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Ultrasonic investigation of amorphous As_2S_3 from 1.5 to 480 K[†]

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The attenuation of longitudinal and shear ultrasonic waves with frequencies between 10 and 450 MHz has been measured in amorphous As_2S_3 at various temperatures between 1.5 and 480 K. It is found that the attenuation is proportional to frequency except below about 30 K where it becomes less frequency dependent the lower the temperature. Below 50 K the attenuation is accounted for quantitatively using recent theory for the attenuation due to stress-relaxation processes each of which involves the thermal phonon-assisted tunneling of a sulfur ion between adjacent positions representable by a double potential-energy well. Tunneling times with a wide range of values occur indicating that there are double wells with various barrier heights and amounts of asymmetry. The probability for the occurrence of double wells is found to be proportional to the product of two Gaussian distributions depending, respectively, on the size of the barrier and the energy difference between the wells of a given pair. The number of double wells per unit volume deduced from fitting our ultrasonic data is consistent with the density of wells deducible from low-temperature specific-heat data of Stephens. Direct evidence that electronic tunneling is not responsible for the low-temperature attenuation has been obtained from measurements which revealed that the attenuation at 4.2 K increased only very slightly with magnetic field up to the highest value used, 133 kOe. Between 50 and 140 K the attenuation is almost independent of temperature and may be due to the combined effects of ions tunneling through and hopping over the potential barriers between the two wells of each of the many double wells in the material although no quantitative justification of this is presented. Above 140 K the attenuation is found to increase with temperature at an ever increasing rate and it is found that 30-MHz longitudinal-wave data can be fitted fairly well all the way up to 480 K by a three-term expression with two of the terms being exponential functions of the negative of the reciprocal temperature. Various possible interpretations of these results are presented but a unique and definitive explanation is not arrived at. However, it does seem that the attenuation involves more than one type of relaxation process and that each process is characterized by a wide range of relaxation times. Jumping of groups of ions over potential barriers may be involved. The velocites of 10-, 30-, and 50-MHz longitudinal waves and of 10- and 30-MHz shear waves have also been measured for a-As_2S_3 samples between 100 and 290 K. It is found that the velocities of both types of waves increase as the temperature decreases in a manner attributable to the anharmonicity of interatomic forces. The velocities increase slightly with frequency thereby providing additional evidence that the attenuation in a-As_2S_3 is *not* due to the Akhieser phonon viscosity mechanism which usually predominates in crystalline dielectric solids at the temperatures in question.

I. INTRODUCTION

Recent measurements[1,2] on vitreous silica and other amorphous substances have shown that the specific-heat and thermal conductivity of these substances exhibit anomalous behavior at very low temperatures. This anomalous behavior has stimulated great interest and a number of theoretical models[3-8] have been proposed to explain it. One of them, the double-potential-well model used by Anderson *et al.*[3] and by Phillips[4] seems to be most successful. In this model an amorphous material is pictured as containing entities each of which has available to it two alternative sites or configurations of nearly the same energy. Each two-site system has been represented by a double well like that shown in Fig. 1. The entities may be atoms, ions, molecules, or groups thereof depending on the substance. Furthermore, it is thought that double wells occur which have various values of barrier height V, energy difference $E_1 - E_2$, and separation d. Transitions of an entity between the two wells of a pair can occur at low temperatures by means of thermal phonon-assisted tunneling through the potential barrier between the wells. The double-well model can account for the anomalous linear term in the heat capacity and the anomalous T^2 dependence of the thermal conductivity at low temperatures. In addition, expressions for two types of ultrasonic attenuation[3,9] have been worked out using this model. They are (i) a resonant absorption process[3,9] at lowest temperatures ($T < 1$ K) in which the attenuation is proportional to ω^2/T (ω is 2π times the ultrasonic frequency) and is amplitude dependent such that if the acoustic power exceeds the saturation level, the $1/T$ dependence is not observable; and (ii) a relaxation mechanism[9] which is very important at low temperatures and may be of some importance up to as high as 100 K. When

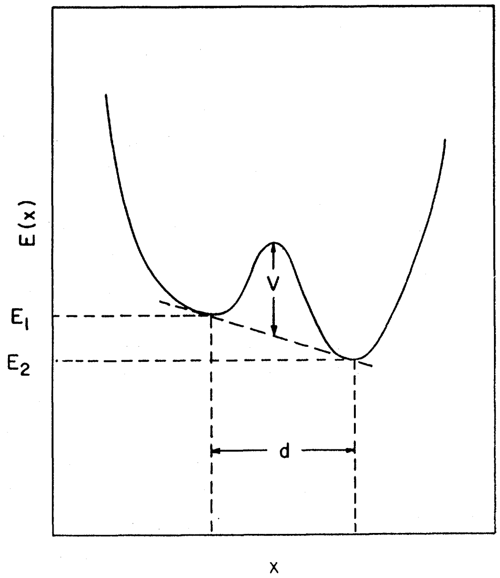

FIG. 1. Diagram (taken from Ref. 3) showing the potential energy of one set of nearly equivalent alternative configurations for an atom (ion) or group of atoms (ions) in a glass plotted as a function of a coordinate along a line connecting two adjacent potential energy minima. Because of the amorphous nature of the glass the double-potential wells at some locations have different values for $E_1 - E_2$ and for V than do the double wells at other locations.

$\omega\tau \ll 1$ the attenuation is linear in ω but independent of T. When, on the other hand, $\omega\tau_m \gg 1$, the attenuation is independent of ω and is proportional to T^3 (τ_m is the minimum value τ can have).

Experiments[10-13] have shown that the resonant absorption process does occur in oxide glasses indicating that two level systems are involved. It has not been determined, however, what the two level systems consist of. Some evidence for type-(ii) attenuation has been found in fused silica.[13]

Amorphous As_2S_3 was selected for our investigation partly because it is available commercially in very high quality—being extensively used for infrared windows in many optical applications. Its quality is, in fact, better than that of most amorphous materials. Data on it should thus provide information about properties intrinsic to the amorphous state itself rather than about properties which are caused by imperfections.

