Phys. Rev. Lett. 34, 721 (1975).

[15]H. Hora, in *Laser Interaction and Related Plasma Phenomena*, edited by H. J. Schwarz and H. Hora (Plenum, New York, 1971), Vol. 1, p. 383.

[16]J. J. Thomson, R. J. Faehl, W. L. Kruer, and S. Bodner, Phys. Fluids 17, 973 (1974).

[17]A. Y. Wong and R. L. Stenzel, Phys. Rev. Lett. 34, 727 (1975).

[18]J. E. Balmer and T. P. Donaldson, Phys. Rev. Lett. 39, 1084 (1977).

[19]T. P. Donaldson, R. J. Hutcheon, and M. H. Key,

J. Phys. B 6, 1525 (1973).

[20]P. Wägli, T. P. Donaldson, and P. Lädrach, to be published.

[21]T. P. Donaldson and I. J. Spalding, Phys. Rev. Lett. 36, 467 (1976).

[22]T. P. Donaldson, M. Hubbard, and I. J. Spalding, Phys. Rev. Lett. 37, 1348 (1976).

[23]T. P. Donaldson, I. J. Spalding, and R. A. Woolley, Opt. Commun. 22, 207 (1977).

[24]R. Decoste and B. H. Ripin, Phys. Rev. Lett. 40, 34 (1978).

Anomalous Absorption in Amorphous Solids at Low Temperature

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Highly absorbing silica-based glasses exhibit a distinct minimum in the temperature dependence of the very-far-infrared absorption coefficient near 10 K. The associated anomalous absorption at lower temperature can be understood by the two-level tunneling model. Different amorphous materials manifest a considerable diversity in the anomalous behavior.

Amorphous solids exhibit thermal and elastic properties at *low* temperatures very different from those of pure crystalline solids. The specific heat is anomalously high and dominated by a term with a linear temperature dependence,[1] indicating the existence of low-energy excitations. Such universal features—like the almost quadratic temperature dependence of the thermal conductivity—independent of structural details have led to the assumption of an universal origin inherent in the disordered state. A statistical distribution of localized two-level tunneling systems[2] (TLS) can describe phenomenologically these anomalous properties at low temperatures. The TLS are viewed as structural or electronic[3] "centers" with two equilibrium configurations, where transitions between the two sites are possible by quantum mechanical tunneling at low temperature and by thermally activated processes at higher temperature. Saturation of the ultrasonic absorption and coherent resonance phenomena[4] have been observed, supporting the tunneling model.

In contrast to the above features the interaction of the electromagnetic field with the TLS is expected to be quite sensitive to the chemical composition of the amorphous material. An anomalous dielectric dispersion[5] as well as a temperature-dependent far-infrared absorption difference[6] has been reported but these measurements dealt

with systems which have small intrinsic dipole moments so that intrinsic effects associated with the TLS were masked by the OH⁻ absorption processes.

For the first time I directly observe an anomalous absorption with an associated minimum in the temperature dependence of the absorption coefficient. Furthermore, highly absorbing glasses have allowed me to observe an anomalous absorption also below 1 K, in contrast to previous results.[6] This Letter is intended (1) to present the experimental data showing the anomalous behavior and the applicability of the two-level tunneling model; (2) to show that several absorption processes contribute to the overall dielectric absorption; (3) to point out the considerable diversity in the anomalous properties of amorphous solids.

A spectrometer system, including a lamellar interferometer, liquid-He³−cooled detector and a separate He³-cooled sample section permitted to measure the transmissivity for temperature between 0.4 and 300 K in the frequency interval from 2 to 20 cm⁻¹ (VFIR). Three main classes of amorphous substances have been investigated: oxide glasses, polymers, and amorphous semiconductors.

The VFIR frequency dependence of the absorption coefficient α of a soda-lime-silica glass (SLS) is shown in Fig. 1 for various tempera-
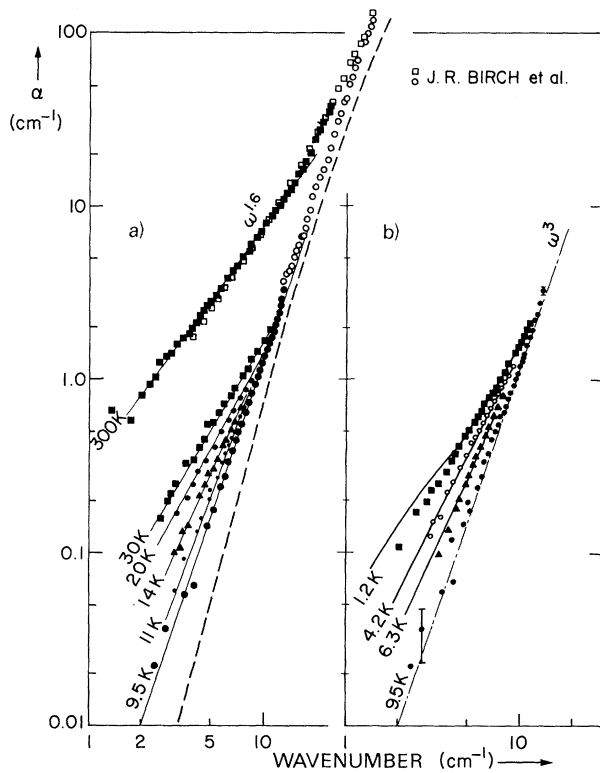
FIG. 1. Absorption coefficient vs wave number for a soda-lime-silica glass (SLS, 17 wt% Na_2O–9 wt% CaO–72 wt% SiO_2–< 2 wt% traces). The dashed curve in (a) represents the background absorption. The solid curves in (b) are a superposition of the resonant tunneling absorption and the background of (a).

