density. Stepwise elution is superior for this purpose to gradient elution, although a very slowly changing gradient might be a useful modification of the technique. The approximate linearity of θ^* with M assures fractions of approximately equal weight when equal increments in eluent concentration are used. Reproducibility of the θ^*-M relation facilitates prediction of elution conditions for a desired fractionation. Fractions obtained are comparable in sharpness to those obtained by other techniques depending on distribution between two phases. Characterization of the breadth of distribution in fractions obtained permits the use of this method for the estimation of molecular weight distribution curves for unfractionated materials on the basis of analytical fractionation results. Fractionation by charge density is also indicated by our data and has been previously demonstrated[4] experimentally for the ionic polysaccharides studied here. Fractionation should, in fact, be much more sensitive to variation in charge density than to molecular weight variation at a single charge density.

Acknowledgment. We wish to acknowledge the importance to this work of the summer undergraduate research programs of the National Institutes of Health (for J. J. L.) and the National Science Foundation (for V. E. L.). We wish to thank John L. Wang, who was also supported by the NSF program, for performance of the light-scattering measurements.

Low-Temperature Microwave Absorption in Insulating Materials

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Contribution from the Institut fuer Polymere der Universität, Marburg, Germany. *Received December 12, 1967*

Abstract: Measurements of the dielectric loss of crystalline and vitreous quartz, polyethylenes of different degree of crystallinity, and one polar polymer at 32 GHz between 4.2 and 300°K are presented and discusssed. In the higher temperature range the loss is interpreted as background loss due to photon–phonon interaction by means of polar impurities in the structure. At low temperatures additional loss is found that yields the same temperature behavior as the mechanical loss at comparable frequencies and is tentatively ascribed to the same intrinsic lattice absorption, coupled over anharmonicity terms to the electromagnetic field.

In the course of our investigations to separate relaxation- and resonance-type dielectric loss at microwave frequencies, temperature-dependent measurements were carried out down to 4.2°K. Here our first experimental results on organic and inorganic polymers shall be presented and discussed. The results give evidence that the dielectric loss, seen at microwave frequencies, is mainly background loss, *i.e.*, loss due to photon–phonon interaction. Additional loss was found at very low temperatures which to a high degree depends on the quality of the lattice. With increasing temperature it reaches a maximum or plateau and then merges into the background loss. It seems to us that here, for the first time, we found evidence for electromagnetic absorption rising directly from the thermal lattice phonons, coupled to the electric field by lattice anharmonicity.

Experimental Section

Measurements were performed on solid disk-shaped samples at 32 GHz in a H_{01n} cavity resonator placed in a liquid helium dewar, which is described in detail elsewhere.[1,2] The resonator plunger, holding the sample, is fixed to the bottom of the mounting tube, which is screwed into the cryostate flange; the resonator itself and the waveguide coupling systems are movable over a micrometer drive on top of the kryostate flange by means of an elastic vacuum connection. The resonance position is read at the micrometer, but the half-width is determined by changing the frequency and reading Δf at half-power points directly on the "Schomandl" frequency stabilization device. Measurements were performed, after evacuating the whole system and cooling down to 4.2°K, with He contact gas at a partial pressure of 10^{-3} torr within and around the resonator. The heating rate is approximately 1°/min, adjusted first by the He boiling rate, later by additional heating. Q of the empty cavity varied from 2.4 to 1.5×10^4 between 4 and 300°K, fluctuating about $\pm 2\%$. The least measurable loss therefore should have the order of magnitude of 5×10^{-6}, which is confirmed by our experimental results.

Results

The measured values of dielectric loss between 4 and 280°K at 32 GHz are shown for quartz (synthetic quartz from Steeg & Reuter), quartz glass, polyethylene (density 0.918 and 0.960, respectively), and polyoxymethylene (Delrin) in Figures 1–4. Dielectric constant values simply follow the density variation, except for the polar polymer, for which they are included in Figure 4 (no significance can be given to the absolute value of ϵ', which is inaccurate up to 10% because of the special resonator design).

The values on quartz show the accuracy and reproducibility of our measurements: no structure of the loss curves can be resolved below 5×10^{-6} ($\cong$70°K). No structure or relaxation peaks are seen in the continuously rising loss curve above 70°K either. This might be surprising, compared with mechanical loss–temperature curves[3,4] and high-frequency measure-

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[1] G. C. Smith and F. H. Mueller, *Kolloid Z.*, **206**, 136 (1965).