Previous ultrasonic studies on a-As_2S_3 have been limited in scope. The attenuation of 20-MHz longitudinal waves over a wide temperature range has been reported,[14] but only a sketchy compilation of its frequency dependence has been made.[14-17]

In this paper, we shall report the results of our measurements of the attenuation of ultrasonic waves in a-As_2S_3 between 1.5 and 480 K and at frequencies between 30 and 450 MHz. A preliminary report of some of our results has been given previously.[18] At low temperature some measurements were made in magnetic fields up to 133 kOe.[19]

Before presenting results of our ultrasonic investigation of a-As_2S_3 we shall summarize some properties of As_2S_3 which are pertinent to our work. Thus, x-ray diffraction studies have shown that crystalline As_2S_3 has the orpiment structure ($P2_1/n$) with lattice parameters[20,21]

$$a = 11.46\ \mathrm{\AA}, \quad b = 9.59\ \mathrm{\AA}, \quad c = 4.24\ \mathrm{\AA},$$

$$\alpha = \gamma = \tfrac{1}{2}\pi, \quad \beta = 90^\circ\ 27'.$$

Each arsenic (As) atom is bonded to three sulphur (S) atoms to form a pyramid. The As atom occupies the apex of the pyramid while the S atoms occupy the corners of its triangular base. Each S atom belongs to two pyramids in order to satisfy the covalent-bonding requirements. The pyramids are arranged in puckered hexagonal rings which extend to form a two-dimensional layer structure.[22] Adjacent layers are held together by weak van der Waals forces. These layers are parallel to the (010) planes. The bases of the pyramids are not parallel to this plane; instead the bases of adjacent pyramids are tilted away from the plane by different amounts.[23] Furthermore, the As atoms can be either above or below the plane. If we designate the As atoms which are above the plane by A and the As atoms which are below the plane by B, then on going around a hexagon the As atoms will appear in the order $AABAAB$ or $BBABBA$. Each As-up pyramid is connected to two As-down pyramids and one As-up pyramid. Each As-down pyramid is connected to two As-up pyramids and one As-down pyramid. The connection is via the S atom which is common to the pyramid in question and a neighboring pyramid. A one-dimensional chainlike structure for As_2S_3 is also possible but no allotropic crystalline form based on such a structure has been found.[24]

Recent x-ray and neutron diffraction studies[25] on amorphous arsenic sulfide close in composition to As_2S_3 indicate the presence of sheets or layers containing As and S atoms whose respective two-fold and threefold covalency requirements are satisfied but that the ring-structure characteristic of the orpiment structure is not preserved. Within a layer there does seem to be a correlation length of 11 Å. The separation between sheets is larger than in orpiment and intersheet correlation perpendicular to the sheets extends for 15 Å. Other investigators[26] have concluded that a-As_2S_3 has a layer structure generally similar to that in orpiment but that sometimes a ring may contain 5 or 7 pyramids instead of 6 as in orpiment.

Rubinstein and Taylor[23] have observed a broad line in the nuclear quadrupole resonance in amorphous As_2S_3 and As_2Se_3. By comparing their amorphous As_2S_3 data with that on the crystalline form, they concluded that it could be interpreted in terms of there being AsS_3 pyramids in the amorphous state which had a distribution of apex angles with halfwidth of about 2°. The average of the apex angles in the crystalline form is about 98°.

Bermudez[27] had made a computer-generated two-dimensional A_2B_3-type disordered-network model for the structure of As_2S_3 and As_2Se_3. From this model he calculated a Raman scattering cross section which is in reasonable agreement with experiment.[28] A graphical representation of this two-dimensional disordered network has been given which is essentially the projection of the As_2S_3 system on to a plane.[24] There are two alternative positions which the sulphur atom can occupy and still produce the same angle for the As-S-As bond. The densities of vibrational states calculated by Bermudez and that deduced from optical[29] or Raman data[28] seem to exhibit: (a) a low-frequency continuum which can be ascribed to the bond (As-S-As) stretching mode, (b) stretching of the S-As-S bond at 310 cm^{-1}, and (c) a peak at 340 cm^{-1} corresponding to an antisymmetric As-S-As bond stretching vibration. Bermudez used a Gaussian distribution of As-S-As bond angles of mean value 150° and a standard deviation of 10°. There is evidence that such a distribution is needed to interpret infrared data.

Much work has been done on the electrical,[30-32] optical,[33-37] and thermal[2,38-41] properties of amorphous As_2S_3. It is found from dc conductivity measurements that a-As_2S_3 has a large electrical activation energy in the range of 2.1–2.3 eV.[31] The ac conductivity is proportional to ω at frequencies up to 10^6 Hz and to ω^2 at frequencies between about 10^8 and 10^{11} Hz. Pollak and Pike,[42] employing the double-well model have shown that a linearly frequency-dependent conductivity can result from an ion hopping over the barrier in a double well. Strom and Taylor[32] suggested that the ω^2 dependence may be due to one-phonon acoustic mode absorption which is induced by disorder in glasses, the reason being that disorder-induced local charge deviation can couple the incident photons to elastic waves in the glass. They claimed that if this interpretation is correct, the increase in value of the T^3 coefficient in the specific heat of amorphous materials over the crystalline counterpart would then be related to the ω^2 absorption in the far infrared. Taylor *et al.*[43] also suggested that the ω^2 dependence in chalcogenide glasses could be due to the low-frequency edge of a Gaussian distribution of harmonic oscillators. Raman[28] and infrared reflectance data[23] on a-As_2S_3 have also been analyzed using a molecular model.[34] The calculated vibration frequencies for a-As_2S_3 agreed well with experimental values.[28] In the calculation it was assumed that the bond bending force constant of the bridging As-S-As bond is much weaker than the bond stretching force constant of the AsS_3 pyramidal molecule.

The molecular model has been criticized[37] because its use of only two or three oscillators to interpret a given infrared (ir) absorption peak is inadequate to account for the wideness of the "base" of the peak. In fact a Gaussian distribution of Lorentzian oscillators has been successful in interpreting each ir peak more completely. The Gaussian distribution needed to explain the peak centered around 340 cm^{-1} has been generated using a two-dimensional A_2B_3 disordered network model[27] as was mentioned previously.

It seems to us that a-As_2S_3 consists of layers containing irregular rings of distorted molecular pyramids of AsS_3. The layers are oriented in a variety of directions thereby producing sample isotropy. The layers are "bonded" together at random points[44] where there are As atoms in octahedral coordination.[45] Furthermore we think that bending of the As-S-As bonds is representable in terms of the motion of a sulfur atom or ion between the two potential wells of a pair.

As will be demonstrated the motion of sulfur ions seems to be mainly responsible for the attenuation at the lower temperatures while the motion of AsS_3 pyramids or groups of such pyramids may be mainly responsible for the attenuation at the higher temperatures.

II. EXPERIMENTAL DETAILS

A. Samples

Amorphous As_2S_3 blanks of grade A or B quality were purchased from the American Optical Corp. Samples suitable for ultrasonic studies were prepared from them by polishing the faces extremely smooth, flat, and parallel. Some of the samples were checked for amorphism using x rays. Laue pictures obtained using x rays revealed no spots nor rings, indicating the absence of crystallinity (at least in the 200-Å depth from which the backscattered x rays originate). Measurements of the intensity of Cu K x rays ($\lambda = 1.54$ Å) as a function of diffraction angle showed very broad maxima. Inspection of the x-ray intensities observed for glassy As_2S_3 and powdered orpiment (crystalline As_2S_3) by others[46] indicates that our x-ray data resemble those for the glass and are quite unlike that of the powdered crystalline As_2S_3. This can be taken as further evidence that our sample is amorphous. One of our samples was analyzed for impurities by mass spectrography at the Battelle Laboratories, Columbus, Ohio. The major impurities found are summarized in Table I. Although our sample contained more Fe (10 ppm) than the especially high-purity a-As_2S_3 prepared by DiSalvo *et al.*[47] (which has about 0.3 ppm of Fe), our sample did have only about the same amount of Fe as their nominally pure sample. The concentrations of Zn, C, and O were not determinable by the mass-spectrographic method. The absorption coefficient for infrared radiation between 7 and 13 μm showed that there are two absorption bands at 8.7 and 10.1 μm. According to Savage and Nielsen[48] and Moynihan *et al.*[49] the absorption at 8.7 μm is due to the presence of oxides. Comparison with the absorption coefficients given by these workers showed that the absorption of our sample is slightly larger than that exhibited by the pure sample of Savage and Nielsen and is considerably less than that exhibited by their impure sample.

