi c = 0.8$ $cm^{-1}$ is

presented for the chalcogenide glasses and compared to existing measurements on oxide glasses and polymers.[3] The disorder-induced coupling to Debye-like modes which accounts for the temperature-independent data above 10 cm$^{-1}$ cannot account for the temperature-dependent absorption observed at lower frequencies. Consequently, the contribution of non-Debye-like modes is considered. Such modes have been modeled as two-level tunneling modes or as damped low-frequency lattice modes (with momentum $q > q_D$, where $q_D$ is the Debye momentum). We examine here to what extent models which are based on these two interpretations of non-Debye-like modes can account for the experimental observations, particularly for frequencies below 10 cm$^{-1}$.

The sample-preparation procedures and the far-infrared and microwave measurement techniques are described in Sec. II followed by the experimental results in Sec. III which are discussed in terms of plausible phenomenological models in Sec. IV. The major results are summarized in Sec. V.

## II. EXPERIMENTAL METHODS

### A. Sample preparation

The chalcogenide glasses $As_2Se_3$ and $Tl_2SeAs_2Te_3$ were prepared by standard quenching techniques[8] from starting material which was normally 99.9999% pure. Disk-shaped samples for the optical-absorption measurements were cut with a wire saw or hot pressed, while thin rods for the microwave perturbation measurements were drawn in liquid form into thin quartz tubes. Waveguide sections lined with Al foil served as forms to melt samples of glass which were cut with a wire saw to be approximately half a waveguide wavelength long and which fit snugly into the microwave cavity. Numerous checks were made to ensure that the measurements were independent of sample preparation.[8] These checks included comparison of hot-pressed and cut samples, measurements on different samples at the same frequency, and comparison of samples prepared under different conditions with different impurity concentrations (e.g., "pure" $As_2S_3$ compared to Servofrax $As_2S_3$ which is doped with Sb). The far-ir absorption in chalcogenide glasses was observed to be insensitive to sample-preparation details. This result contrasts with observations in evaporated Ge films,[4] in which case the far-ir absorption changed dramatically in intensity for different evaporation rates. The latter result was interpreted in terms of the existence of voids in the evaporated films and the variation of void size and density with evaporation rate. The absence of voids in chalcogenide glasses has been well established.[9]

### B. Far-infrared measurements

The conductivity $\sigma$ or absorption coefficient $\alpha [n\alpha(\text{cm}^{-1}) = 120\pi\sigma(\Omega^{-1}\text{cm}^{-1})$, where $n$ is the index of refraction] in the frequency range 8–150 cm$^{-1}$ was determined from reflection and transmission measurements. From the reflectivity, the dielectric constant $\epsilon'(\omega) = n^2$ is obtained. The absorption coefficient $\alpha$ is obtained from the usual expression for the transmission $T$ through a plane parallel slab of thickness $d$.[10] For normal incidence, the expression for $T$ in the high-absorption region $(\alpha d \gg 1)$ is

$$T = (1 - R)^2 e^{-\alpha d}/(1 - R^2 e^{-2\alpha d}) , \qquad (1)$$

where $R = |(1 - n)/(1 + n)|^2$ is the single surface reflectivity at normal incidence. An alternate method for measuring $\alpha$ without separate determination of the reflectivity is to measure $T$ for several samples of different thicknesses $d$. Good agreement was found for the absorption coefficients obtained with either method. In general, approximately five different samples of varying thicknesses were required to span the 1–100-cm$^{-1}$ range.

The optical source in these measurements was an optically pumped pulsed far-infrared molecular-gas laser[11] (see Fig. 1). A compensated InSb surface channel detector[12] was used in the frequency region below 150 cm$^{-1}$ and a Ga-doped Ge photodetector above 150 cm$^{-1}$. The high intensity and monochromaticity of the optically pumped far-ir laser allowed accurate absolute measurements of the conductivity with a spectral resolution limited only by the availability of different laser lines.[13] In the following study approximately 20 different laser lines have been used which provide adequate resolution of the observed broad far-infrared absorption features between 10 and 150 cm$^{-1}$.

The range from 20 to 200 cm$^{-1}$ was also examined with a Michelson interferometer. Although absolute determinations of the absorption coefficient with this technique are less certain than with the laser, spectral features over a wide frequency range can be determined rapidly.
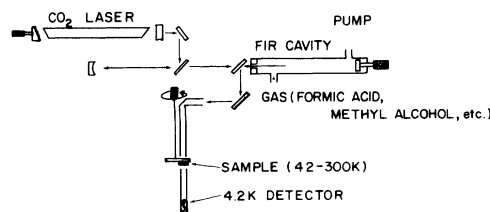


FIG. 1. Far-infrared optically pumped gas laser system. The $CO_2$ laser is used to pump the gas in the electrodeless far-infrared (FIR) cavity.

## C. Microwave measurements

Results below 5 cm$^{-1}$ were obtained by means of microwave techniques (Fig. 2). A perturbative method[4,14,15] was used for the highly conducting glass $Tl_2SeAs_2Te_3$ at all frequencies between 3 and 75 GHz (0.1–2.5 cm$^{-1}$) and for $As_2Se_3$ above 30 GHz (1 cm$^{-1}$). Whenever the conductivity was too small to be measured reliably with the perturbation method, it was necessary to use a nonperturbative approach.[15] The perturbative and nonperturbative techniques differ only with respect to the assumptions made about the magnitude and distribution of the microwave fields in the sample under investigation. In the perturbation technique the field distribution is assumed unchanged by the introduction of the sample. This condition is realized when a rodlike sample is placed at a maximum of the electric field with the rod axis parallel to the field in a $Te_{10_m}$ rectangular cavity, where $m$ is typically 3 to 10. A necessary condition for the perturbative approach to hold is that $(\nu - \nu_0)/\nu \ll 1$ and $Q^{-1} \ll 1$, where $\nu_0$ and $\nu$ are the unperturbed and perturbed cavity resonant frequencies, respectively, and $Q$ is the quality factor of the perturbed cavity. The perturbative method allows direct determination of the real ($\epsilon'$) and imaginary ($\epsilon''$) parts of the dielectric constant:

