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Anelastic and Dielectric Relaxation of Excess Vibrational Modes in Silica*

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Anelastic and dielectric measurements of fused-silica and soda-silica glasses have been made at low temperatures. The results indicate the presence of distinct relaxation processes at ~11 and ~35°K. It is suggested that these relaxations are due to vibrational modes in excess of the usual Debye spectrum. The existence of these additional modes, or "Einstein modes," has already been deduced from low-temperature specific-heat measurements. A simple theoretical treatment of a charged harmonic oscillator coupled to the strain through a Grüneisen constant shows that anelastic and dielectric relaxations are expected from an excess mode of this kind. Very general considerations of the interactions between the "Einstein oscillator" and the bulk phonons suggest that the relaxation time τ describing the approach to equilibrium of the perturbed oscillator is of the form $\tau=\tau_0 e^{Q/kT}$. This expression is found to be in good agreement with the experimental observations. For the 11°K relaxation $Q=0.0140\pm0.0008$ eV, while for the 35°K relaxation $Q=0.053\pm0.007$eV.

INTRODUCTION

SPECIFIC-HEAT measurements have established the fact that many amorphous substances exhibit substantial positive deviations from ideal Debye behavior at low temperatures. In some cases, it has been shown, using Raman data, that low-frequency lattice vibrational modes exist as well. The work of Flubacher, Leadbetter, Morrison, and Stoicheff,[1] incorporating both types of measurement, shows that the excess low-temperature specific heat of vitreous silica can be explained in terms of excess low-frequency vibrational modes not present in crystalline quartz. In essence, the vitreous silica lattice frequency spectrum is visualized as the Debye spectrum $[N(\omega)\propto\omega^2]$ with additional Einstein contributions at several low frequencies. For silica, Flubacher *et al.* find that the specific heat can be described by including three additional Einstein vibrational modes corresponding to temperatures ($\hbar\omega/kT=1$) of 13, 32, and 58°K. Similar excess-specific-heat behavior is observed in vitreous germania by Antoniou and Morrison,[2] in glycerol glass by Craig, Massena, and Mallya,[3] and in polystyrene, polymethyl methacrylate, and polyvinyl acetate by Choy, Hunt, and Salinger.[4] The excess specific heat is in all cases attributed to excess low-frequency modes.

Numerical calculations by Dean[5] have shown that the vibrational spectra of disordered solids are not smooth, but instead are very irregular. Recently, Rosenstock and McGill,[6] extrapolating from a theoretical analysis of a one-dimensional model, predict that peaks are to be expected, in general, in the frequency spectrum of disordered solids. The simplified models used above to explain the excess specific heat have, thus, considerable theoretical justification.

In the same temperature region, and extending to somewhat higher temperatures, the amorphous oxides exhibit characteristic broad mechanical-loss peaks which have been extensively investigated.[7–12] Fine *et al.*[9] suggested the possibility that the characteristic mechanical loss maximum in silica occurred because of unusual vibrational modes; i.e., that the origin of anomalies in the mechanical loss and the excess specific heat (subsequently measured) were structurally connected. Other investigators have also suggested that some structural entity is responsible for the excess specific heat and the mechanical-loss maximum without, however, considering any specific mechanism. A recent discussion of anomalous properties of amorphous oxides by Krause and Kurkjian,[13] for example, points out that very low-frequency Raman spectra (indicating the presence of low-frequency vibrational modes) occur whenever a characteristic mechanical-loss maximum is observed for these oxides.

Precision mechanical-loss measurements of amorphous silica and several Na_2O-SiO_2 glasses are presented in this paper. The accuracy of the measurements is such that new details of the low-temperature mechani-

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* Based on thesis submitted by W. W. Scott to the University of Pennsylvania in partial fulfillment of requirements for the Ph.D.

[1] P. Flubacher, A. J. Leadbetter, J. A. Morrison, and B. P. Stoicheff, J. Phys. Chem. Solids **12**, 53 (1959).

[2] A. A. Antoniou and J. A. Morrison, J. Appl. Phys. **36**, 1873 (1965).

[3] R. S. Craig, C. W. Massena, and R. M. Mallya, J. Appl. Phys. **36**, 108 (1965).

[4] P. Choy, R. Hunt, and G. L. Salinger (private communication).

[5] B. Dean, Proc. Roy. Soc. **A254**, 507 (1960).

[6] H. B. Rosenstock and R. E. McGill, Phys. Rev. **176**, 1004 (1968).

[7] J. W. Marx and J. M. Silverstone, J. Appl. Phys. **24**, 81 (1953).

[8] H. J. McSkimin, J. Appl. Phys. **24**, 988 (1953).

[9] M. E. Fine, H. Van Duyne, and N. T. Kenney, J. Appl. Phys. **25**, 402 (1954).

[10] O. L. Anderson and H. E. Bommel, J. Amer. Ceram. Soc. **38**, 125 (1955).

[11] J. T. Krause, J. Am. Ceram. Soc. **47**, 103 (1964).

[12] H. E. Bommel and K. Dransfeld, Phys. Rev. **117**, 1245 (1960).

[13] J. T. Krause and C. R. Kurkjian, J. Am. Ceram. Soc. **51**, 226 (1968).

cal-loss curve are revealed, thereby allowing a clearer correlation between the specific heat and the mechanical-loss behavior. In addition, precision dielectric measurements in the same frequency range indicate a correlation of dielectric behavior with mechanical-loss behavior. A theoretical analysis is given which shows that a charged harmonic oscillator (a representative model of a low-frequency mode) mechanically coupled to the "lattice" through a Grüneisen constant γ can interact with an electric or a strain field and give dielectric and mechanical loss.

Therefore, it is possible to explain the excess specific heat and certain features of the dielectric and mechanical behavior in SiO_2 and Na_2O-SiO_2 glasses by assuming the presence of several discrete modes in addition to the normal modes of the elastic continuum. (The elastic-continuum approximation at these low temperatures is considered valid.[1]) The model, which explicitly assumes the same structural unit responsible for some features of specific heat, mechanical loss, and dielectric loss, requires that the relaxation time τ, describing interactions between the harmonic oscillator and the continuum modes, be greater than $1/\omega_0$, where ω_0 is the angular frequency of the harmonic oscillator.