tures. No marked change in the character of the frequency dependence occurs between 300 and 30 K, although the absolute value of α decreased considerably. A pronounced change in the frequency dependence results with further reduction of the temperature. A very striking experimental result is the minimum in the absorption coefficient observed at a temperature $T_{min} \approx 9$ K; below this temperature the *absorption increases with decreasing temperature* to the lowest temperatures measured (0.4 K). At T_{min} the absorption coefficient varies as the cube of the frequency. This frequency dependence has been found in all water-free glasses measured, however its physical significance has not been estabilished.[7-9]

Figure 1 allows me to distinguish between several absorption mechanisms. The temperature-independent contribution can be explained by the interaction of light with the Debye phonons of the solid via the elastic strain field of the TLS. This produces a FIR absorption proportional to the phonon density of states. In order to account for

the power law $\alpha \propto \omega^s$ with $s \geq 3$, a correlation among centers is required. To *estimate* the temperature-independent contribution we follow Schlömann[10] who calculated the dielectric susceptibility in a lattice with a disordered charge distribution due to various correlations among the charge deviations. The dielectric absorption with an exponential correlation may be written approximately as

$$\alpha \approx \frac{2(\epsilon + 2)^2}{3^3 c \sqrt{\epsilon}\, v_t{}^3} \frac{\langle g^2 \rangle}{m} \omega^2 \left[1 - \left(1 + \frac{\omega^2}{\omega_0{}^2} \right)^{-2} \right], \quad (1)$$

where $\omega_0/2\pi = v_t/l$ and c is the speed of light. In a soda-lime-silica glass the transverse velocity of sound is $v_t \approx 3 \times 10^5$ cm/sec, and a separate measurement for the dielectric constant gives $\epsilon = 2.58$. With a correlation length $l = 30$ Å the frequency dependence of the absorption is $\alpha \propto \omega^4$ for $\omega/2\pi c \ll 33$ cm^{-1} and $\alpha \propto \omega^2$ for $\omega/2\pi c \gg 33$ cm^{-1}. For the quotient $\langle q^2 \rangle / m$ I assume a charge deviation q of ± 1 electron charge per average mass m corresponding to a sodium atom. The computed background absorption according to Eq. (1) is shown in Fig. 1(a) (dashed curve).

Figure 1(b) shows very clearly the anomalous dielectric absorption; the absorption coefficient increases with decreasing temperature. More accurate measurements of the temperature dependence were possible by varying only the temperature of a given sample, thereby compensating for the temperature-independent background absorption. Extensive frequency- and temperature-dependent measurements on highly absorbing glasses have allowed us to identify the different contributions due to the direct coupling of light to the TLS. (Weakly absorbing glasses hardly allow the determination of the anomalous properties.) I now compare the different processes predicted by the tunneling model[2,11] with the experimental results, namely, (I) resonant tunneling, (II) relaxation due to phonon-assisted tunneling of the TSL, and (III) relaxation due to thermal activation processes (nondiffusive hopping) of the structural centers. The resonant part of the absorption of a two-level tunneling system (incident VFIR radiation less than 1 nW/cm^2) is[5]

$$\alpha_{res} = 4\pi^2 n_e \mu'^2 \omega \tanh(\hbar\omega/2kT)/\sqrt{\epsilon}\, c, \quad (2)$$

where n_e, the density of states coupling to the electric field, is initially assumed to be constant. μ' denotes the induced electric dipole moment of the TLS without local-field correction and spatial averaging. The dipole matrix element is depen-