$$\epsilon' = 1 + \frac{\nu - \nu_0}{2\nu} \frac{V}{v} , \quad \epsilon'' = \frac{1}{4} \frac{Q - Q_0}{Q_0 Q} \frac{V}{v} ,$$

where $V$ and $v$ are the volumes of the cavity and the sample, respectively. In practice, for the case of low conducting dielectrics, the condition $Q^{-1} \ll 1$ is easily satisfied, but whenever the fractional frequency shift $(\nu - \nu_0)/\nu$ becomes >0.1 the perturbative approach is no longer reliable and a nonperturbative technique is required to measure the microwave conductivity. In this case, a sample was molded to fit the waveguide cross section and then was cut to a length equal to $\frac{1}{2}\lambda_s$, where $\lambda_s$ is the microwave wavelength in the sample. Both $\epsilon'$ and $\epsilon''$ can in principle be determined with this technique, however some rather complicated equations need to be solved. If, on the other hand, the

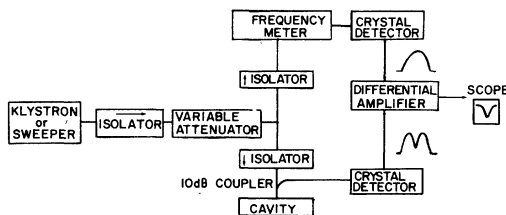real part of the dielectric constant at low frequencies is determined separately, as in a far-infrared reflectivity experiment or with a separate perturbative measurement, then the wavelength of the microwave radiation, and hence the field distribution in the sample, can be determined easily. We have utilized this nonperturbative method to measure the microwave conductivity of $As_2Se_3$ at 25 GHz over the temperature range 25–300 K and at 9 GHz (300 K only).

## III. EXPERIMENTAL RESULTS

The frequency dependence of the far-ir absorption for the two chalcogenide glasses $As_2Se_3$ and $Tl_2SeAs_2Te_3$ is shown in Fig. 3. Our results for these chalcogenide glasses are also compared with an average curve for glassy $SiO_2$ (Optasil) obtained from a number of different sources,[5,6,16,17] some of which limited their measurements to a narrow
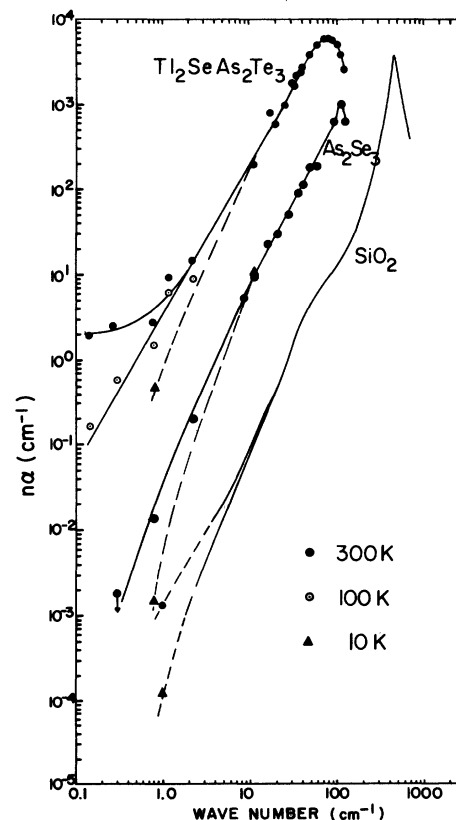


FIG. 3. Measured product of absorption coefficient $\alpha$ and index of refraction $n$ versus frequency. In terms of the complex dielectric constant $\epsilon = \epsilon' + j\epsilon''$, where $n = \sqrt{\epsilon'}$, $n\alpha$ (cm$^{-1}$) $= 120\pi\sigma$ ($\Omega^{-1}$cm$^{-1}$) $= 30\omega\epsilon''$. The $\blacktriangle$ point for $As_2Se_3$ at 0.76 cm$^{-1}$ is measured at 25 K. Note that for $As_2Se_3$ at 10 cm$^{-1}$ the 300- and 10-K data points are nearly identical.



FIG. 2. Microwave spectrometer for the frequency range 3–150 GHz (0.1–5 cm$^{-1}$).

TABLE I. Measured coefficient $K_0$ and exponent $\beta$ from temperature-independent (4–300 K) far-infrared (10–100 cm$^{-1}$) absorption $n\alpha = K_0(\hbar\omega)^2$. Local-field correction $\kappa^2 = [\frac{1}{3}(n^2 + 2)]^2$, $n$ is the low-frequency index of refraction, $c_3$ is the low-temperature specific-heat coefficient (from Ref. 27). Near constancy of $K_0/\kappa^2 c_3$ demonstrates near constancy of matrix element for disorder-induced coupling to Debye modes in predominantly covalently bonded solids.

| Material | $\beta$ | $K_0$ ($10^{29}$ erg$^{-2}$cm$^{-1}$) | $\kappa^2$ | $C_3$ ($10^2$ erg g$^{-1}$ K$^{-4}$) | $K_0/\kappa^2 C_3$ ($10^{26}$ erg$^{-3}$ g cm$^{-1}$K$^{+4}$) |
|---|---|---|---|---|---|
| Tl$_2$SeAs$_2$Te$_3$ | 1.9 | 615 | 107 | 7.0 | 8.2 |
| As$_2$Se$_3$ | 2.0 | 17.5 | 15.2 | 2.5 | 4.6 |
| Se | 1.7 | 16.4 | 8.8 | 1.9 | 9.8 |
| As$_2$S$_3$ | 2.0 | 9.0 | 10.7 | 1.3 | 6.5 |
| PMMA [a] | 1.9 | 4.5 | 3.2 | 2.9 | 4.8 |
| GeO$_2$ | 2.0 | 3.7 | 5.4 | 0.26 | 26.5 |
| B$_2$O$_3$ | 2.0 | 1.1 | 3.1 | 1.1 | 3.2 |
| SiO$_2$ | 2.0 | 0.5 | 3.7 | 0.20 | 7.0 |

[a] PMMA, poly(methylmethacrylate).

frequency range. The absorption observed in these three amorphous materials above 10 cm$^{-1}$ is temperature independent and approximately proportional to the square of the frequency. This behavior is in contrast to that observed in the corresponding crystalline materials (such as crystalline As$_2$Se$_3$ or SiO$_2$) in which the absorption over the same frequency range is both strongly dependent on temperature and at least an order of magnitude weaker.