B. Experiment

The attenuation was measured by observing the decay in the amplitude of the train of echoes produced by each 2-μsec-wide pulse of ultrasonic waves generated in X-cut or AC-cut quartz transducer crystals by a pulse of rf. The quartz transducers had chrome-gold-plated electrodes and were purchased from the Valpey Fisher Co. From 100 K up, phenyl salicylate (Salol), Dow Corning 200 fluids, and Plexol were used to bond transducers to the sample with varying degree of success. Below 77 K, 4-methylpentene-1 was the only material which produced a suitable bond. The electronic equipment consisted of a Matec 1204 Master Synchronizer and Exponential Generator, a Matec 6000 R. F. Pulse Generator and Receiver, a Matec 2470 Attenuation Recorder, Weischell tuning stubs, a Tektronix 585 Scope, and either a Leeds and Northup Speedomax W Multipoint Recorder or a Hewlett Packard 7000A X-Y Recorder. Temperatures below room temperature were obtained by using a commercial variable-temperature metal Dewar flask made by Cryogenic Associates. The temperature of the sample was measured by means of a Cryocal germanium-resistance thermometer. This Ge thermometer was calibrated from 1.5 to 100 K by comparison with a calibrated unit obtained from the manufacturer. From 50 to 300 K, temperatures were measured with an Artonix platinum thermometer. Sample temperatures above 4.2 K were obtained by using a constantan heater controlled by a Princeton Applied Research Model 152 controller which used a gallium arsenide diode as a sensor.

Some data were obtained with the sample in a magnetic field at liquid-helium temperatures using an Intermagnetics General Corp., IGC 31010, 140-kG, 2-in.-diam bore superconducting solenoid. The sample temperature was determined by the boiling point of the liquid helium in which the sample was immersed, and was measured at zero field using a germanium thermometer. No attempt was made to control the temperature. The magnetic field strength was measured using a calibrated magnetoresistance probe (IGC 31011).

TABLE I. Impurity concentration ratios in amorphous As_2S_3, sample No. 7, obtained from mass-spectrographic analysis performed by Battelle Columbus Laboratories, Columbus, Ohio.

Impurity element	$N_I/(N_{As}+N_S)$ [a] (ppm)
Al	1
Sb	200
B	0.002
Ca	6
Cl	14
F	1
Fe	9
K	13
Ru	0.3 to 3
Si	1
63 others	below detection limit [b]

[a] N_I, N_{As}, and N_S are the number of impurity, arsenic, and sulfur atoms, respectively.

[b] Detection limits ranged from a low of 0.05 ppm for Be to a high of 11 ppm for Sc.

III. RESULTS

The velocities of longitudinal and shear waves of different frequencies, measured using the pulse-echo-overlap method, are shown in Figs. 2 and 3. Note that the velocities increase somewhat with decreasing temperature or increasing frequency.

In Fig. 4 is shown the attenuation of 30-MHz longitudinal waves from 140 to 480 K. It can be seen that the attenuation increases ever more steeply as the temperature is increased. Similar results had been found previously for 20-MHz longitudinal waves by Krause *et al.*[14]

In Fig. 5 is shown the attenuation of longitudinal waves at different frequencies from 1.5 to 50 K. The attenuation is almost independent of temperature at the higher temperatures. However, when

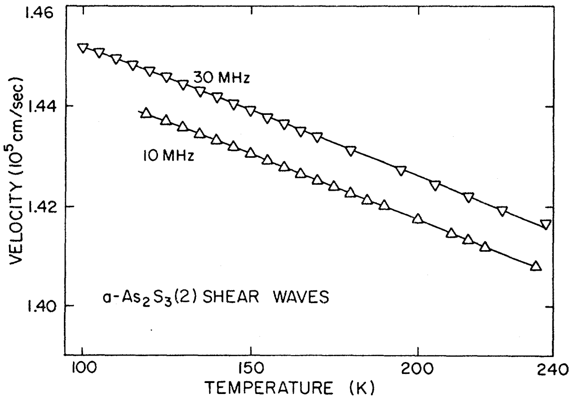

FIG. 2. Velocities of 10- and 30-MHz shear waves in amorphous As_2S_3, sample No. 2, vs temperature.

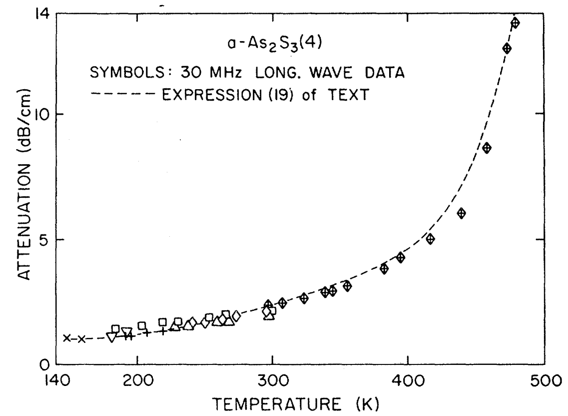

FIG. 4. Attenuation of 30-MHz longitudinal waves in amorphous As_2S_3, sample No. 4, from 140 K to near the glass temperature. The symbols represent data points obtained with various types of bonds as follows: □◇ salol; +× DC 200 fluid, 100 cS; ▽ DC 200 fluid, 1000 cS; and ⊕ DC 710. (DC stands for Dow Corning and cS for centistoke.) The dashed line is an empirical fit of the three-term expression (19) of the text which contains a constant term and two terms which are exponential functions of $-1/T$, where T is the absolute temperature.

the temperature is decreased sufficiently, the attenuation begins to decrease with decreasing temperature doing so more strongly the higher the frequency and the lower the temperature. Figure 6 shows that the attenuation is linear in frequency at high temperatures and low frequencies and has a smaller frequency dependence at the lower temperatures.

In Fig. 7 the frequency dependence of the attenuation of longitudinal and shear waves at different temperatures are shown as log-log plots. The slopes of these plots were obtained by performing least-square fits to the data. All the slopes are very close to unity. The frequency dependence of the attenuation at the temperature in question can be represented by the relation

$$\alpha = A(T)\omega^s , \quad (1)$$

where $s = 1.02 \pm 0.03$ within 2 standard deviations. Three separate, previously reported, values of the attenuation[15-17] are very similar to ours although there are some slight differences. The differences are not understood, but we think they may be due to differences in the preparation procedures for different sample lots, possibly at the annealing stage.