dent on initial and final states; therefore only TLS with symmetric or slightly asymmetric potentials will contribute to the resonant absorption process. The solid curves in Fig. 1(b) represent a fit to the experimental data, obtained with Eq. (2) superimposed on the background absorption. A value of 9×10^{-4} cgs units is assumed for $n_e \mu'^2$ (e.g., $\mu' = 1$ D, $n_e = 9 \times 10^{32}$ erg^{-1} cm^{-3}). More complete details of the anomalous absorption are given in Fig. 2 for a soda-silica (SS) glass: $Na_2O \cdot 3SiO_2$ [note that $\Delta\alpha$ in Fig. 2(a) is anomalous also below 1 K, this is also true for the seven other glasses measured]. At low temperatures the absorption difference $\Delta\alpha = \alpha(T) - \alpha(T_R)$, T_R is the reference temperature, is fitted with a single parameter according to Eq. (2). This anomalous behavior has been found in all highly absorbing glasses and allows me to rule out the excited-state transition model proposed by Mon, Chabal, and Sievers[6] [note that $\Delta\alpha$ in Fig. 2(b) of Ref. 6 is positive].
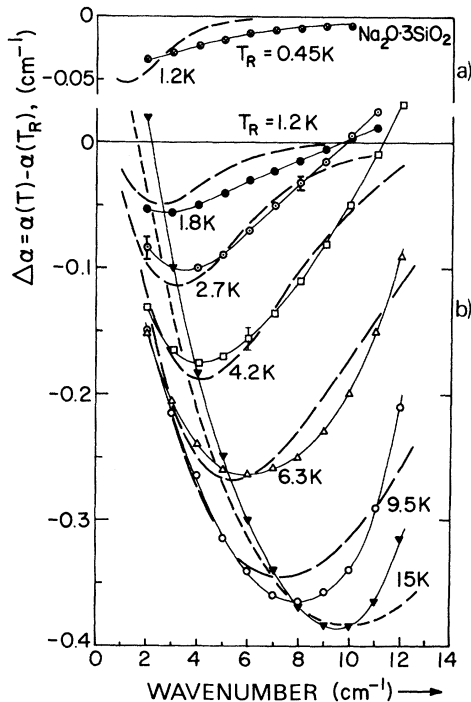

FIG. 2. Absorption difference vs wave number for soda-silica glass (SS, $Na_2O \cdot 3SiO_2$). This glass is hygroscopic. The samples have been prepared carefully and cut ultrasonically in a water-free slurry. The experimental data (points and solid curves) for 1.2, 1.8, and 2.7 K are compared with a single parameter fit describing the resonant tunneling absorption ($n_e \mu'^2$ = 1.4×10^{-3} cgs units). The computed curves for higher temperatures contain process (I) through (III).

For the lower-temperature curves in Fig. 2(b), we see that $\Delta\alpha$ becomes positive above 9 cm^{-1}. This behavior can be understood by process II, the relaxation due to phonon-assisted tunneling[11]:

$$\alpha_{rel} = A \int_0^\infty dE \, \frac{\exp(E/kT)}{kT[1 + \exp(E/kT)]^2} \, \frac{\omega^2 \tau_1}{1 + \omega^2 \tau_1^2}. \quad (3)$$

The relaxation strength A containing the permanent dipole coupling constant $n_e \mu^2$ is used as adjustable parameter. The relaxation time τ_1 $= a \tanh(E/2kT)/E^3$ was derived, neglecting multiphonon interactions, under the assumption of symmetric potentials ignoring the slower relaxation by asymmetric potentials. The calculated absorption difference resulting from both tunneling processes is included in Fig. 2(b) for 4.2, 6.3, and 9.5 K. The parameters are $n_e \mu'^2 = 1.4 \times 10^{-3}$ cgs units, $A = 1.3 \times 10^{-12}$ cm^{-1} sec, and $a = 4.2 \times 10^{-56}$ erg^3 sec.

For temperatures higher than T_{min} both Figs. 1 and 2 display a positive shift in the frequency dependence. I assign this effect to process III. The relaxation absorption for thermally activated transitions is

$$\alpha_{hop} = (h/T) \int_0^\infty dV \, P(V) \omega^2 \tau / (1 + \omega^2 \tau^2), \quad (4)$$

where h is the hopping relaxation strength. From ultrasonic measurements[12] I adopt the distribution function of potential barrier heights V: $P(V)$ $= \exp[-(V - V_m)^2/V_0^2]$ with $V_m = 550$ K, $V_0 = 410$ K, and $P(V) = 0$ if $V < 50$ K. For thermal activation the relaxation time is $\tau = \tau_0 \exp(V/kT)$, $\tau_0 \approx 10^{-13}$ sec. The absorption due to the hopping relaxation ($h = 3 \times 10^{-12}$ cm^{-1} sec) is also included in the computed curves in Fig. 2 and begins to give a substantial contribution at 15 K.