EXPERIMENTAL RESULTS

The SiO_2 samples used in these experiments were of Corning high-purity fused silica. All glasses were prepared from laboratory-grade Na_2CO_3 and SiO_2 powders which were premixed and melted in an Al_2O_3 container under an argon atmosphere. 0.5% As_2O_3 was added to all the melts to assist in bubble elimination. The glasses were melted by means of an induction coil and a graphite susceptor to 100°C above the reported liquidus line, held for $1\frac{1}{2}$ h, and then poured on a graphite block which was quickly placed in a muffle furnace at 400–450°C and furnace cooled.

Mechanical-loss measurements were made using a new and very sensitive vibrating-reed method described elsewhere.[14] Essentially, the sample is cut into a three-pronged tuning-fork configuration with the two side prongs clamped. The center prong is, thus, free to vibrate at the resonant frequency, which can be measured with an accuracy of one part in 10^6. The rate of decay is recorded and, thence, the mechanical loss. Losses down to 2×10^{-6} have been reproducibly measured at 4.2°K. Dielectric measurements were made using a General Radio 1615-A ratio-arm capacitance bridge. Gold-paste electrodes with guard rings were utilized, and the samples were usually 0.2–0.3 mm thick with a surface area of about 1 cm^2.

The general features of the mechanical behavior of silica and Na_2O-SiO_2 glasses up to 400°K is shown in Figs. 1(a) and 1(b): Figure 1(a) shows the relative temperature dependence of the real part of the elastic constant $C_{4.2}/C_T=(f_T/f_{4.2})^2$, where C_T and f_T are the real part of the elastic shear constant and the resonant frequency, respectively, at a given absolute temperature T. Figure 1(b) shows the temperature dependence of the loss $\tan\delta$ ($\tan\delta=C'/C$, where C and C' are the real and imaginary parts of the elastic constant). The general features of the dielectric behavior over a wide temperature range are shown in Figs. 2(a) and 2(b), where the relative temperature dependence of the real part of the dielectric constant $K_T/K_{4.2}$ and temperature dependence of the loss $\tan\delta=K'/K$ is shown. For fused silica, the drop in mechanical modulus, with minimum value at about 60°K, is well known, and the other simultaneous anomalous properties have been discussed.[15]

The mechanical and dielectric behavior of concern occurs at low temperatures, and are shown in Figs. 3 and 4. (The behavior of these glasses in the higher-temperature region has been extensively investigated but will not be discussed in this paper.) "Double knees" may be seen in the continuously decreasing (real part of the) elastic constant, indicating the presence of a relaxation process centered by visual inspection at temperatures ~11°K. Two double knees may be seen in the continuously increasing (real part of the) dielectric constant, which indicate the presence of two relaxation processes, one centered by visual inspection at temperatures ~15°K and the other at temperatures ~37°K. The imaginary parts of the mechanical modulus and dielectric constant clearly show structure, as shown in Figs. 3(b) and 4(b), but they do not give so precise an estimate of the temperatures at which the relaxation process occurs.

It has been found that the dispersions shown in Figs. 3 and 4 are characteristic of the SiO_2 network and not the network modifiers. As can be seen in Figs. 3 and 4, increasing Na_2O content in the Na_2O-SiO_2 glasses did not eliminate or significantly alter the mechanical or dielectrical relaxation under discussion. In addition, experiments on complex glasses (Corning 7070 and 7050 glasses containing B_2O_3, Al_2O_3, Li_2O, and K_2O) also showed these relaxations to be present. This insensitivity to chemical variations implies that these relaxations should be independent of the degree of phase separation, and this was confirmed experimentally. It was also found that these relaxations were independent of the fictive temperature. The present results, therefore, indicate that the discrete relaxation processes are characteristic of the SiO_2 network, and the characteristics of this network establish the temperatures at which the relaxation processes are manifest.

From Figs. 2–4, the mechanical and dielectric behavior of fused-silica and silica-base glasses may be described in terms of a broad continuous background together with at least two relaxation processes at ~11 and ~30°K at audio frequencies. (Recently, Jones

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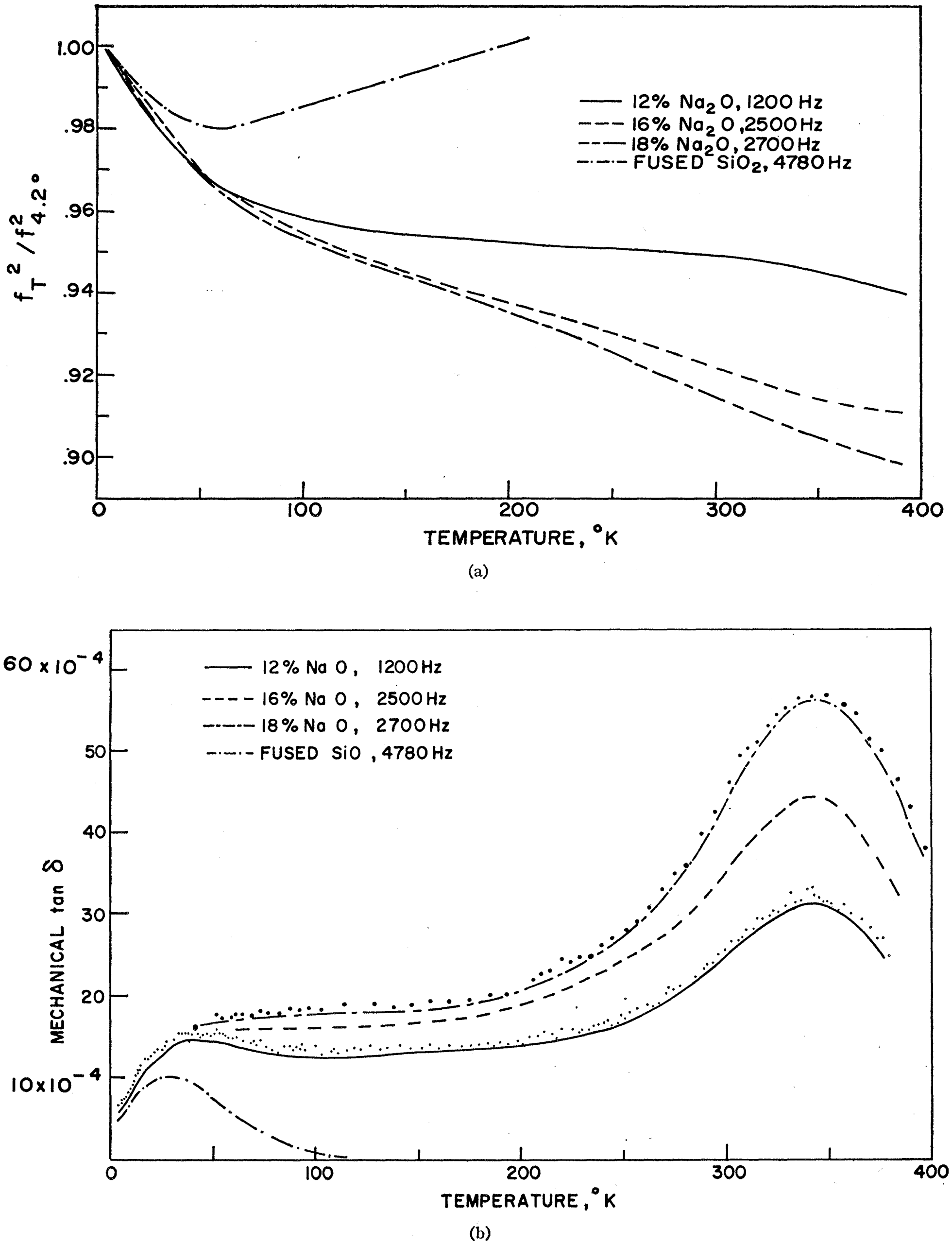
[14] W. W. Scott and R. K. MacCrone, Rev. Sci. Instr. **39**, 821 (1968).