We have observed that the attenuation of 30-MHz ultrasonic waves in a-As_2S_3 at 4.2 K is affected slightly by a magnetic field—at 133 kG the increase in attenuation was about 0.6% ± 0.7% in the case of longitudinal waves and about 2% ± 1% in the case of shear waves.

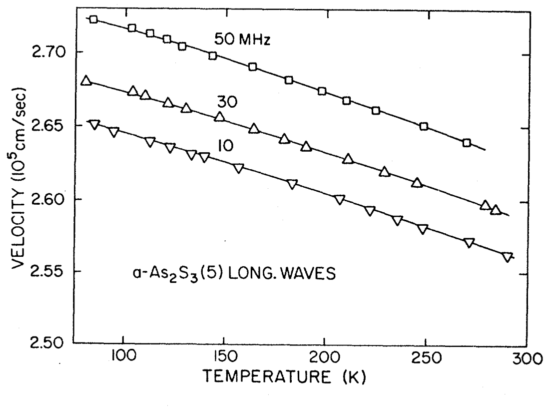

FIG. 3. Velocities of 10-, 30-, and 50-MHz longitudinal waves in amorphous As_2S_3, Sample No. 5, vs temperature.

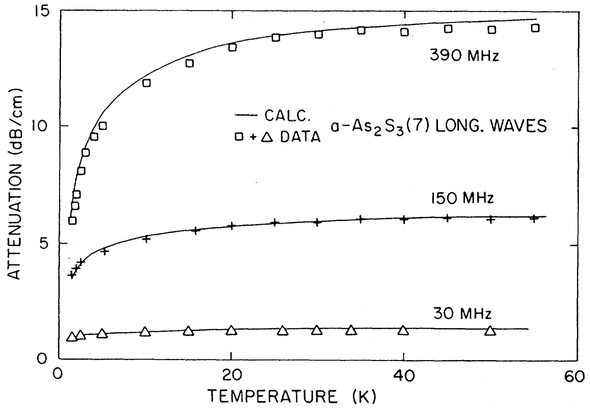

FIG. 5. Attenuation of longitudinal waves in amorphous As_2S_3, sample No. 7, between 1.5 and 50 K. The curves were calculated using the thermal phonon-assisted ionic tunneling time given by Eq. (6) of the text in the attenuation formula given in Eq. (7) of the text.

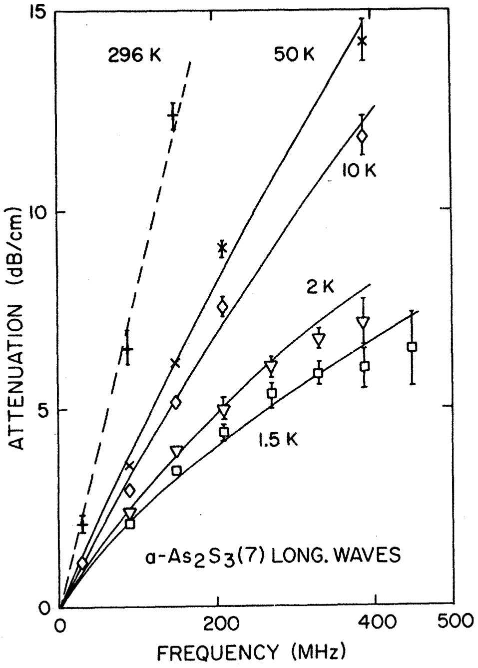

FIG. 6. Attenuation versus frequency for longitudinal waves in amorphous As_2S_3, sample No. 7, at various temperatures.

IV. DISCUSSION

The linear frequency dependence which we observed for the attenuation in a-As_2S_3 at ordinary temperatures is similar to that observed previously in many other glasses[50] and in amorphous polymers.[51-53]

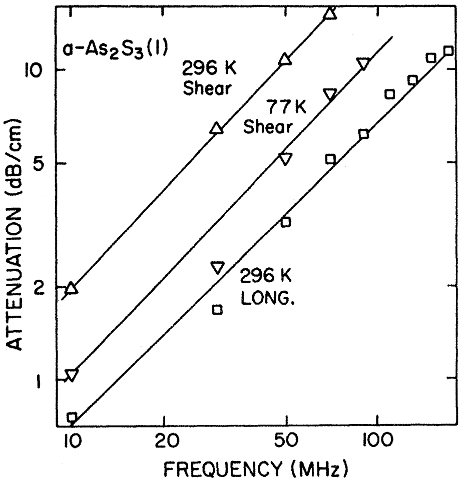

FIG. 7. Log-log plot of attenuation vs frequency in amorphous As_2S_3, sample No. 1. Shear-wave data are shown for 77 and 296 K and longitudinal-wave data are shown for 296 K. The slopes of the straight lines through the shear-wave data are 1.05 at 296 K and 1.08 at 77 K. The slope of the straight line through the longitudinal-wave data is 1.02.

It is known that relaxation processes can give rise to sound absorption. The attenuation associated with an elementary relaxation process is given by

$$\alpha_j = R_j\,\omega^2\tau_j/(1+\omega^2\tau_j^2)\,, \qquad (2)$$

where R_j is the relaxation strength divided by the wavelength of the ultrasonic wave, τ_j is the relaxation time characteristic of the elementary relaxation process, and ω is the angular frequency of the ultrasonic wave.

The theory for the Akhieser-type relaxation process due to thermal phonon interaction has been worked out for the crystalline case by various authors.[54-58] For our purposes it is adequate to use formulas for the attenuation given by Woodruff and Ehrenreich.[55] They found that

$$\alpha = (\gamma^2 C_v T/2\rho v^3)\omega\tan^{-1}(2\omega\tau)\,, \qquad (3)$$

when there is no local temperature change due to the ultrasonic strain (i.e., $\Delta T \approx 0$) and only umklapp scattering of thermal phonons by each other is important. Woodruff and Ehrenreich also found that when $\omega\tau \ll 1$,

$$\alpha = (\gamma^2 C_v\, T/3\rho v^3)\omega^2\tau\,, \qquad (4)$$

provided that $\Delta T \neq 0$ (but again only umklapp scattering is important). Equation (4) is a special case of the general relaxation form given by Eq. (2) for the $\omega\tau \ll 1$ case. γ is an anharmonicity parameter similar to the Grüneisen "constant," τ is the thermal-phonon lifetime which can be estimated from the measured thermal conductivity κ, heat capacity C_v, and velocity of sound v using the relation

$$\kappa = \tfrac{1}{3} C v^2 \tau\,. \qquad (5)$$

If $\omega\tau \gg 1$, α is proportional to ω according to Eq. (3). It should be noted, however, that when $\omega\tau \gg 1$ direct scattering of ultrasonic phonons by thermal phonons becomes predominant, and although Eq. (3) can account for the frequency dependence sometimes observed for the attenuation, it does not ordinarily account for the temperature dependence observed for α. Using values of κ, C_v, and v from the literature,[59] we find that for the ultrasonic frequencies employed in this work, $\omega\tau \ll 1$, and both Eqs. (3) and (4) give an attenuation proportional to ω^2, which does not agree with the observed frequency dependence. In addition, for ordinary values of γ, the attenuation calculated from Eqs. (3) and (4) is much smaller than the attenuation which is observed in amorphous materials. Thus if τ is the same for all thermal processes as is assumed in the derivation of Eqs.