So far I have presented data for two silica-based glasses. Figure 3 shows the $\Delta\alpha = \alpha(4.2$ K$)$ $- \alpha(1.2$ K$)$ data of many amorphous materials. This graph displays the diversity in the anomalous properties. In particular silica, often regarded as a prototype for glass studies, has a weak dielectric absorption readily influence by water content. Adding network modifier (e.g., Na_2O) to oxide glasses results in an increasing dielectric absorption which is dependent on the amount and type of modifier. An absorption coefficient ranging over two orders of magnitude is readily obtained in this manner as shown in Fig. 3. I find a very different frequency dependence for amorphous semiconductors at low temperatures. $\Delta\alpha$ of amorphous Se in Fig. 3 is typical and representative for the absorption of several chalcogen-
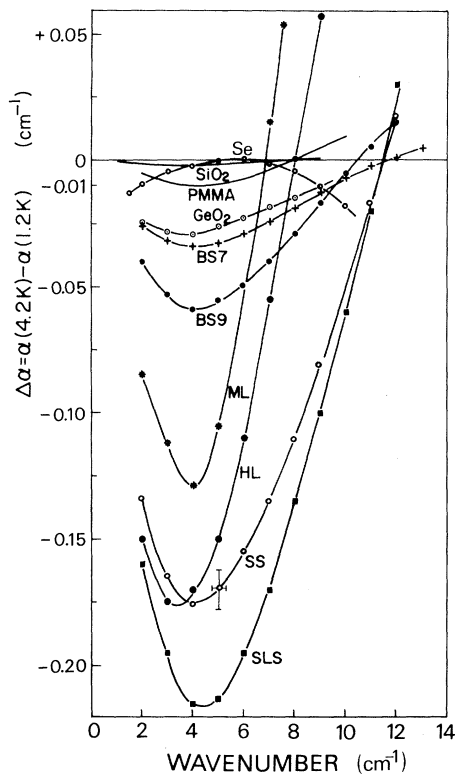
FIG. 3. Frequency dependence of $\Delta\alpha = \alpha(4.2$ K$)-$ $\alpha(1.2$ K$)$ for a variety of amorphous materials. BS7, 28 wt% B_2O_3–2 wt% Ti_2O–70 wt% SiO_2; BS9, 13 wt% B_2O_3–4 wt% Na_2O–82 wt% SiO_2–1 wt% traces; HL, 83 wt% PbO–10 wt% B_2O_3–6 wt% SiO_2–1 wt% traces; ML, 60 wt% PbO–10 wt% BaO–30 wt% SiO_2; PMMA, poly-methyl methacrylate; GeO_2, water-free germania.

ide glasses studied. The low-frequency part $(\omega/2\pi c < 6$ cm$^{-1})$ can be understood by the previously described resonant tunneling process. Above 6 cm^{-1} I find another anomalous absorption (the absorption increases with decreasing temperature), which could be due to resonant tunneling of electronic origin.

In conclusion, the present results show that an anomalous absorption governs the low-temperature dielectric behavior and is characteristic of the disordered state. Although the results sup-

port the two-level tunneling model, a refinement is needed for a full quantitative agreement (Figs. 1 and 2 show that the density of states decrease rapidly above 10 cm^{-1}). I believe that the fascinating diversity in the low-temperature dielectric behavior among different amorphous solids might lead towards a microscopic picture of the structural and electronic centers.

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[1]R. O. Pohl and G. L. Salinger, Ann. N. Y. Acad. Sci. 279, 150 (1976).

[2]P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. 25, 1 (1972); W. A. Phillips, J. Low Temp. Phys. 7, 351 (1972).

[3]P. W. Anderson, Phys. Rev. Lett. 34, 953 (1975).

[4]B. Golding and J. E. Graebner, Phys. Rev. Lett. 37, 852, 1105(E) (1976).

[5]M. von Schickfus, S. Hunklinger, and L. Piché, Phys. Rev. Lett. 35, 876 (1975); M. von Schickfus and S. Hunklinger, J. Phys. C 9, L439 (1976).

[6]K. K. Mon, Y. C. Chabal, and A. J. Sievers, Phys. Rev. Lett. 35, 1352 (1975).

[7]J. R. Birch, A. F. Harding, N. R. Cross, and D. W. E. Fuller, Infrared Phys. 16, 421 (1976).

[8]U. Strom and P. C. Taylor, in Structure and Excitation of Amorphous Solids (Williamsburg, Virginia, 1976), AIP Conference Proceedings No. 31, edited by G. Lucovsky and F. L. Galeener (American Institute of Physics, New York, 1976), Vol. 31, p. 273.

[9]R. H. Stolen, Phys. Chem. Glasses 11, 83 (1970), and references therein.

[10]E. Schlömann, Phys. Rev. 135, A413 (1964).

[11]J. Jäckle, Z. Phys. 257, 212 (1972).

[12]S. Hunklinger and W. Arnold, Phys. Acoust. 12, 155 (1976); N. Theodorakopoulos and J. Jäckle, Phys. Rev. B 14, 2637 (1976).