[15] O. L. Anderson and G. T. Dienes, in *Non-Crystalline Solids*, edited by V. D. Frechette (John Wiley & Sons, Inc., New York, 1960).



(a)

(b)

FIG. 1. (a) Relative variation of elastic moduli with temperature for fused-silica and sodium-silicate glasses. (b) Mechanical tanδ of fused-silica and sodium-silicate glasses up to 400°K.

et al.[16] have shown a third ultrasonic absorption process at temperatures ~4°K, and a dielectric relaxation was observed in the same region by Jaeger,[17] cf. Krause.[11]) The continuous background depends upon the cation content and is not of concern here. The low-temperature discrete relaxation processes, however, seem to be characteristic of the SiO_2 network. In the following sections, a model is proposed that accounts for these low-temperature relaxations as well as the observed excess specific heat. The model presupposes the existence of additional modes and assumes that each excess mode frequency is related to the strain through a Grüneisen constant γ_d. Upon the adiabatic application of a stress, the frequency of the excess mode is altered so that the mode is no longer in thermal equilibrium with the continuum phonons. The transfer of energy into or out of the mode as equilibrium is established is

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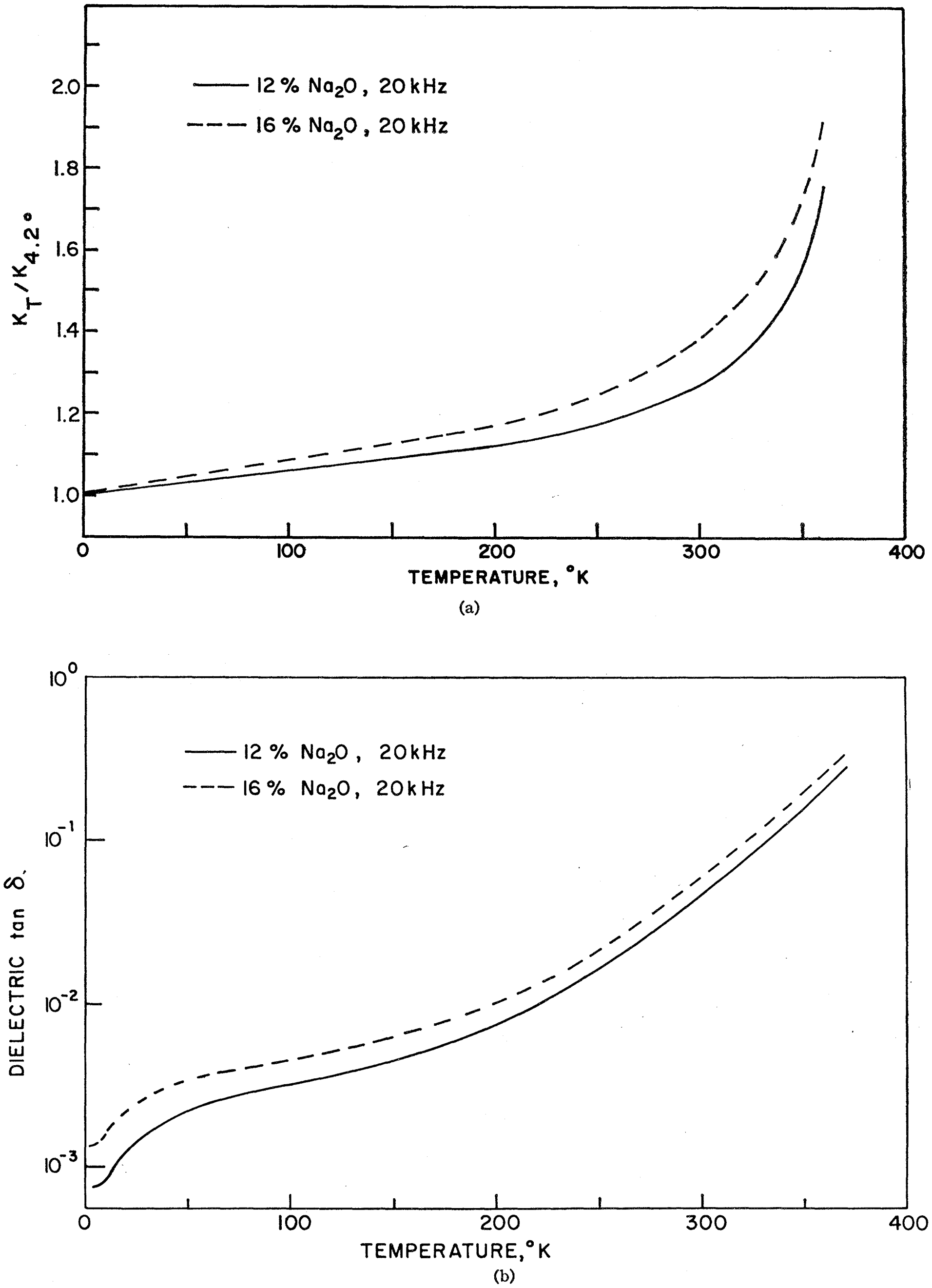
[16] C. K. Jones, P. G. Klemens, and J. A. Rayne, Phys. Letters **8**, 31 (1964).