The analysis of the far-ir absorption solely in terms of a contribution which varies smoothly with the square of the frequency is oversimplified since there is evidence for structure in the far-ir spectra of some of the oxide glasses and polymers. Nevertheless, we concentrate on the broad underlying frequency dependence of the far-ir absorption because it appears to be characteristic of the amorphous phase and should yield information about the effect on the optical matrix elements of the loss of long-range order without particular regard for the details of the local structural order.

Above 10 cm$^{-1}$, the magnitude of the far-ir conductivity can be written

$$n\alpha = K_0(\hbar\omega)^\beta, \quad \omega/2\pi c > 10 \text{ cm}^{-1}, \quad (2)$$

where $K_0$ is a constant for each amorphous material (independent of temperature and frequency) and $\beta \lesssim 2.0$. In Table I are listed values of $K_0$ and $\beta$ obtained from our measurements for poly(methylmethacrylate) (PMMA), As$_2$Se$_3$, As$_2$S$_3$, and Tl$_2$SeAs$_2$Te$_3$ and those abstracted from other published data[3,5,6,16,17] for SiO$_2$, B$_2$O$_3$, and GeO$_2$. [The value $\beta = 1.9$ for the material PMMA represents a more accurate value than the value (1.7) previously published.[1]] The materials in Table I are predominantly covalently bonded. Glasses such as 3SiO$_2 \cdot$ Na$_2$O which contain some highly ionic

bonding configurations, exhibit a far-ir absorption and hence values of $K_0$ which are considerably larger than the values of $K_0$ listed in Table I. This enhanced coupling can be attributed to the ionic character of the alkali constituent.[6]

The frequency region below 10 cm$^{-1}$ has not been previously studied in chalcogenide glasses in any detail. There exist several microwave measurements by Amrhein and Müller[3] on the temperature dependence of the absorption in selected polymers. In addition, Mon et al.[16] have reported far-ir measurements over the range 2–100 cm$^{-1}$ in PMMA, GeO$_2$, and SiO$_2$ for temperatures between 1.2 and 10 K and at 300 K. However, these authors con-
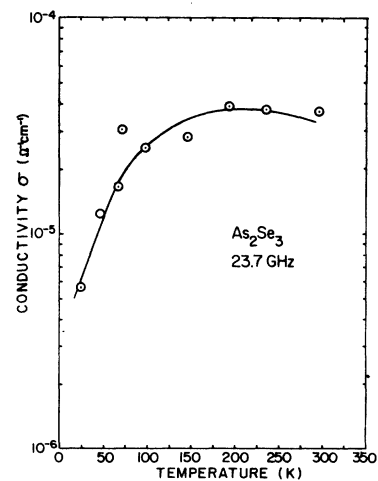


FIG. 4. Measured microwave conductivity $\sigma$ vs temperature for As$_2$Se$_3$ glass at 23.7 GHz (0.79 cm$^{-1}$). The solid line represents a model fit [Eq. (11)] with $p(E)$ Gaussian and $E_M = 550$ K, $E_0 = 320$ K, $\tau_0 = 7 \times 10^{-13}$ sec (see text for definitions of parameters).
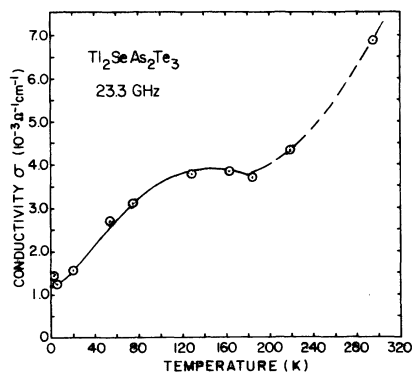
FIG. 5. Measured microwave conductivity $\sigma$ vs temperature for glassy $Tl_2SeAs_2Te_3$ at 23.3 GHz (0.78 cm$^{-1}$). The solid line is a fit to Eq. (11) with $p(E)$ Gaussian and $E_m = 550$ K, $E_0 = 410$ K, $\tau_0 = 5 \times 10^{-13}$ sec. The dotted line represents a thermally activated electronic band-type conductivity $(\sigma \sim \exp(-\epsilon/kT)$, where $\epsilon = 0.35$ eV and $\sigma \sim 4 \times 10^{-3} \, \Omega^{-1} \text{cm}^{-1}$ at 300 K).



FIG. 7. $n\alpha/\omega^2$ ($n\alpha$ taken from Fig. 3) vs wave number $(\omega/2\pi c)$ for glassy $As_2Se_3$ and glassy $SiO_2$. Plot illustrates constancy of matrix element $K_0$ [Eq. (2)] above $\sim 10$ cm$^{-1}$ and the frequency dependence of the optical coupling at lower frequencies. The dash-dotted curves represent the one-phonon matrix elements $K_0 g(\omega l/V_D)$ calculated from Eq. (7) with $l = 9$ Å for $As_2Se_3$ and $l = 18$ Å for $SiO_2$.

centrate on the subtle temperature variation of the absorption observed between 1.2 and 10 K, and do not attempt to interpret the strong temperature dependence that is observed between 300 and 10 K.