[2] E. M. Amrhein, H. Röder, and F. H. Mueller, *Z. Angew. Phys.*, **24**, 18 (1967).

[3] H. J. Maris, Ph.D. Thesis, University of London, 1963.

[4] D. B. Fraser, "Physical Acoustics," Vol. IV, W. P. Mason, Ed., Academic Press, Inc., New York, N. Y., 1967.

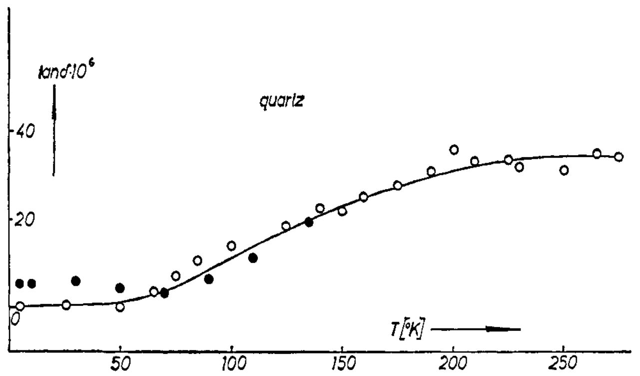

Figure 1. Dielectric loss of synthetic quartz at 32 GHz (limit of accuracy, tan $\delta = 5 \times 10^{-6}$): ○ and ●, two different measurements with same sample.

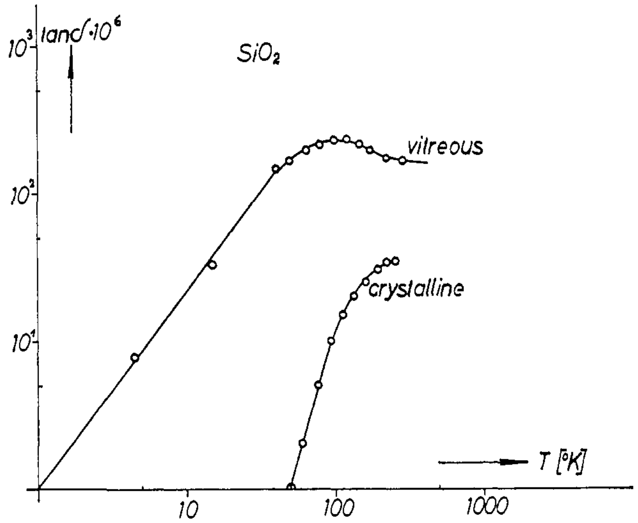

Figure 2. Dielectric loss of quartz glass and quartz (same as in Figure 1) at 32 GHz.

ments[5] in the megacycle region. It can possibly be explained by the fact that the electric field in all experiments lay in planes perpendicular to the *c* axis.

All data presented have some features in common. Amorphous materials exhibit a distinct dielectric loss at very low temperatures, which finally decreases toward zero according to a power temperature law. At medium temperatures there is a region of very poor temperature dependence or better a "well" in the loss–temperature curves, and at still higher temperature loss increases again, following again a T^n law, the exponent n, however, being a different one. In order to demonstrate clearly the differences in temperature dependence, the data are plotted on double logarithmic scale. In Figure 5 mechanical loss–temperature curves from Maris[3] are reproduced for comparison.

Discussion

For an interpretation of the results, we wish to distinguish between the high- and low-temperature part of the loss curves. The high-temperature loss (not shown in the SiO_2 samples), which increases with T^n (n varying between 1.5 and 2.5), will be called "background loss;" the low-temperature loss, superimposed on the background loss, shows a maximum and decreases toward zero for $T \rightarrow 0$ with, again, a T^n law, but n varying between 1 and 4 according to the lattice quality. We will call this loss "intrinsic phonon loss."