[17] R. E. Jaeger, J. Am. Ceram. Soc. **51**, 57 (1968).



(a)

(b)

FIG. 2. (a) Relative variation of the dielectric constant with temperature for two sodium-silicate glasses. (b) Dielectric tanδ of two sodium-silicate glasses up to 400°K.

an entropy-generating process, and gives rise to a mechanical loss for sinusoidally applied stress. Akhieser[18] has considered the case of mechanical loss due to heat flow between the different phonon branches; the model here is much simpler.

It is further assumed that the vibrational mode involves charge motion. Thus, an adiabatically applied electric field would then perturb the harmonic-oscillator energy levels and again thermal nonequilibrium would occur, with entropy generation as equilibrium is established. Thus, the model predicts that a sinusoidally applied electric field will also result in a dielectric loss.

Model

Let us suppose that there exists in the amorphous material a particular local structure with a characteristic vibration frequency ω_0, cf. Ref. 6. A simple model,

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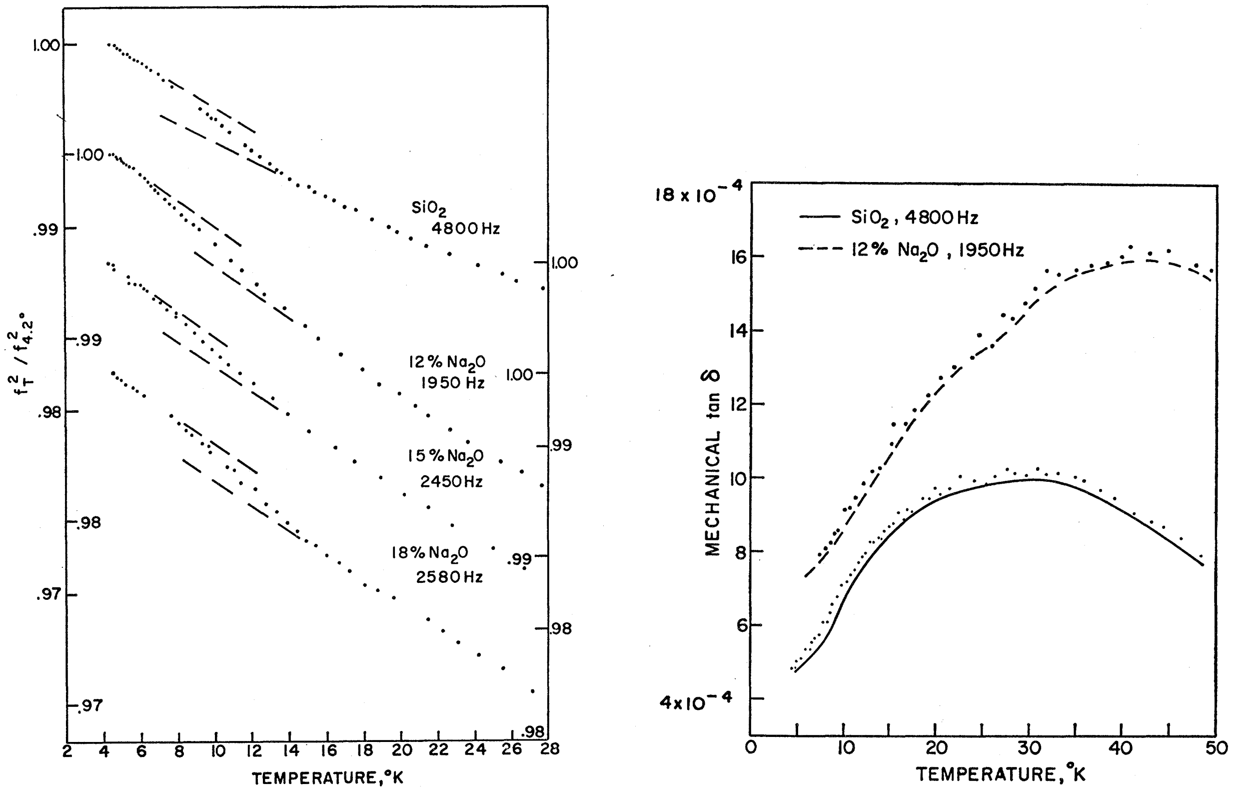
[18] A. Akhieser, J. Phys. USSR 1, 277 (1939).



(a) (b)

FIG. 3. (a) Low-temperature change in the elastic modulus of silica and sodium-silicate glasses indicating a relaxation process at 10–12°K. The dashed lines are extrapolations of the behavior at temperatures above and below the temperature of the relaxation. (b) Low-temperature mechanical-loss data for silica and a sodium-silicate glass. The best fit to the experimental points has been drawn displaced from the actual position for clarity.

similar to that discussed by Rosenstock,[19] is sketched in Fig. 5, where for simplification we consider displacement in one dimension only.

Qualitatively, it can be concluded that the effect of this attached harmonic oscillator of mass m and spring constant u, on the normal modes of vibration of the linear chain with units of mass M and spring constant U, decrease as the ratios $m/M \rightarrow 0$ and $u/U \rightarrow 0$. A crude but plausible assumption is that the chain and harmonic-oscillator interactions are perturbation interactions only. This implies that the local structure vibrates as an almost independent Einstein oscillator. Krumhansl[20] has pointed out that many localized modes behave as if they were simple Einstein oscillators and discusses theoretically how this occurs.