In Figs. 4 and 5 we present the temperature dependence of the absorption at 0.8 cm$^{-1}$ (24 GHz) for glassy $As_2Se_3$ and $Tl_2SeAs_2Te_3$. In $As_2Se_3$ (Fig. 4) the absorption is relatively independent of temperature between 300 and 100 K, but decreases rapidly
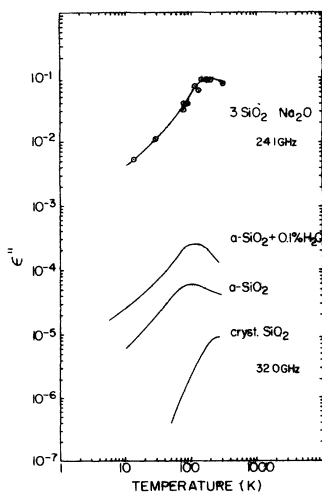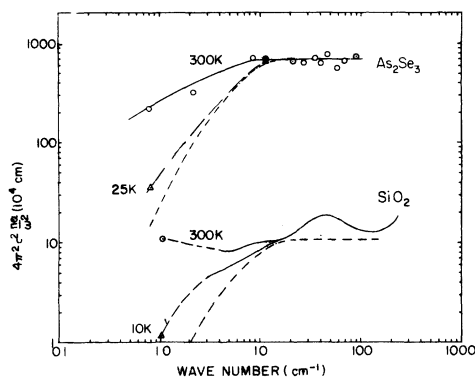


FIG. 6. Imaginary part of dielectric constant $\epsilon''$ [$\epsilon'' = 3 \times 10^{10} n\alpha (\text{cm}^{-1})/\omega(\text{sec}^{-1})$] vs temperature for crystalline $SiO_2$, amorphous $SiO_2$, amorphous $SiO_2$ with 0.1% $H_2O$ (all from Ref. 3) at 32.0 GHz, and for the partially ionic glass $3SiO_2 \cdot Na_2O$ at 24.4 GHz. All curves for the glasses can be fitted with Eq. (11) and $E_m = 500$–550 K, $E_0 = 300$–430 K, and $\tau_0 = (1$–$2) \times 10^{-13}$ sec.

with decreasing temperature below 100 K. At the lowest temperatures, the absorption again becomes less temperature dependent as can be best seen from the data at 0.8 cm$^{-1}$ for $Tl_2SeAs_2Te_3$ in Fig. 5.[18]

In Fig. 6 our measurements for glassy $3SiO_2 \cdot Na_2O$ at 24 GHz are compared to measurements by Amrhein and Müller[3] for glassy $SiO_2$ (Optasil), glassy $SiO_2 + 1200$ ppm $H_2O$ (infrasil), and crystalline quartz. The temperature dependence of the microwave absorption in these oxide glasses exhibits features qualitatively similar to those observed in the chalcogenide glasses (Figs. 4 and 5), with the exception that the flat temperature dependence over the approximate range 100–300 K in the chalcogenide glasses is replaced by a slight bump in the absorption versus temperature plots of Fig. 6 near 100 K. There is also some evidence for a residual absorption at low temperatures ($\sim$10 K) similar to that which is observed in the chalcogenide glasses. In Fig. 7 a replot of the data of Fig. 3 is presented in which the absorption $n\alpha$ is divided by the factor $(\omega/2\pi c)^2$. For simplicity, only $SiO_2$ and $As_2Se_3$ are shown. Figure 7 emphasizes the departure at low frequencies of the low-temperature absorption from the quadratic dependence on frequency. Although the exact frequency dependence of the low-temperature absorption is not well established because of the limited data, it is evident from Fig. 7 that the frequency dependence of $n\alpha$ at 10 K is considerably stronger than quadratic below 1 cm$^{-1}$ but very nearly quadratic above 10 cm$^{-1}$ for both glasses. In the case of glassy $SiO_2$, the broad structure centered near

50 cm$^{-1}$ is a complicating feature; nevertheless, a relatively frequency-independent region in the $n\alpha/\omega^2$ plot is evident between 15 and 150 cm$^{-1}$ in this material.

If the absorption due to the thermal excitation of carriers into the conduction band[19] is ignored, the far-infrared absorption in chalcogenide glasses over the frequency range $0.1 < \omega/2\pi c < 100$ cm$^{-1}$ can be expressed in the following empirical form:

$$n\alpha = K(\omega, T)(\hbar\omega)^2 , \tag{3}$$

where $K$ approaches the temperature- and frequency-independent value $K_0$ of Eq. (2) for frequencies above 10 cm$^{-1}$.

## IV. DISCUSSION

No microscopic theory for the optical response of amorphous materials at far-infrared frequencies presently exists. Nevertheless, comparison of a phenomenological model to be outlined here with the experimental data suggests that the observed far-ir absorption is due to a disorder-induced interaction of the optical radiation with the lattice excitations of the amorphous solid. Other interpretations do not appear to account for the main features of the data. For example, an absorption $\sim\omega^2$ is predicted for the case of direct optical transitions between localized electronic states.[20] However, the magnitude of the experimental absorption in the $10^{10}$–$10^{12}$-Hz range is at least an order of magnitude larger than is predicted by the electronic model.

The possibility of disorder-induced optical absorption in crystals in the far-infrared spectral range was treated by Vinogradov[21] in terms of a charge-defect model. The role of correlation effects induced by lattice interactions between defects was subsequently examined by Schlömann.[22] There exists at present no firm experimental evidence for the existence of these disorder-induced effects in crystals. (We are not referring here to the observation of the distinct vibrational defect modes as discussed, for example, in the review by Barker and Sievers in Ref. 2.) Bagdade and Stolen[6] later suggested that the disorder-induced absorption model could be applied to explain the far-infrared absorption in glasses. In oxide glasses the absorption above 30 cm$^{-1}$ was found to be temperature independent and greatly enhanced over the corresponding crystalline materials—quite suggestive of Vinogradov's and Schlömann's predictions. It was also thought that correlation effects were observed,[6] but the identification of such effects was greatly obscured by the presence of far-infrared optical modes as well as the limitation to the frequency region above 15 cm$^{-1}$.