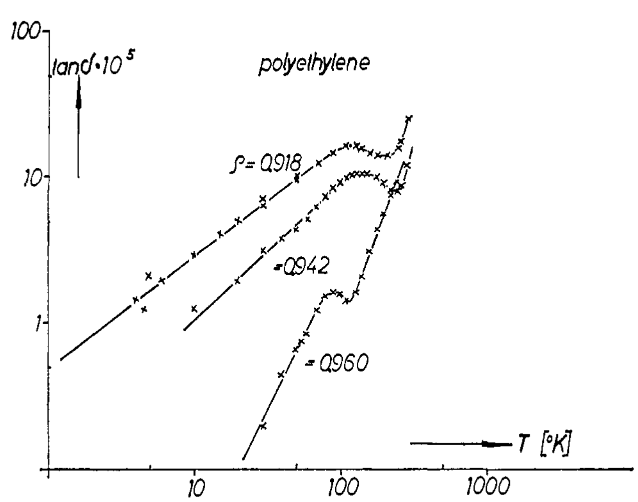

Figure 3. Dielectric loss of three polyethylene samples at 32 GHz; ρ = density; crystal content ~40 and 75% for ρ = 0.918 and 0.960, respectively.

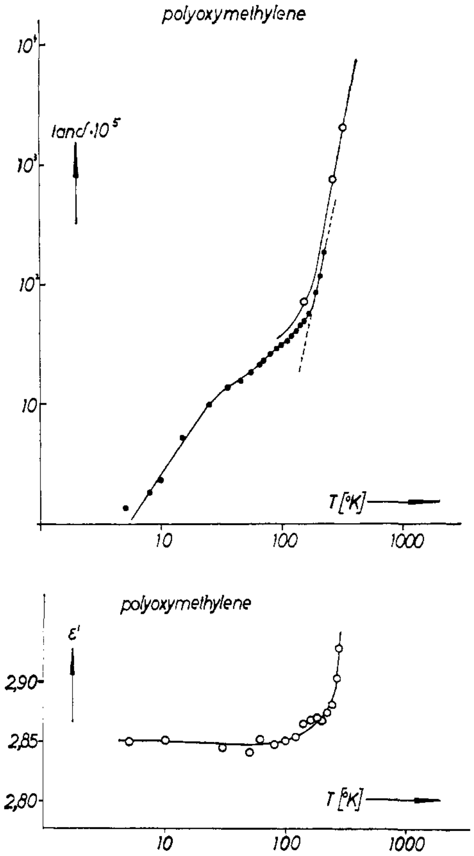

Figure 4. Dielectric loss (top) and dielectric constant (below) of polyoxymethylene (Delrin) at 32 GHz; open circles are measurements by Smith and Mueller[1] in a high-temperature cavity at the same frequency.

The "Background Loss." This has been discussed in detail for a series of organic and inorganic dielectrics.[6] It follows the power temperature law up to the glass-transition temperature in all amorphous or partially crystalline materials. It can clearly be separated

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[5] J. M. Stevels and J. Volger, *Philips Res. Rept.*, 17, 283 (1962).

[6] E. M. Amrhein and F. H. Mueller, *Trans. Faraday Soc.*, in press.

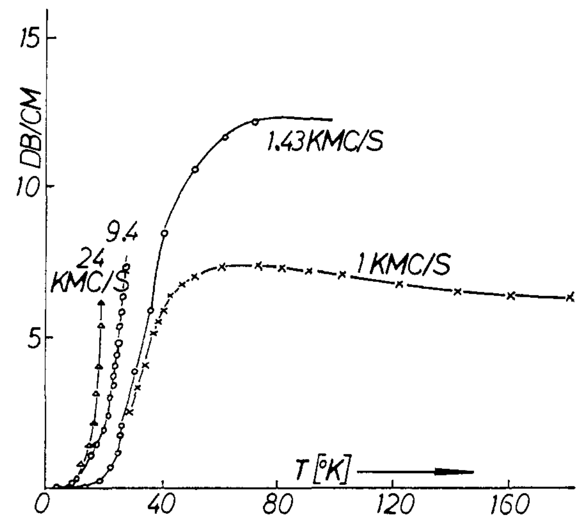

Figure 5a. General temperature dependence of attenuation of shear waves in quartz (from Maris[3]): H. E. Bommel and K. Dransfeld, *Phys. Rev.*, **117**, 1245 (1960); E. H. Jacobsen, "Quantum Electronics," Columbia University Press, New York, N. Y., 1960, p 468.