(3) and (4), the attenuation in amorphous substances is not due to the Akhieser relaxation process involving the interaction between thermal phonons.

Consider again Eq. (2). The attenuation given by it reaches a maximum when $\omega\tau_j = 1$. However, if a distribution of relaxation times exists, there will be a series of terms similar to the expression in Eq. (2) each having a different value of τ_j. The resultant attenuation will be proportional to ω if the τ_j's have a wide range of values. We think this is why the attenuation observed in many amorphous materials has a linear frequency dependence since a wide distribution of relaxation times can be justified physically. We shall discuss this further later.

The velocities shown in Figs. 2 and 3 increase in a manner similar to that expected due to the anharmonicity of interatomic forces.[60] The increase in velocity with increasing frequency implies, as did our attenuation data, that Akhieser-type relaxation due to thermal phonon interactions is not the predominant source of attenuation. This inference is made because, if the Akhieser process were predominant, no appreciable dispersion in velocity would be expected when $\omega\tau \ll 1$. From the values of the velocities of 30-MHz longitudinal and shear waves which were measured for our samples at 100 K, we obtain a value of 163 K for the elastic Debye temperature in fairly good agreement with the value of 170 K quoted by Stephens.[2]

Our low-temperature attenuation data showed no evidence for the amplitude-dependent attenuation due to resonant absorption of ultrasonic phonons.[10-13] Such attenuation occurs at lower temperatures, higher frequencies, and lower acoustical power than those which we have used.

Our attenuation data at low temperatures can be interpreted by means of Jackle's theory[9] for relaxation due to thermal phonon-assisted tunneling of ions between alternative positions representable by a double potential well. For a given pair of wells the phonon-assisted tunneling time τ_t is given by[9]

$$\tau_t^{-1} = \left(\frac{B_l^2}{v_l^5} + \frac{2B_t^2}{v_t^5}\right)\frac{\Delta^2 E}{2\pi\rho\hbar^4}\coth\left(\frac{E}{2kT}\right), \tag{6}$$

where $E = (\epsilon^2 + \Delta^2)^{1/2}$, $\epsilon = E_1 + \hbar\omega_1 - E_2 - \hbar\omega_2$, $\Delta = \hbar\omega_0 e^{-\lambda}$, and $\lambda \approx \frac{1}{2}(2mV/\hbar^2)^{1/2}d$. B_l and B_t are the deformation potentials for longitudinal and transverse phonons, respectively. E_1 and E_2 are the energies of the bottoms of well 1 and well 2 of a pair; ω_1 and ω_2 are the zero-point vibrational frequencies of the atom in wells 1 and 2 and they are both expected to be approximately equal to ω_0 which we take to be 10^{13} rad/sec; d is the separation between the two wells of a pair. A wide distribution in the values of τ_t can arise if double wells at various locations are characterized by suitably different values of λ and E. When τ_t has a wide range of values and $\omega\tau_t \ll 1$ for all τ_t of interest, the attenuation turns out to be proportional to frequency and almost independent of temperature[9] thus accounting qualitatively for the behavior of the attenuation in the upper part of the temperature range shown in Fig. 5.

In the case when $\omega\tau_t \gg 1$, the attenuation is independent of frequency and has a T^3 dependence.[9] Our experiment was not carried down to low enough temperatures to reach the frequency-independent T^3 temperature-dependent region which has been observed in fused silica.[10-13] However, from Figs. 5 and 6 we can see that we may be approaching that regime.

In order to account for our low-temperature attenuation data we used an expression based on the work of Jackle,[9] namely,

$$\alpha = \frac{B^2}{2\rho v^3 kT}\int\int P(\epsilon,\lambda)\,\mathrm{sech}^2\left(\frac{E}{2kT}\right) \times \frac{\epsilon^2}{E^2}\,\frac{\omega^2\tau_t}{1+\omega^2\tau_t^2}\,d\epsilon\,d\lambda\,. \tag{7}$$

$P(\epsilon, \lambda)$ is proportional to the probability of the occurrence of double wells which have an energy difference of ϵ between the two wells in a double-well and a tunneling parameter λ. More specifically we chose

$$P(\epsilon,\lambda) = N_{\text{total}}\,P(\epsilon)P(\lambda), \tag{8}$$

with

$$P(\epsilon) = [\exp(-\epsilon^2/2\sigma_\epsilon^2)]/(2\pi)^{1/2}\sigma_\epsilon$$

and

$$P(\lambda) = \{\exp[-(\lambda-\lambda_0)^2/\sigma_\lambda^2]\}/(2\pi)^{1/2}\sigma_\lambda\,.$$

The latter distribution is really less *ad hoc* than it might appear to be at first sight since a one-parameter alternative distribution

$$P'(\lambda) = (2\lambda^3/\lambda'^2)\exp(-\lambda^2/\lambda_0'^2) \tag{9}$$

has the same shape as our $P(\lambda)$ when $\lambda' = 8.1$. N_{total} is the total number of wells in a unit volume of material, and σ_ϵ and σ_λ are the widths of the ϵ and λ distributions. The integral in Eq. (7) was evaluated numerically by means of a CDC 6500 computer using an integration routine from the library of the Purdue Computer Science Center. A lower limit of $\lambda = 3$ was used in performing the integration because the tunneling rate formula, Eq. (6), is valid[3,6] only down to a value of λ of about that size. An upper limit of $\lambda = 12$ was used because we found that almost all of the attenuation calculable from Eq. (7) using $P(\epsilon, \lambda)$ was included for such an upper limit. For comparison it should be noted that Anderson *et al.*[3] suggested that $\lambda_{min} = 5$ and $\lambda_{max} = 20$. The limits we choose for λ imply that the number of wells per unit volume having a suitable value of λ is $\int\int N_{total} P(\epsilon)P(\lambda)\, d\epsilon\, d\lambda = 0.66\ N_{total}$.