Our approach here is to review briefly the charge-fluctuation model, to suggest why this model may be applied to amorphous solids, and finally to examine the predictions of the model. It will be shown that our extensive frequency range (1–100 cm$^{-1}$) provides a more meaningful test for correlation effects. We will further show that the temperature-dependent optical absorption observed at frequencies below 10 cm$^{-1}$ can be interpreted in terms of the charge-fluctuation model provided the existence of highly damped non-Debye-like modes is stipulated.

We proceed by expressing the disorder-induced far-ir absorption $\alpha(\omega, T)$ in the following form[22]:

$$\alpha(\omega, T) = \sum_q c(q)\rho(q, \omega) , \tag{4}$$

where the summation is taken over all phonon wave vectors $q$ (a summation over various phonon branches is also assumed but not indicated). In Eq. (4), $c(q)$ is the phonon-photon coupling coefficient and $\rho(q, \omega)$ is the oscillator response function of the system. For damped lattice oscillators we have $\rho(q, \omega) \propto [\omega^2 - \omega^2(q) + i\gamma\omega]^{-1}$. For a model of disorder-induced charge fluctuations the coupling coefficient in Eq. (4) becomes[22]

$$c(q) = \text{const} \times g(q) , \tag{5}$$

where $g(q)$ is the correlation factor proposed by Schlömann. This factor arises from the assumption of charge neutrality on a scale of a correlation length $l$. Consequently, statistically distributed charges of opposite sign will reduce the optical absorption whenever the regions of charge interact. Such interaction takes place when the phonon wavelengths are larger than the average charge separation, i.e., at sufficiently low frequencies. An explicit expression for $g(q)$ is found by assuming a specific form of the compensating charge distribution which surrounds a given charge fluctuation. For a compensating charge distribution which falls off exponentially as $\exp(-r/l)$ it is found that[22]

$$g(q) = 1 - (1 + q^2 l^2)^{-2} , \tag{6}$$

i.e., the normalized Fourier transform of $\exp(-r/l)$. It has been shown that charge distributions other than the exponential type do not significantly alter the functional form of $g(q)$.[6]

Equations (4)–(6) have been derived for defects in crystals. The same model can be applied to amorphous systems provided the averaging implied by the summation in Eq. (4) is properly done and if average quantities such as an average correlation length $l$, average effective charges $e^*$, etc., can be defined. In addition, information must be available about the nature of the lattice excita-

tions, in particular the dispersion relations and the density of states. This type of information is very incomplete for amorphous solids and we must generally base our conclusions on a comparison of model and experiment. It is convenient to separate the experimental results into temperature-dependent and temperature-independent portions. The reason for this separation is made evident by noting that for Debye modes ($q \equiv q_D \equiv \omega/V_D$, in a crystalline matrix the sum over $q$ in Eq. (4) yields[22]

$$n\alpha(\omega, T) = K_0(\hbar\omega)^2 g(q_D) , \qquad (7)$$

where $K_0$ is a constant which is *independent* of temperature and frequency, provided the physical quantities entering $K_0$ such as optical dipole moments and index of refraction $n$ are independent of temperature (generally a good approximation for glassy solids at far-ir frequencies). Thus, according to this model, a temperature independent far-ir absorption is tied to the excitation of Debye-like modes with momenta $q_D = \omega/V_D$. An absorption which is strongly temperature dependent, as observed in glasses at frequencies below 10 cm$^{-1}$, cannot be related directly to Eq. (7) unless additional assumptions about the phonon lifetimes and dispersion relations are made.

### A. Temperature-independent absorption

Equation (7) was derived for a Debye density of states. Is such an assumption realistic for a glass? In the limit where the phonon wavelength $\lambda \gg l$, the amorphous solid is well approximated by an elastic continuum and Debye-like sound waves will exist, even at frequencies as high as $\sim 1$ cm$^{-1}$ as has been verified by Brillouin scattering.[23] At higher frequencies, (>10 cm$^{-1}$) experimental evidence for Debye-like modes is less direct, as from analyses of thermal transport results.[24,25] There is evidence[26,27] for remnants of "crystal-like" (but not crystalline) order on a scale of 10–20 Å. Hence Debye-like excitations, although severely damped, can exist at a frequency of $\sim 30$ cm$^{-1}$ where the Debye phonon wavelength in $As_2Se_3$ is on the order of 10 Å. Thus, at least in the limiting cases of high and low frequencies as defined above, the summation in Eq. (4) can be performed and Eq. (7) is expected to apply to amorphous solids.

We wish to compare the frequency dependence and the magnitude of $n\alpha(\omega)$ as predicted by the charge-fluctuation model. The frequency dependence is controlled by the factor $\omega^2 g(q_D)$. At high frequencies $(\omega l/V_d \gg 1)$, $\omega^2 g(q_D) \rightarrow \omega^2$ and at low frequencies $(\omega l/v_D \ll 1)$, $\omega^2 g(q_d) \rightarrow \omega^4$. The $\omega^4$ dependence of $\alpha(\omega)$ (i.e., a coupling coefficient proportional to $\omega^2$) is due to the $q^2$ dependence of the