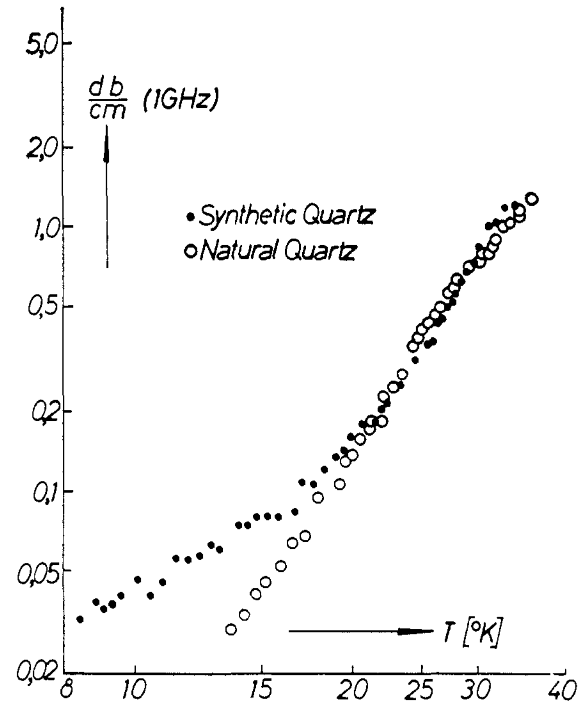

Figure 5b. Low-temperature results of attenuation of shear waves in quartz (from Maris[3]).

from relaxation losses by means of its characteristic temperature dependence. It is nearly independent of frequency but seems to rise with frequency toward the millimeter wavelength range. Its magnitude depends strongly on the amount of dipolar (or ionic) groups in the structure (not markedly on crystal content) and, regarding one dipole in different molecular surroundings, on the mobility of this dipole. The nature of this background loss was therefore explained as a photon–phonon interaction, *i.e.*, as due to the coupling of the electromagnetic field to low-frequency acoustical modes by means of the considered anharmonic polar units. Until now there was no explanation of the fact that at microwave frequencies the background loss bended off from the T^n line toward very low temperatures, showing a new type of loss coming into play. By measurements down to 4°K, it was possible to form an idea of the nature of this loss.

The Low-Temperature "Intrinsic Loss." This is interpreted as being due to thermal lattice vibrations (phonons) analogous to the attenuation of ultrasonic waves in a dielectric crystal.[3,4,7] The coupling between the electromagnetic field and the phonon states which finally dissipate the energy must be of a different type in this case compared with the case of the background loss. For the background loss it obeys the same mechanism which, in ionic crystals, gives rise to the side-band absorption of the Reststrahlen maxima and, in covalent crystals, to the defect-induced second-order absorption.[8] It is by means of the virtual excitation of an optically active oscillator (a high-frequency optical mode) that the photon energy is transferred to the low-frequency phonon modes. Decay of the excitation takes place through creation of two (or more) phonons, the energy of which is balanced by the incident photon energy. The coupling to the phonon states is due to anharmonic potential or to a higher order dipole moment. In the former case the excited oscillator might be an ion, in the latter case an electron. But always the virtual excitation of an optical mode is essential. Of course, the question rises as to under what conditions a direct collision with the low-frequency phonon modes might be possible. It cannot be expected unless the lifetime of the phonon states is longer than or at least equal to the period of the applied field. For the millimeter-wave absorption this means that the mean phonon lifetime must exceed 10^{-10} sec, so that a direct interaction (or scattering) can take place; *i.e.*, the temperature must be below 50–100°K. This is well known from the attenuation of acoustic waves in insulating crystals (see below). We suggest that the additional dielectric low temperature loss is due to the same effect: a direct collision of the incident radiation (now photons) with the thermal lattice vibrations. This interaction should be possible as soon as any asymmetry in the lattice provides a coupling between the electromagnetic and potential energy. We were led to this conclusion first by the fact that, as in the case of mechanical loss, this low-temperature loss proved to be an "intrinsic lattice property," and second by the close similarity of the loss–temperature curves of quartz at comparable frequencies in both the electrical and mechanical cases.

The T^n Region and Maximum. For the quartz crystal, in which the "phonon loss" seems to be the only important one over the whole temperature range of our investigation, a more detailed discussion is possible. In the mechanical case the attenuation is due to collisions between the low-energy phonons which constitute the ultrasonic wave and the higher energy thermal phonons of the lattice. This picture holds true as long as $\omega\tau \gg 1$ (ω = angular frequency of the applied mechanical field; τ = mean time between collisions of the thermal phonons). The quantum mechanical treatment[7] then yields, for simple collisions involving three phonons, an absorption proportional to ωT^4, as it

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(7) R. Orbach, Ph.D. Thesis, University of California, 1959.