On this assumption, we shall consider the interaction of the additional harmonic oscillator of frequency ω_0 with an applied mechanical stress σ and an applied electric field F. The effect of an adiabatically applied stress or electric field is to produce a nonequilibrium energy state of the oscillator. This results in a difference between the unrelaxed and relaxed elastic constants C_∞ and C_0, and dielectric constants K_∞ and K_0. The approach to equilibrium, the relaxation, is a very complex process, and we will discuss qualitatively the possibility of a "relaxation-time" behavior, where τ follows one of the expressions

$$\tau=\tau_0 e^{Q/kT} \quad \text{or} \quad (\tau_0\theta/T)e^{Q/kT}.$$

Anelastic Relaxation

The particular thermoelastic behavior of interest here may be most simply described by assuming a Grüneisen constant γ_d $[\omega=\omega_0(1+\gamma_d\epsilon)]$ and thermal coefficient of expansion α_d per unit concentration of defect. Here, ω is the frequency of vibration of the structural unit when the specimen is in a state of strain ϵ. Thus, following Zener,[21] we write

$$\epsilon=C_0\sigma+N\alpha_d T' \tag{1}$$

for the strain relative to the standard state, with the stress $\sigma=0$, $T'=T_0-T=0$. Here, C_0 is the relaxed

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[19] H. B. Rosenstock, J. Phys. Chem. Solids **23**, 659 (1962).

[20] J. A. Krumhansl, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum Publishing Corp., New York, 1968), p. 17.

[21] C. M. Zener, *Elasticity and Anelasticity of Metals* (Chicago University Press, Illinois, 1965), p. 69ff.

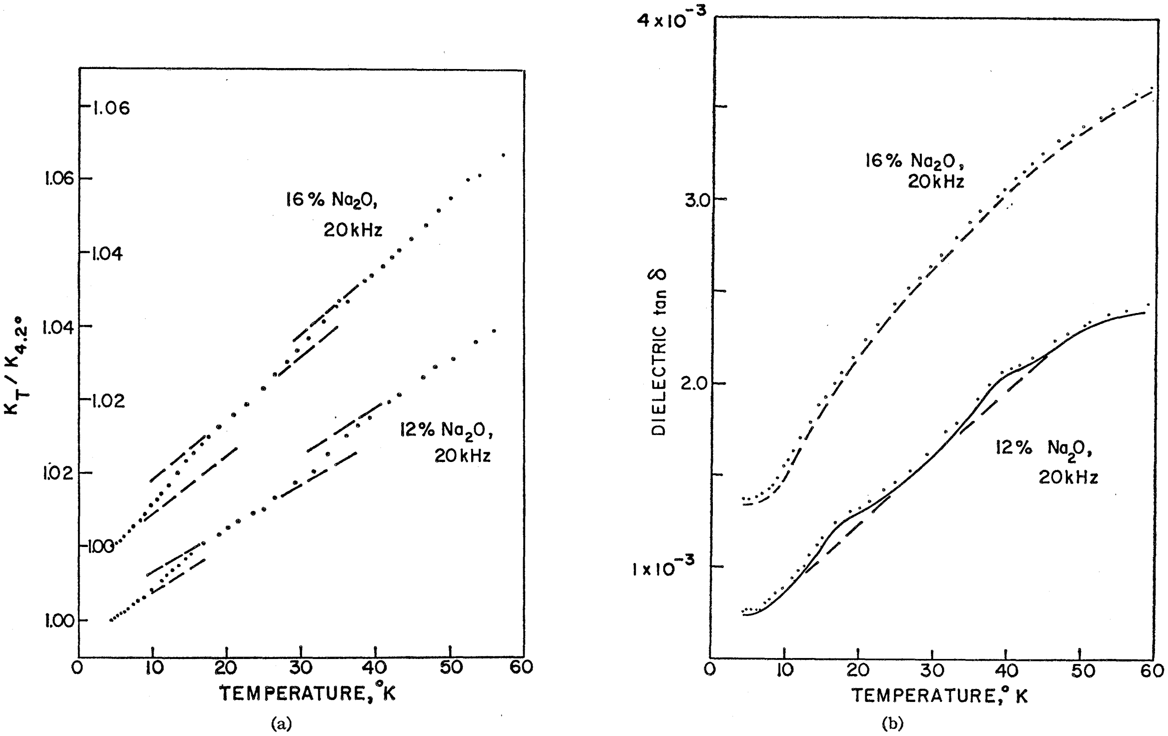

FIG. 4. (a) Low-temperature change in the dielectric constant for two sodium-silicate glasses indicating two relaxation processes at ~12 and ~35°K. The dashed lines are extrapolations of the behavior at temperatures above and below the temperature of the relaxation. (b) Low-temperature dielectric-loss data for two sodium-silicate glasses showing two relaxation processes. The best fit to the experimental results has been drawn displaced from the actual position for clarity. The dashed line on the 12% Na_2O curve indicates the presumed background.

"isothermal" elastic constant and $N\alpha_d$ the coefficient of thermal expansion due to the defects. This equation implies that we are considering a simple model of N defects embedded in an isothermal reservoir with elastic constant C_0 and zero coefficient of thermal expansion; this arbitrarily sets the background thermoelastic loss of the reservoir (specimen) to be zero. Terms describing a background thermoelastic loss could have been included in the above equations; for simplicity, they have been omitted.