photon-phonon coupling coefficient which is a general feature of optical-acoustical interactions in the hydrodynamic regime. We refer here to the model of Martin and Brenig[28] concerning Brillouin scattering in a disordered medium. As seen in Table I the functional form of $\alpha(\omega)$ for $\omega/2\pi c > 10$ cm$^{-1}$ is $\omega^\beta$ with $\beta \lesssim 2.0$. This dependence is emphasized for $As_2Se_3$ and $SiO_2$ in Fig. 7 by dividing $\alpha(\omega)$ by $\omega^2$. The application of Eq. (7) to the entire frequency region below 100 cm$^{-1}$ yields the dash-dotted curves in Fig. 7, which are normalized to the magnitudes of the data above 10 cm$^{-1}$. There is considerable uncertainty about this type of fit in $SiO_2$, as has been discussed earlier in this paper. The dash-dotted curves were calculated with the Debye sound velocities $V_D = 1.2 \times 10^5$ cm/sec for $As_2Se_3$ and $V_D = 4.1 \times 10^5$ cm/sec for $SiO_2$. The only adjustable parameter is $l$. The values of $l = 9$ Å for $As_2Se_3$ and $l = 18$ Å for $SiO_2$ were chosen to agree best with the temperature independent data above 10 cm$^{-1}$ and the $T \rightarrow 0$ extrapolation of the microwave results in Figs. 5 and 6. The calculated curves in Fig. 7 represent the temperature-independent disorder-induced one-phonon absorption. The upper bounds of $l$, defined by the microwave data at 20 $K$, are 20 and 40 Å for $As_2Se_3$ and $SiO_2$, respectively. Lower bounds are determined by the onset of the temperature-independent $\alpha \sim \omega^2$ regime at $\omega \gtrsim 10$ cm$^{-1}$. Using Eq. (7), these minimum values of $l$ are 5 Å for $As_2Se_3$ and 10 Å for $SiO_2$. The significance of the difference between the values of $l$ for $As_2Se_3$ and $SiO_2$ cannot be assessed here because of the uncertainites involved in these quantities. However, it is evident that in each case correlation lengths exist which are considerably larger than a single interatomic spacing (i.e., $\sim 2$–3 Å). We further note that, although it is by no means certain that correlation lengths determined for a given glass by different experimental techniques should be the same, the correlation lengths determined here are consistent with those inferred from some x-ray diffraction studies on the same materials.[27] It is also illustrative to relate the correlation length $l$ to the concentration of charged regions $N$. The simplest possible relationship is $N \approx l^{-3}$, from which are obtained values of $N$ for $SiO_2$, and $As_2Se_3$ of 1.2 and 8.0 $\times 10^{20}$ cm$^{-3}$, respectively.

For comparison of the magnitude of the absorption with the charge-fluctuation model we write the explicit form for the constant in Eq. (7) as

$$K_0 = [(e^*)^2 N/\hbar^2 \rho c](1/V_D^3)\kappa^2 , \qquad (8)$$

where $\kappa^2 = [\frac{1}{3}(n^2 + 2)]^2$ is the local-field correction,[29] $c$ is the speed of light, $\rho$ is the mass density, and $N$ designates the density of charge fluc-
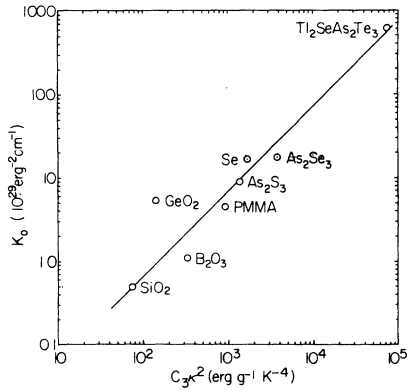
FIG. 8. Comparison of measured coefficient $K_0$ of far-infrared $\omega^\beta$ absorption ($\beta \sim 2.0$) with coefficient $c_3$ of low-temperature $T^3$ term of specific heat (from Ref. 27). Values for the local-field correction $\kappa^2 \left[\frac{1}{3}(n^2+2)\right]^2$ are given in Table I.

tuations of magnitude $|e^*|$. Taking the value of $K_0$ obtained for $SiO_2$ as listed in Table I and $\rho$ = 2.2 g cm$^{-3}$, $V_D = 4.1 \times 10^5$ cm sec$^{-1}$, $\kappa^2 = 3.7$, we find $Ne^{*2} = 1.3 \times 10^{20} e^2$ cm$^{-3}$, where $e$ is the electronic charge. Combining this result with our previous estimate of $N = 1.2 \times 10^{20}$ cm$^{-3}$ for $SiO_2$, we conclude that the charge fluctuations in $SiO_2$ are on the order of a single electronic charge. The same calculation of $As_2Se_3$, with $\rho = 4.0$ g cm$^{-3}$, $V_D = 1.2 \times 10^5$ cm sec$^{-1}$, $\kappa^2 = 15$, yields $Ne^2$ = $0.8 \times 10^{20} e^2$ cm$^{-3}$, and since $N \sim 8 \times 10^{20}$ cm$^{-3}$ this implies $e^{*2} \sim 0.1 e^2$ or local charge fluctuations of $|e^*| \sim 0.3e$. Thus, although the magnitudes of the far-ir absorption in glassy $As_2Se_3$ and $SiO_2$ differ by two orders of magnitude, the optical coupling coefficients $\propto N(e^*)^2$ and effective charges are very comparable. Similar values of the disorder-induced coupling are exhibited by other amorphous solids. In order to illustrate this behavior we rewrite Eq. (8) in terms of the coefficient $c_3$ of the $T^3$ contribution to the Debye specific heat as

$$K_0 = 5.7 \times 10^6 N(e^*/e)^2 \kappa^2 c_3,$$

where we have normalized the average effective charge to the electronic charge and where $K$ and $c_3$ are in units of erg$^{-2}$ cm$^{-1}$ and erg g$^{-1}$K$^{-4}$, respectively. Thus a plot of $K_0$ vs $\kappa^2 c_3$ as in Fig. 8 provides information about the magnitude of $N(e^*)^2$ for different amorphous solids. These data are well approximated by a straight line of unit slope which implies a direct correlation between the optical matrix element ($\propto K_0$) and the Debye density of states ($\propto c_3$), provided local-field effects ($\propto \kappa^2$) are taken into account.