Values for B_l, B_t, σ_ϵ, σ_λ, and λ_0 were determined to give a best fit to the 150-MHz longitudinal wave data. The values are $N_{total} = 2.7\times 10^{19}$ cm^{-3}, $\sigma_\epsilon = 0.04$ eV, $\sigma_\lambda = 4$, $\lambda_0 = 10$, $B_l = 1$ eV, and $B_t = \frac{1}{2}$eV. λ_0 corresponds to the most probable value of λ which is involved in Eq. (6). If the tunneling particle is the sulphur atom, and if $d = 1$ Å, this value of $\lambda_0 = 10$ implies a value of $V_0 = 0.025$ eV for the most probable barrier height between wells. This value of V_0 is reasonable in view of the feeling[4] that the maximum value of V should be of the order of thermal energy at the glass temperature. For a-As_2S_3 this would mean a V_{max} of about 0.041 eV. Our value of V_0 is also consistent with the size of the barrier V_b calculable[61,62] for two symmetric, harmonic wells spaced a distance d of 1 Å apart, with each well representing the potential energy of a sulfur ion vibrating with a zero-point frequency ω_0 of 10^{13} rad/sec. Specifically, $V_b = \frac{1}{4}M\omega_0^2 d^2 = 0.042$ eV, where M is the mass of sulfur. It should also be noted that calculation of V_b in this manner implies a tunneling parameter λ_b of $M\omega_0 d^2/4\hbar$ with a value of 12.7 which is surprisingly close to the maximum value of λ which is needed to fit Eq. (7) to our low-temperature attenuation data.

The set of values for B, σ_ϵ, σ_λ, and λ_0 obtained by fitting the 150-MHz attenuation versus temperature data was then used to calculate the attenuation expected for 30- and 390-MHz longitudinal waves. A comparison of the calculated and the experimental values is shown in Fig. 5. The solid curves indicating the calculated attenuation fit the data points (given by the symbols) very well. Similar agreement is obtained for shear waves.

One estimate of the physical significance of the fit is obtained by comparing the value of N_{total} which we obtained from fitting our attenuation data with that implied by specific-heat data. Stephens[2] has measured the specific heat of amorphous As_2S_3 and found that at very low temperatures it can be represented by

$$C_v = C_1 T + C_3 T^3\,, \tag{10}$$

where for a-As_2S_3 $C_1 = 14$ erg g^{-1}K^{-2} or 45 erg cm^{-3} K^{-2}. We identify $C_1 T$ with the specific heat derived from the double-well model,[3] i.e., $\frac{1}{6}\pi^2 k^2 n(0)T$, where k is Boltzmann's constant and $n(0)$ is the constant value which the density of double wells is assumed to have for ϵ between 0 and some maximum value ϵ_{max}. Above ϵ_{max} the density of wells is considered to be zero. Since ϵ is the difference in energy between a state located in one well and that located in the other well of a given pair, simple geometrical considerations imply that $\epsilon_{max} = xV_{max}$, where $0 < x < 1$ and V_{max} is the maximum potential energy barrier which occurs. With $V_{max} \approx 0.041$ eV we have for the number of wells per cm^3,

$$N_{total} \approx n(0)xV_{max} \simeq \frac{6C_1}{\pi^2 k^2}\, xV_{max} \simeq 9.4\times 10^{19} x \text{ cm}^{-3}\,.$$

Equating this expression to the value of N_{total} deduced from our attenuation data (i.e., 2.7×10^{19} cm^{-3}), we obtain a very reasonable value of 0.29 for x.

Stephens also showed that the very-low-temperature heat capacity of some amorphous solids could be fitted by the three-term expression

$$C_v = C_1' T + C_2' T^2 + C_3' T^3\,. \tag{11}$$

Some authors have suggested that the T^2 term is due to vibrational modes having two degrees of freedom and that the T^3 term equals that expected for a Debye model. It has been shown[8] that the heat capacity anomalies can be accounted for in terms of localized modes arising because there is order within three or four atomic distances of a given atom. For fused silica a contribution to the density of vibrational states which is proportional to frequency has been deduced from Raman data. Barber[63] claimed that such a linear frequency dependence contributes to the T^2 term and that theoretical calculations relevant to glasses having tetrahedral atomic configurations can account for the T^2 term in the heat capacity.

No linearly-frequency-dependent contribution to the density of vibrational states has yet been deduced for a-As_2S_3. However, if we assume that for a-As_2S_3 the $C_3' T^3$ term equals the heat capacity calculable from the Debye model with a Debye temperature deduced from the velocities of longitudinal and shear ultrasonic waves which are measured at 100 K, it is found that Eq. (11) does fit the heat capacity of Stephens's purest sample with $C_1' = 8.8$ erg g^{-1}K^{-1} and $C_2' = 35.4$ erg g^{-1}K^{-2}. The presence of the T^2 term supports the notion that extra vibrational states are connected with motions within layers which are not only weakly bonded by van der Waals forces to adjacent layers as in the crystalline form but, furthermore, must be bonded at only a few random locations.[44]

If, as before, we attribute the $C_1' T$ term to the tunneling of ions between potential wells, the number of double wells is now equal to $C_1'/C_1 = 0.63$ times the number derived from Eq. (10) implying that $x \approx 0.43$. This value of x is also quite reasonable.

The heat capacity data also has some implications for the thermal phonon-assisted tunneling time τ_t. This is because the latter depends on the density of phonon states. [In Eq. (6) it is assumed that this density is simply that given by the Debye model.] Stephens deduced a density of states $g(\omega)$ by requiring that *both* terms in Eq. (10) be accounted for by it. He found

$$g(\omega) = a + (b + b_D)(\hbar\omega)^2 \tag{12}$$

where $b_D(\hbar\omega)^2$ is the Debye density of phonon states and a and $b + b_D$ give rise respectively to the C_1T and C_3T^3 terms into which the heat capacity can be analyzed.

Following Anderson *et al.*[3] we consider the quantity a to be dependent on the density of potential wells so that the true density of vibrational states is given by $(b + b_D)(\hbar\omega)^2$. Consequently, the new tunneling rate is given by

$$\tau_{nt}^{-1}(E_j) = (b + b_D)/[b_D]\,\tau_t^{-1}(E_j), \tag{13}$$

where τ_t^{-1} is given by Eq. (6). Using the Stephens heat capacity[2] we find that for a-As_2S_3, $(b+b_D)/b_D = 1.8$. Thus, if $b(\hbar\omega)^2$ does describe the density of extra vibrational states τ_{nt}^{-1} has a value 1.8 times that of τ_t^{-1} given by Eq. (6). We do not need to recalculate the attenuation using τ_{nt} because the tunneling rate depends on other quantities such as the deformation potentials B_l and B_t and $\Delta = \hbar\omega_0 e^{-\lambda}$ whose values are not precisely known so that the 1.8 factor can be considered to be already absorbed in these quantities. (It might also be argued that the extra states may not involve phonons which assist the tunneling of ions.)