A temperature difference between the Einstein oscillator and the reservoir may be included by an adiabatic strain, i.e.,

$$\partial T'/\partial t=(\partial T'/\partial\epsilon)_{\text{adiabatic}}d\epsilon/dt=-\beta d\epsilon/dt. \tag{2}$$

On the usual assumption that thermal relaxation follows a relaxation-time equation, i.e., that

$$\partial T'/\partial t=-T'/\tau, \tag{3}$$

the well-known relaxation expression[21]

$$\epsilon/C_0+\tau\dot{\epsilon}C_\infty=\sigma+\tau\dot{\sigma} \tag{4}$$

is obtained, where

$$C_\infty=C_0/(1+N\alpha_d\beta) \tag{5}$$

is the unrelaxed elastic constant. Now,

$$\begin{aligned}\beta&=-(\partial T/\partial\epsilon)=(\partial T/\partial U)_\epsilon(\partial U/\partial\omega)_T(\partial\omega/\partial\epsilon)\\&=\omega_0\gamma_d(\partial U/\partial\omega)_T/C_v\\&=\hbar\omega_0\gamma_d/2k(e^z-2z-e^{-z})/2z^2,\end{aligned} \tag{6}$$

where U is the energy of the mode, C_ϵ is the specific

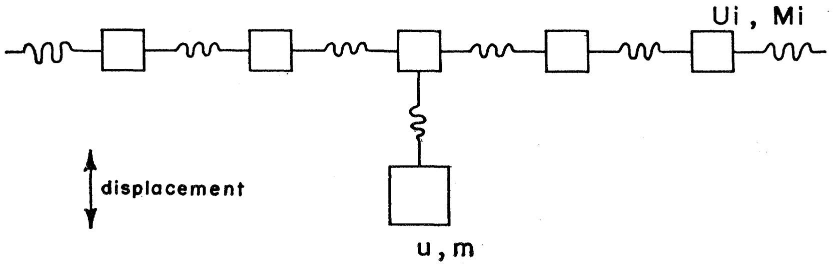

FIG. 5. Structural model.

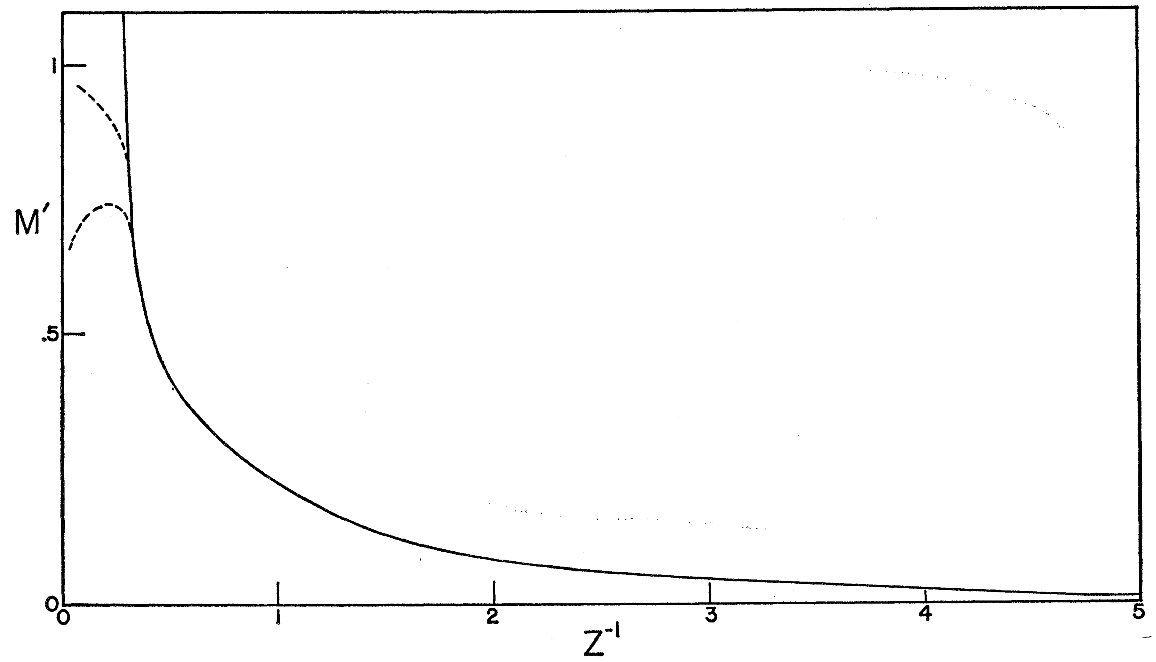

FIG. 6. Temperature dependence of the function $M'(z)$.

heat at constant ϵ, the last expression applies specifically to an Einstein oscillator with $z=\hbar\omega_0/kT$, and we have set $C_\epsilon=C_v$.

Thus, $(C_0-C_\infty)/C_\infty$, the fractional change in the elastic constant observed an infinite time after the application of a stress, is given by

$$(C_0-C_\infty)/C_\infty=N\alpha_d\beta=(N\alpha_d\gamma_d\hbar\omega_0/2k)M'(z)\,, \quad (7)$$

where $M'(z)=(e^z-2z-e^{-z})/2z^2$. The function $M'(z)$ is shown plotted as a function of $z^{-1}=kT/\hbar\omega_0$ in Fig. 6.

This expression is probably quite good at higher temperatures as $z\rightarrow 0$. At lower temperatures, however, as $z\rightarrow\infty$ the above expression diverges because we have not taken into account the temperature dependence of the coefficient of thermal expansion $N\alpha_d$. Now, $N\alpha_d(T)\rightarrow 0$[22] at low temperatures, so that $N\alpha_d M'(z)$ will remain finite as $T\rightarrow 0$. Two possibilities are shown (dotted line in Fig. 6). Thus, according to this analysis, the application of a stress will cause a change in the elastic constant, the magnitude of which decreases with increasing temperature.

Dielectric Relaxation

A harmonic oscillator with charge e in an applied electric field experiences the perturbation $H'=eFr$. The only nonvanishing matrix elements $H'_{m,n}$ are[23] $H'_{n-1,n}=n^{1/2}\mu F$ and $H'_{n,n+1}=(n+1)^{1/2}\mu F$, where

$$\mu^2=\hbar e^2/2m\omega_0.$$

Thus, a second-order perturbation to the unperturbed energy $E_n{}^0=(n+\frac{1}{2})\hbar\omega_0$ results and this gives rise to a change in the Gibbs free energy. The free-energy change may be calculated by the method of "thermodynamic perturbation"[24]

$$\Delta G=\sum_n V_{nn}W_n+\sum_n\sum_m\frac{|V_{nm}|^2}{E_n{}^0-E_m{}^0}W_n-\frac{1}{2kT}\sum_n V_{nn}{}^2W_n+\frac{1}{2KT}(\sum_n V_{nn}W_n)^2,$$

where

$$W_n=\exp[(G_0-E_n{}^0)/kT]. \quad (8)$$

In this case,

$$\Delta G=\frac{N\mu^2F^2}{-\hbar\omega_0}. \quad (9)$$

Since

$$\Delta\chi=-\tfrac{1}{2}\partial^2\Delta G/\partial F^2,$$

we find

$$\Delta\chi=\frac{N\mu^2}{-\hbar\omega_0}. \quad (10)$$

This shows that a charged harmonic oscillator has a temperature-independent dielectric response.