The solids included in Fig. 8 are predominantly covalently bonded. It is evident from Fig. 6 that

the addition of highly ionic constituents such as $H_2O$ or alkali ions greatly enhances the optical absorption. For example, in glassy $3SiO_2 \cdot Na_2O$ the value of $Ne^{*2}$ is about a factor of 50 greater than in glassy $SiO_2$.[1,17] Since $c_3$ and $\kappa^2$ are both essentially the same in these two materials, the Na-containing silicate glass will fall considerably above the straight line in Fig. 8. In general, materials which are predominantly covalent fall near the line of unit slope in Fig. 8; solids with some highly ionic bonds fall well above the line in the upper left quarter of the plot; partially crystalline solids generally fall below the line of unit slope, as is the case for the partially crystalline polymer polystyrene.[1]

The results of the preceding discussion show that the magnitude of $Ne^{*2}$ is found to vary by at most a factor of 10 for a diverse group of predominantly covalently bonded amorphous solids. In fact, within the subgroup of chalcogenide glasses, $Ne^{*2}$ is of constant magnitude within a factor of 2. This insensitivity of the far-ir absorption in amorphous materials to structural details is reminiscent of the structural insensitivity of the magnitude of the anomalous low-temperature specific heat, which has been interpreted as due to highly anharmonic tunneling modes. It is tempting to suggest that charges or dipole moments associated with the anharmonic modes may be at least partially responsible for the enhanced temperature-independent far-ir optical absorption described in this paper. This argument finds some support in the comparison of the low-temperature ($< 1$ K) dielectric and acoustic measurements with the relatively high-temperature ($> 10$ K) far-ir absorption data. From application of the charge-fluctuation model to the far-ir absorption we estimated $e^* \approx (0.3-1.0)e$ when the total density of charged regions was $N \approx 10^{20}$ cm$^{-3}$. The energy densities of configurational modes commonly found for glasses[27,28] are $10^{17}-10^{18}$ K$^{-1}$ cm$^{-3}$ which imply that there are in this case also $10^{19}-10^{20}$ cm$^{-3}$ states contributing up to energies of about 100 K. Thus an effective charge in the range $(0.1-1.0)e$ is suggested for the two-level configurational states. The expected dipole moment $p$ is then on the order of $p \sim e^*$ which, for $r \approx 1$ Å and $e^* = 0.5e$, yields $p \approx 2.5D$. This is of comparable magnitude to those values of $p$ determined from very-low-temperature microwave and far-infrared measurements.[16,30]

### B. Temperature-dependent absorption

Although the far-ir absorption in amorphous solids is independent of temperature above $\sim 10$ cm$^{-1}$, below 10 cm$^{-1}$ the absorption is temperature dependent, particularly for temperatures

below 100 K. Possible interpretations of this temperature-dependent optical absorption include (i) highly damped phonon modes, (ii) multiphonon processes, (iii) resonant coupling to atomic configurational modes, and (iv) relaxation processes involving configurational modes. We consider briefly the applicability of these four processes as explanations for the temperature dependence of the microwave absorption in glasses.

(i) The finite lifetimes of phonons were not considered in the previous section. We further distinguish the damping of Debye-like modes (sound waves) and the finite lifetime of more localized non-Debye-like modes. Thermal conductivity and Brillouin measurements are primarily sensitive to Debye-like modes. Thermal conductivity measurements suggest that the phonon mean free path $\Lambda$ is relatively short above 30 cm$^{-1}$ (<50 Å) but increases rapidly with lower temperature and frequency below 10 cm$^{-1}$. In fact, Brillouin-scattering results[23] at 300 K in oxide glasses suggest that $\Lambda > 1000$ Å at frequencies ~1 cm$^{-1}$. Since temperature-dependent effects on the conductivity are expected for $\Lambda \sim l$, these effects are most likely restricted to the frequency region around ~10 cm$^{-1}$. At the lower microwave frequencies, damped non-Debye-like modes may contribute to the optical absorption. Such modes have been proposed by Fulde and Wagner[31] in order to account for the enhanced low-temperature specific heat in amorphous solids. Winterling[32] considered such modes in the qualitative interpretation of the temperature-dependent low-frequency (~5-cm$^{-1}$) Raman-scattering measurements in SiO$_2$ which are quite analogous to the far-ir optical-absorption measurements. As proposed by Fulde and Wagner, these modes are described in terms of the spectral distribution $\rho(q, \omega)$ for large $q$, low $\omega$.[31] In other words, at a given frequency $\omega$ there exists a distribution of lattice modes with momenta $q \gtrsim q_D$. The lifetimes of such modes are expected to decrease with increasing temperature. Winterling[32] considered the qualitative effect of varying lifetimes on the distribution function $\rho(q, \omega)$. The form of the Raman-coupling coefficient, which is similar to $c(q)$ in Eq. (4), was assumed to be $\propto q^2$. This is strictly valid only for Debye phonons in the long-wavelength limit.

We propose that the non-Debye-like modes with $q > q_D$ may have a significant effect on $c(q)$. Qualitatively, our argument is as follows. At any given temperature and frequency there exist lattice modes with a distribution of momenta $q$. Let the average of this distribution be $\bar{q}$. At low temperatures the lattice modes are essentially Debye-like with $\bar{q} = q_D$ and thus $c(q) \propto g(q_D) = 1 - (1 + q_D^2 l^2)^{-2}$. At higher temperatures, more localized and highly

damped modes contribute and $\bar{q} > q_D$, so that $g(\bar{q}) > g(q_D)$. For example, for As$_2$Se$_3$ at $\omega/2\pi c = 1$ cm$^{-1}$, $q_D \simeq 1.6 \times 10^6$ cm$^{-1}$. For $l = 10^{-7}$ cm, then $q_D l = 0.16$ and $g(q_D) = 0.025$. At some higher temperature, we may have $\bar{q} = 10^7$ cm$^{-1}$, then $\bar{q} l = 1$ and $g(\bar{q}) = 0.75$. We may speculate on the functional form of $\bar{q}(T)$. For frequencies below 10 cm$^{-1}$ the condition $\hbar \omega \ll kT$ holds generally for $T > 10$ K. If modes with $\bar{q} > q_D$ obey Bose statistics, (although such modes may be highly damped,) then for all temperatures >10 K the number density of lattice modes is proportional to $T$. If the phonon mean free path $\Lambda$ is limited by phonon-phonon collisions, as in crystals at high temperatures, then $\Lambda(\bar{q}) \sim 1/T$. For highly damped modes the phonon mean free path is comparable to the spatial extent of the mode, i.e., $\Lambda(\bar{q}) \sim 1/\bar{q}$.[33] Comparison of these relations suggests that $\bar{q}(T) \propto T$. This relationship, together with the assumption that the dominant temperature dependence in Eq. (4) is due to $c(q)$, leads to an $\alpha(T)$ curve very much as is observed for As$_2$Se$_3$ in Fig. 4.