In order to be better able to interpret our attenuation data on a-As_2S_3 we shall consider the behavior of other glasses at moderately low temperatures. Many glasses show an attenuation maximum in this temperature range.[64-69] However, we have not observed such a maximum in amorphous As_2S_3 nor did Krause *et al.*[14] A rather small but wide attenuation peak has been observed at 54 MHz in amorphous As_2Se_3 between about 5 and 80 K.[69] The peak appears on top of a fairly temperature-independent background attenuation. Because of the similarity in structure between the As_2S_3 and As_2Se_3, one would be inclined to think that the "background" attenuation in amorphous As_2Se_3 is similar in nature to that observed in amorphous As_2S_3 and is due to the same phonon-assisted tunneling mechanism, whereas the peak proper may be due to the relaxation associated with the hopping of ions over barriers which have a narrower range of *lower* heights than in a-As_2S_3. Perhaps the attenuation peak in As_2Se_3 might be due to impurities. It would be interesting to know if these impurities might cause a Schottky-type anomaly in the heat capacity.

An attenuation peak has been observed in fused silica which is apparently due to OH^- impurities.[66] However, Anderson and Bommel[64] have interpreted a broad attenuation maximum in fused silica in terms of the relaxation of oxygen atoms in the Si-O-Si bond. The deformation of the bond angle requires energy and can be regarded as the height of the barrier which the oxygens have to jump over. The attenuation maximum is too broad to be fitted by a single relaxation peak, and in order to produce a good fit, Anderson and Bommel assumed the existence of six thermally activated relaxations each of which has a different activation energy between 1 and 1.5 kcal/mole and a different relaxation strength. By invoking the possible existence of a much wider distribution of relaxation times for a-As_2S_3 than that found for fused silica, we can explain qualitatively the absence of an analogous attenuation maximum in a-As_2S_3 below 140 K. The force constant associated with the bending of the As-S-As bond is much smaller than that associated with the S-As-S bond,[33,34] and consequently it is most likely that the moving particles are sulfur atoms (or ions). The positions describable by the two wells of each double potential well are then identified with the nearly equivalent alternative positions for the sulfur atoms. The barrier between the wells is caused by the energy required to straighten out the As-S-As bond. This energy is proportional to the angle of displacement of the sulphur atom. Because of the weak van der Waals bonding between layers at a few random locations,[44] there will be a wide distribution in the angle of displacement and hence a wide distribution of relaxation times.

We turn now to the rise in the attenuation which we observed in a-As_2S_3 above 140 K as shown in Figs. 4 and 8. Between 140 and 300 K the rise in attenuation was accounted for previously[18] by assuming that associated with each of the many double potential wells in the material there is a relaxation process in which an ion jumps over the barrier between the two wells of the double well. It was also assumed that various barrier heights occur and that the number of wells with a given barrier height V can be expressed in terms of the number of wells having a given barrier parameter λ. The latter number is proportional to the $P(\lambda)$ distribution function in Eq. (8) which we used to calculate the low temperature tunneling attenuation. The formula which was used for the hopping attenuation is

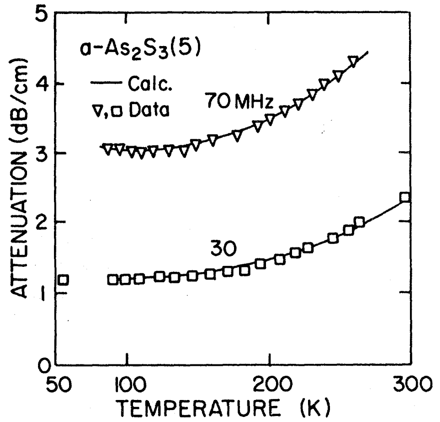

FIG. 8. Attenuation of 30- and 70-MHz longitudinal waves in amorphous As$_2$S$_3$, sample No. 5, between 50 and 300 K. The symbols represent the experimental data and each curve gives the sum of the attenuation calculated for thermally activated hopping over potential energy barriers by using either Eq. (15) or Eq. (18) of the text and a background attenuation which is independent of temperature.

$$\alpha_{\rm hop} = C \int \frac{\omega^2\tau}{1+\omega^2\tau^2} P(\lambda)d\lambda , \tag{14}$$

with the hopping relaxation time τ being given by

$$\tau = (10^{-13}\ {\rm sec})e^{V/kT} . \tag{15}$$

In Eqs. (14) and (15), $V = 2\lambda^2\hbar^2/Md^2$. We found[18] that using a fixed value of $d = \frac{1}{4}$ Å we could calculate curves which fitted the attenuation data very well as shown in Fig. 8 provided that λ_0 and σ_λ in $P(\lambda)$ had values of 15 and 3, respectively.

Since the above values of d and λ_0 are different than those needed to fit the attenuation at low temperatures, we surmise that different kinds of moving entities and potential barriers are involved in the hopping attenuation instead of the sulfur ions which seem to be involved in the low temperature (tunneling) attenuation. To obtain an idea of the possible nature of the entities involved in hopping, we note that with $d = \frac{1}{4}$ Å a value of 15 for λ_0 implies that $(2MV)^{1/2} \approx 30\hbar/(\frac{1}{4}\times 10^{-8}) = 1.27 \times 10^{-17}$ erg sec cm^{-1}, and if $V \lesssim kT_{\rm glass} \approx 0.041$ eV, then $M = 1.23\times 10^{-21}$ g or 736 atomic mass units. Such a large mass would seem to imply that the hopping entity is comprised of a group of ions which move as a unit. Furthermore, in view of the structure of a-As$_2$S$_3$ the group would most likely contain six AsS$_3$ pyramids on the average. (We took the mass of each pyramid to be that of AsS$_{3/2}$ since each S is shared by two pyramids.) Such a number of pyramids is reasonable in terms of the maximum number consistent with the 11-Å in-layer correlation distance[25] in a-As$_2$S$_3$. The hopping motion might be analogous to the rigid layer mode vibrations in crystalline orpiment.[70]

In order for Eq. (14) to fit the rise in attenuation between 140 and 300 K, C had to have a value of 6.3×10^{-7} dB sec cm^{-1}. Since C is just N times the factor in front of the integral in Eq. (7), where N is the number of entities per unit volume, the above value of C implies that $NB^2 = 4.8\times 10^{19}$ cm^{-3} eV^2. If we assume that the deformation potential B has the fairly large value of 30 eV then there are $N = 5.3\times 10^{16}$ groups of pyramids per unit volume involved. Such a value for N means that a not unreasonable 0.008% of the atoms in the sample is involved in this type of relaxation process. Before concluding that hopping of groups of pyramids is indeed responsible for the measured rise in the attenuation between 140 and 300 K we shall discuss two alternative ways of fitting this rise.

The first alternative again assumes that there is a relaxation process which involves over-the-barrier hopping with a relaxation time given by Eq. (15) and that various values of V are possible. However instead of using a distribution in λ, we use a distribution in V. The first distribution in V which we have tried is based on the $P'(\lambda)$ distribution given by Eq. (9). Specifically we assumed that the probability that there are wells with barrier heights between V and $V + dV$ is given by $P'(V)dV = (V/V_0^2)e^{-V/V_0}dV$. This form of $P'(V)$ did not allow us to fit the observed rise in the attenuation. However a related distribution $P(V)$ did permit such a fit between 100 and 300 K. The distribution is given by

$$P(V) = (V^3/6V_0^4)e^{-V/V_0} \tag{16}$$

and the formula for the attenuation is

$$\alpha_{\rm hop} = C_R \int P(V) \frac{\omega^2\tau}{1+\omega^2\tau^2}\, dV . \tag{17}$$

In Eq. (17) we used τ as given by Eq. (15).