Relaxation Time

To evaluate τ, it is necessary to know not only the normal modes of the system but also the details of the

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[22] We assume that the Nernst Heat Theorem is valid in this connection, although there is doubt that the configuration entropy → 0 as $T\rightarrow 0$.

[23] L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Co., New York, 1935), Chap. III.

[24] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Ltd., London, 1958), Chap. 32, p. 93ff.

interactions between the "oscillator-type" modes and "chain-type" modes. We shall avoid the mathematical complexities and uncertainties by confining our attention to the harmonic oscillator, whose first perturbation term is $H'=C/3!(u-u_j)^3$, and approach a description of the qualitative behavior by assuming that we can write u and u_j in terms of the normal coordinates of an isolated harmonic oscillator and isolated linear chain.

On this assumption,

$$H'=\frac{C}{3!}\left[\left(\frac{h}{2m\omega_0}\right)^{1/2}(a+a^*)\right.$$
$$\left.-\left(\frac{1}{N}\right)^{1/2}\sum_k\left(\frac{h}{2M\omega_k}\right)^{1/2}(a_k+a_{-k}^*)e^{ikx_i}\right]^3,$$

where a, a_k and a^*, a_k^* are the annihilation and creation operators[25] for the oscillator and mode k, respectively.

Expansion of H' gives interaction terms involving all combinations of the annihilation and creation operators, but which nevertheless include two types:

$$H_1'\propto aa^*a_{-k}^*e^{ikx_i}$$

and

$$H_2'\propto aa_ka_{-k'}^*e^{i(k-k')x_i}.$$

The first describes interactions in which two oscillator modes interact with one chain mode, while the second describes interactions in which one oscillator mode interacts with two chain modes. The conservation of energy restricts the frequency ω_k in the first case to ω_0, while in the second case, the restriction is much less severe, namely, $\omega_k-\omega_{k'}=\omega_0$. This means that phonons ω_k, $\omega_{k'}\gg\omega_0$ are also effective in the interaction. Since only a relatively few phonons satisfy the first criterion while relatively many satisfy the second, we assume that the rate of reaction is dominated by the second interaction, namely, two-chain–one-oscillator phonon interactions, the possibility of interaction being proportional to the number of phonons of each involved. Thus,

$$\tau^{-1}\propto n_{\text{osc}}n_kn_{k'}$$
$$\propto(e^{\hbar\omega_0/kT}-1)^{-1}(e^{\hbar\omega_k/kT}-1)^{-1}(e^{\hbar\omega_k/kT}-1)^{-1}$$

average over all phonon occupation numbers. Thus, we suggest

$$\tau^{-1}\propto(T\tau_0^{-1}/\theta)e^{-2\hbar\bar{\omega}/kT}\quad\text{for}\quad\hbar\omega_0/kT\ll1\tag{11}$$

and

$$\tau^{-1}\propto\tau_0^{-1}e^{-2\hbar\bar{\omega}/kT}\quad\text{for}\quad\hbar\omega_0/kT\gg1.\tag{12}$$

To obtain these equations, we have assumed that phonons with frequency ω_k, $\omega_{k'}>kT/\hbar$ are mainly responsible for establishing equilibrium, and that the average over all ω_k's may be approximated by an average frequency $2\bar{\omega}$.

Comparison with Experiment

The previous sections have shown that a number of Einstein oscillators (or excess vibrational modes within a narrow frequency range) can give rise to both mechanical and dielectric relaxations. For a sinusoidally applied stress, the complex elastic constant $C(\omega)+iC(\omega)$ is, thus, given by the usual Debye equations

$$[C(\omega)-C_\infty]/(C_0-C_\infty)=1/(1+\omega^2\tau^2)$$

and

$$[C'(\omega)]/(C_0-C_\infty)=\omega\tau/(1+\omega^2\tau^2).$$

$(C_0-C_\infty)/C_\infty$ is given by Eqs. (6) and (7), τ given by Eq. (11) or (12). Analogous expressions exist for the complex dielectric constant $K(\omega)+iK'(\omega)$, the magnitude of $(K_0-K_\infty)/K_\infty$ being given by Eq. (10). Since $(C_0-C_\infty)/C_\infty$, $(K_0-K_\infty)/K_\infty\ll1$, we have for $\tan\delta$, for example,

$$\tan\delta\approx\frac{C_0-C_\infty}{C_0}\,\frac{\omega\tau}{1+\omega^2\tau^2},$$

where δ is the loss angle.

We suggest that the mechanical relaxations of Fig. 3, at temperatures of ~11 and ~35°K correspond to particularly prominent "spikes" in the phonon density-of-states distribution curve. Indeed, the frequency spread may in some cases be so narrow that "Einstein modes" may be an appropriate description. The fact that each of these spikes gives rise to a dielectric relaxation, Fig. 4, indicates that charge motion is also involved.

The anelastic and dielectric measurements indicate the presence of a process at ~11°K equally well. In contrast, the dielectric measurements of the 35° process show a relatively sharp peak (see also measurements by Volger and Stevels[26]) while the anelastic measurements indicate a broad spectrum of relaxation between 30 and 50°K. This suggests the possibility that several fairly closely spaced vibrational modes are involved here, with only one, however, involving charge motion. Each of the modes gives rise to a mechanical relaxation, and, hence, a broad mechanical spectrum arises, while only one of the modes is dielectrically active, and sharper dielectric relaxation is observed.

It is interesting to estimate the value of the dielectric relaxation

$$(\chi_0-\chi_\infty)=N\mu^2/\hbar\omega_0=Ne^2/2m\omega_0^2,$$

where N is the number of vibrational units. Using the values of N and ω_0 determined by Leadbetter *et al.*[1] from specific-heat measurements, we find the values of $\chi_0-\chi_\infty$ shown in Table I with the values of m used in this estimate. Also shown in Table I are the corresponding experimentally observed values of $\chi_0-\chi_\infty$. Good agreement between theory and experiment is evident.