(8) H. Bilz, The Scottish University Summer School in Physics, Aberdeen 1965; and "Festkörperprobleme," Vol. VI, Vieweg Verlag, Braunschweig, Germany, 1967, p 222.

is found in quartz crystals at low temperatures. For $\omega\tau \leqq 1$ ($\lambda >$ mean phonon path), no direct interaction occurs between the sound phonons and lattice phonons, but rather a modulation of the phonon energies by the sound wave, and the relaxation of the phonons back to their equilibrium states gives rise to the observed absorption. This absorption is proportional to τT and is, as long as $\tau \sim 1/T$ (in good crystals), independent of temperature. Considering the variation of $\omega\tau$ with temperature, the total shape of the loss–temperature curves (Figure 5a) can thus be explained. Figures 1 and 2 demonstrate the same temperature dependence in the case of dielectric absorption: at low temperatures a T^4 law and then the gradual transition to a rather temperature-independent value. From this it seems reasonable to assume that it is the same mechanism which gives rise to absorption in both cases.

The Exponent n ($1 < n \leqq 4$). Maris[8] and also Fraser and Spencer[9] reported a flattening of the loss–temperature curves in the ultrasonic absorption with increasing defects in the crystal structure. The same is found in the dielectric case comparing, *e.g.*, the quartz and quartz glass curves of Figure 2. It seems to us that this feature can be generalized, that the exponent n, characterizing the intrinsic phonon absorption, is a new and sensitive means to characterize a "lattice quality." In this line, the "lattice" of the quartz glass does not show as much deviation from the ideal crystal lattice of SiO_2 as, for instance, the over-all lattice quality of a still 40% crystalline polyethylene sample. This close similarity in the structures of crystalline and amorphous SiO_2 has often been suggested[10] by different approaches. The sensitivity of the exponent n on the lattice quality is clearly marked in the example of the different polyethylenes. n can be chosen as a measure of the degree of crystallinity (which again determines the order in the amorphous as well as in the crystalline phase[11]). The polyoxymethylene fits well into this line, with a crystal content of about 70% and a slope slightly less than the 75% crystalline polyethylene. This again demonstrates that absorption of electromagnetic radiation in the considered range of frequency and temperature is not dependent on polar units in the structure but is, in fact, an intrinsic lattice property.

Summarizing we may say that there seemed to be enough evidence for us to consider it worthwhile to present our interpretation of microwave low-temperature absorption for further discussion and measurements.

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(9) D. B. Fraser and W. J. Spencer, to be published.

(10) F. Oberlies and A. Dietzel, *Glastech. Ber.*, **30**, 37 (1956).

(11) H. G. Killian, *Faserforsch. Textiltech.* **15**, 537 (1964); W. Glenz, H. G. Kilian, and F. H. Mueller, *Kolloid Z.*, **206**, 104 (1965).

The Structures of Norbornane and 1,4-Dichloronorbornane as Determined by Electron Diffraction

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Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received December 29, 1967*

Abstract: The structures of norbornane and 1,4-dichloronorbornane in the vapor state, as determined by electron diffraction, provide geometric parameters (i) for calculating strain and nonbonded interaction energies in a representative rigid bicyclic hydrocarbon, and (ii) for assessing the influence on the skeletal structure due to substitution of highly electronegative groups at the 1,4 positions. Sectored diffraction photographs obtained at Cornell University and at the University of Oslo of the same samples gave scattered intensity which were in complete agreement both in magnitude and angular scale over the regions they overlapped. The strain energy for norbornane as calculated according to the scheme of Allinger was compared with the experimentally determined value.

Bicyclic molecules, particularly derivatives of bicyclo[2.2.1]heptane, have held a prominent position in the investigation of phenomena associated with nonclassical ions.[1] While the interpretation of these phenomena is still controversial,[2] there is general agreement that the properties depend critically on the detailed geometry of the molecules. In general, those properties of bicyclic compounds wherein they differ from the corresponding acyclic alkanes find rationalization in terms of several types of "strain" imposed by their geometries. Bicyclic molecules are of interest also because, compared to acyclic molecules, the relatively rigid structures of the carbon skeletons lead to unambiguous orientations and magnitudes of separation of substituents. The absence of complications from having to consider averages over several widely different conformations has made this group of molecules useful for testing numerous theories.[3]

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(1) T. P. Nevell, E. DeSalas, and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939).

(2) (a) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; (b) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).