Assuming that the attenuation is the sum of that calculated using Eq. (17) and a temperature-independent linearly-frequency-dependent term with a value equal to that of the attenuation measured at 100 K, we can again calculate curves to fit our data provided that $V_0 = 0.8$ eV. These curves are the ones shown in Fig. 8 which were initially calculated using Eq. (14). Such an extremely large value of V_0 is hard to account for. Perhaps it could represent the barrier to some kind of relaxation of a structure which involves the flexing of the network of AsS$_3$ pyramids in a layer with dimensions of the order of 11-Å in-layer correlation length. Since a value of 2.2×10^{-5} dB sec cm^{-1} for C_R was needed to fit the rise in the experimental attenuation between 100 and 300 K then

$NB_R^2 = 1.7\times 10^{21}\ \mathrm{cm}^{-3}\,\mathrm{eV}^2$. By assuming the deformation potential associated with this relaxation process has a value of 100 eV we find that $N = 1.7\times 10^{17}\ \mathrm{cm}^{-3}$ or about 0.02% of the atoms in a cubic centimeter of material. Since either Eq. (14) or (17) can fit the rise in attenuation between 100 and 300 K if suitable but different values are chosen for the parameters involved, it may mean that more than one type of hopping is involved or that the deformation potentials should not be assumed to be independent of barrier height. There is indeed a precedent[14] for the relaxation strength to depend on the value of the activation energy involved in τ. Before concluding that either Eq. (14) or (17) implies a certain origin for the rise in attenuation above 140 K we shall discuss another way of fitting this temperature rise.

We have found that the rise in attenuation of 30-MHz longitudinal waves can be fitted fairly well from 140 K all the way to 480 K by means of the expression

$$0.98 + 36.8\,e^{-0.086\ \mathrm{eV}/kT} + 1.05\times 10^{7}\ e^{-0.58\ \mathrm{eV}/kT}, \tag{18}$$

where 0.98, 36.8, and 1.05×10^7 have units of dB/cm. How well expression (18) fits the data is shown in Fig. 4. It is not clear what the significance of this empirical fit is. It might mean that there are three types of processes two of which either must involve only certain thermally excited states or else must have coupling constants with appropriate exponential temperature dependences. The second term in (18) might be attributable to a small group of thermally excited AsS_3 pyramids and the third term in (18) to some kind of more massive structural relaxation.

It should be noted that for other frequencies besides 30 MHz we do not know if a three-term expression similar to (18) would fit the attenuation in the same temperature range where (18) fits the 30-MHz data. This is because, with the exception of the 20-MHz data by Krause *et al.*, measurements at other frequencies have been made (by us) only up to about 300 K and a constant term plus one exponential term suffice to fit our attenuation data in this more limited temperature range.

In view of the preceding discussion it should be evident that we have no definitive interpretation of the attenuation above 140 K. Hopefully, some of the elements in our discussion might prove useful in searching for such an interpretation.

Next we would like to consider the possibility that electronic effects are contributing to the attenuation. Approximate expressions for the absorption of sound due to electronic hopping have been worked out.[71] They are

$$\alpha \sim \exp(-\mathrm{const}\ \omega^{-1/3})\left(1 - \frac{\sin(\omega\tau)^{2/3}}{(\omega\tau)^{1/3}}\right), \tag{19}$$

when $\omega \gg \omega_0$, and

$$\alpha \sim \omega^2(\ln\omega)^4\left(1 - \frac{\sin\varphi}{\varphi}\right), \tag{20}$$

when $\omega \ll \omega_0$. In Eq. (19), $\varphi = (\omega/\omega_c)\ln(J/\omega)$ and ω_0, ω_c are characteristic frequencies of the theory, and J is an exchange integral occurring in the theory. It is obvious that the attenuation which we have observed does not have the frequency dependence implied by Eq. (19) or (20).

The very slight dependence of the attenuation on magnetic field strength at 4.2 K (see Sec. III) also seems to indicate the unlikelihood that electronic effects are important for the low-temperature attenuation. Since we do not think that the slight increase in attenuation with magnetic field is an intrinsic effect, we should like to comment on the likelihood that impurities are responsible for it. First of all, we recall that our a-As_2S_3 sample which was analyzed by mass spectroscopy contained about 10 ppm of Fe (see Table I). Such a concentration of Fe in a-As_2S_3 has been found to cause a measurable Curie-law-type of magnetic susceptibility at low temperatures.[47] Experiment has shown that Fe^{2+} impurities cause a magnetic field dependence of the hypersonic attenuation in crystalline MgO at low temperatures.[72] Most of the conditions of the MgO experiment (higher Fe concentration, crystalline material, higher frequencies, and lower magnetic field strengths) are so different from ours however that it does not seem justified to conclude that impurities are responsible for the slight field dependence of the attenuation. Instead the attenuation of a-As_2S_3 samples with various known amounts of Fe should be investigated carefully as a function of magnetic field strength.

V. CONCLUSION

Our low-temperature attenuation data on a-As_2S_3 support the concept that in glasses there are certain atoms (or ions) each of which has available to it two alternative sites of almost the same energy which are representable by a double potential well. Furthermore, with the assistance of thermal phonons an atom (or ion) can tunnel through the potential barrier between the two wells. We conclude that in a-As_2S_3 there are double wells with a wide variety of barrier heights and energy differences and that the probability of occurrence of wells with given characteristics is proportional to the product of two Gaussians—one of these being a function of the energy difference between states in the two wells of a pair and the other being a function of the tunneling parameter for the barrier between the two wells of a pair.

On the basis of the extremely slight effect of a magnetic field on the attenuation at 4.2 K we conclude that electronic tunneling is relatively unimportant for the low-temperature attenuation.

At somewhat higher temperatures our attenuation data indicate that thermally activated hopping of ions over potential barriers with a wide range of barrier heights may take place along with the tunneling process.

We tentatively conclude that above 140 K thermally activated jumps of groups of $\mathrm{AsS_3}$ pyramids over potential barriers with a variety of heights may be taking place. However, the actual temperature dependence of the attenuation in the entire range from 140 to 480 K is difficult to understand, especially since the attenuation has a linear frequency dependence at least up to 300 K. We feel that inferences about the nature of atomic relaxation processes at these temperatures ought to be subjected to further investigation.

From our velocity data between 100 and 290 K it can be concluded that in a-$\mathrm{As_2S_3}$ the anharmonicity of interatomic forces is not unusual and that thermal phonon viscosity effects are not important.

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