Although these details are quite speculative, we stress our main argument that the model of disorder-induced charge fluctuations, if combined with the optical excitation of highly damped and relatively localized lattice excitations, can account for the low-frequency (<10-cm$^{-1}$) temperature-dependent optical absorption (or Raman scattering). This approach is attractive in that a single model [Eq. (4)] can explain the dominant temperature and frequency dependences observed in far-ir absorption.

(ii) Amrhein and co-workers[3] have reported results on organic polymers similar to those reported in this paper for inorganic amorphous solids, but their results for the region $\lesssim 1$ cm$^{-1}$ were interpreted in terms of three-phonon difference processes. We have attempted to fit the experimental data in Figs. 4 and 5 with the appropriate phonon difference equations[3] for different sets of phonon frequencies without success. Although the rapid drop of the absorption with decreasing temperature below ~80 K can be reproduced, the absorption curves over the entire temperature range, particularly the broad maximum around ~150 K, cannot be accounted for in terms of the phonon difference model. We conclude that although phonon difference processes may be important in certain types of disordered materials, such as impurity-doped alkali halides and perhaps partially crystalline polymers, they are unlikely to play a significant role in the microwave and far-ir optical-absorption spectra of chalcogenide glasses.

(iii) The existence of highly anharmonic modes in glasses appears well established by low-tem-

perature ultrasonic-attenuation experiments.[34] It is, however, difficult to attribute the temperature-dependent absorption observed above ~20 K at wave numbers below 10 cm$^{-1}$ to the resonant absorption of photons by such modes. The optical excitation of a system of two-level oscillators results in an optical absorption which diminishes with increasing temperature,[16] which is opposite to the experimental observations (Figs. 4 and 5).

(iv) A relaxation mechanism which couples photons to anharmonic configurational modes has been proposed[33,35] to explain the low-frequency light-scattering properties of glasses.[32] The philosophy of this approach is to fit the temperature dependence of the low-frequency Raman scattering intensity $I(\omega, T)$ using the energy density of tunneling modes as deduced from ultrasonic attenuation measurements.[32] If the microwave and far-ir absorption and the Raman scattering intensities are related as[17] $n\alpha(\omega, T) \propto \omega I(\omega, T)/f(\omega, T)$ (i.e., if the electric polarizability and ir effective charge are independent of temperature and frequency), then the predicted absorption due to this mechanism becomes

$$n\alpha \sim \beta\omega^2 \int dE\, p(E)\, \frac{\tau(E)}{1 + \omega^2\tau^2(E)}, \tag{10}$$

where $\beta = (kT)^{-1}$, $p(E)$ is the energy density of two-level states with barrier height $E$, $f(\omega, T)$ is the Stokes or anti-Stokes thermal occupation factor and $\tau(E)$ is a relaxation time for the two-level states, which is taken to be of the form $\tau(E) = \tau_0 \exp(\beta E)$. The simplest approximation to $p(E)$ is to assume that $p(E) = \text{const}$. For this case Eq. (10) is formally identical to the expression for the ac conductivity for frequencies ~$10^5$ Hz as proposed by Pollak and Pike.[36] With the assumption that the barrier heights $E$ range in magnitude considerably above and below the temperatures of interest (10–300 K), a constant $p(E)$ in Eq. (10) yields $n\alpha \sim \omega$ independent of temperature. This result does not agree with any of the observed far-infrared and microwave data.

The temperature dependence of the Raman scattering intensity in $SiO_2$ at 5 cm$^{-1}$ has been fit[33] using a Gaussian form for $p(E) \sim \exp[-(E - E_m)^2/E_0^2]$, where $E_m$, $E_0$ [and $\tau_0$ in the expression for $\tau(E)$] are taken from fits to the temperature de-

pendence of the ultrasonic attenuation. Although a similar fit to the temperature dependence of the far-ir absorption below 10 cm$^{-1}$ can be obtained with slightly different ($\pm 20\%$) values of $E_m, E_0$, and $\tau_0$ from those which best fit the ultrasonic attenuation data[37] (Figs. 4–6), this distribution function *does not* reproduce the observed frequency dependence which is $\gtrsim \omega^2$. One could construct a more complicated distribution function which would fit both the frequency and temperature dependences of the data, but without supporting evidence for such a function this exercise is of questionable significance.

## V. CONCLUDING REMARKS

The microwave and far-ir absorption in glasses can be separated into temperature-dependent and independent contributions. The temperature-independent absorption has been interpreted in terms of a coupling of photons to Debye phonons which occurs as a result of disorder-induced local variations in static or dynamic charge $e^*$. These charge fluctuations can be characterized by an average correlation length $l$ which is on the order of 10–20 Å. In this phenomenological interpretation, the frequency dependence of the absorption depends on the magnitude of the phonon wavelength with respect to $l$. The temperature-dependent absorption observed in the microwave region (~1 cm$^{-1}$) was interpreted in terms of the temperature-dependent lifetime of non-Debye-like modes. Such modes are modeled as highly damped low-frequency lattice excitations or as two-level quantum-mechanical modes. These results suggest that microwave and far-ir optical absorption may provide a sensitive tool for the study of low-frequency lattice excitations in amorphous solids. However, before such measurements may be fully exploited, a comprehensive framework for the description of elementary lattice excitations in amorphous systems is required.

## ACKNOWLEDGMENTS

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