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[25] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1963), Chap. 1.

[26] J. Volger, J. M. Stevels, and C. van Amerongon, Philips Res. Rept. **10**, 260 (1955).

TABLE I. Theoretical and experimental dielectric relaxation strengths in fused SiO_2 (see text).

Oscillator[a] (°K)	N[a]	m (a.m.u.)	$\chi_0-\chi_\infty$ (theor)	$\chi_0-\chi_\infty$ (expt)
13	4.8×10^{18}	16	3.3×10^{-3}	1.27×10^{-3}
32	1.2×10^{20}	92	2.4×10^{-3}	$2.0\ \times10^{-3}$
58	8.4×10^{20}			Not observed

[a] Reference 1.

Since the vibrating structural units are not known, the values of m to be used can only be guessed at. The values used here were arbitrarily chosen to correspond to the mass of an oxygen[27] atom and the mass of an SiO_4 tetrahedron. It would not be realistic, however, to consider masses smaller or larger by an order of magnitude. Thus, since the respective masses m can only realistically lie between close limits and cannot be arbitrarily varied, we conclude that the agreement between theory and experiment is most significant. It is unfortunate that a relaxation was not observed in these experiments at about 55°K, thus not giving complete correspondence with Leadbetter *et al.*[1]

The magnitude of the anelastic relaxation is not so readily evaluated. However, approximating $N\alpha$ by the difference between the coefficients of thermal expansion of fused silica and quartz at 10°K[15], $\approx1\times10^{-6}$, and using the value -4 for the Grüneisen constant, we find

$$(C_0-C_\infty/C_\infty)_{\text{calc}}\approx2.9\times10^{-3}.$$

This value should be compared with the experimentally observed value

$$(C_0-C_\infty/C_\infty)_{\text{expt}}\approx2.0\times10^{-3}.$$

Agreement is most satisfactory, in view of the relatively crude estimate.

The relaxation time τ is related to the resonant scattering of phonons discussed by Wagner[28] and which is manifest in thermal-conductivity measurements.[29–31] Using the empirically determined value of τ of Walker,[30] namely,

$$1/\tau\approx10^{-44}\omega_0{}^4,$$

we find $\tau=3.5\times10^{-5}$ sec for $\hbar\omega_0/k\approx10$°K. Although the form of this expression is not the same as the Arrhenius expression which describes our results (see below), we nevertheless feel that the estimate indicates that our relaxation time $10^{-3}\sim10^{-4}$ sec is at least realistic.

The temperature at which the maximum in the mechanical loss and dielectric loss occurs is found from the condition $\partial\tan\delta/\partial T=0$. [At this temperature, the relaxation of the real part of the modulus is about one-half (see Ref. 20).] Differentiating the complete expressions for $\tan\delta$ leads to conditions with intractable solutions, so we resort to the simple Debye criterion $\omega_m\tau=1$ and use the "peak shift" method (in which the temperature at which the maximum occurs increases with increasing frequency of measurement ω_m) to determine the "activation energy" $2\hbar\bar{\omega}=Q$. This procedure implies the assumption that the temperature dependence of C_0-C_∞ is slow compared to the temperature dependence of the Debye term $\omega\tau/1+\omega^2\tau^2$.

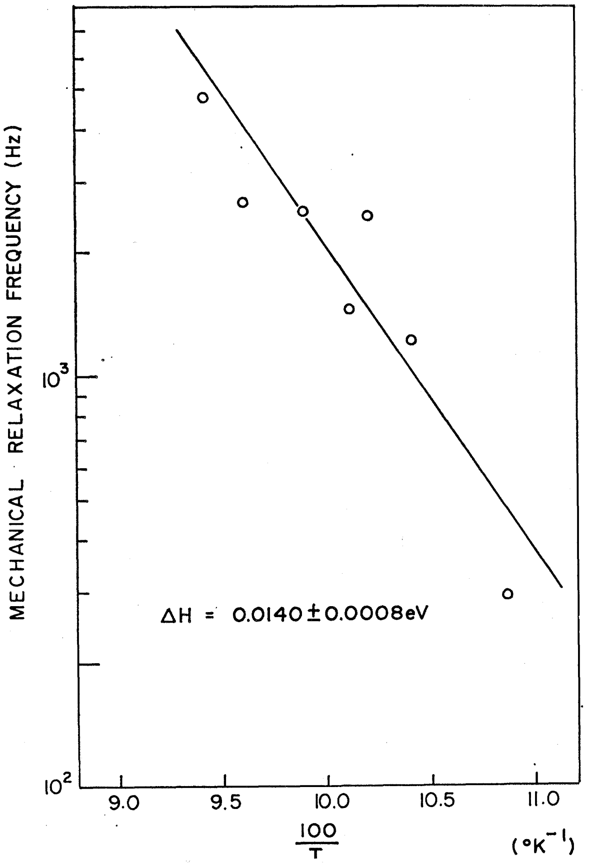

FIG. 7. Experimental $\ln\omega_m$ versus $1/T$ for the low-temperature relaxation indicating an activation energy of 0.0140±0.0008 eV.

The Arrhenius plot for the 11°K dispersion is shown in Fig. 7. A least-squares fit to the expression $\tau=\tau_0\exp(Q/kT)$ leads to the values $\tau_0=2.5\times10^{-11}$ sec, $Q=0.0140\pm0.0008$ eV. This activation energy indicates that the frequencies of the phonons interacting with the oscillator are $\omega\sim1.1\times10^{13}$ sec^{-1}. It is interesting that this process was predicted by Clark and Strakna[27] from a mathematical analysis of the data of Anderson and Bommel,[10] although it was not observed experimentally as a discrete process. Figure 8 shows the Arrhenius plot for the 30°K dispersion. A least-squares fit of these experimental values leads to $\tau=8.7\times10^{-14}$ sec, $Q=0.053\pm0.007$ eV, indicating that the frequencies of the phonons interacting with the oscillator are $\omega\sim4.2\times10^{13}$ sec^{-1}. The data for both relaxation proc-

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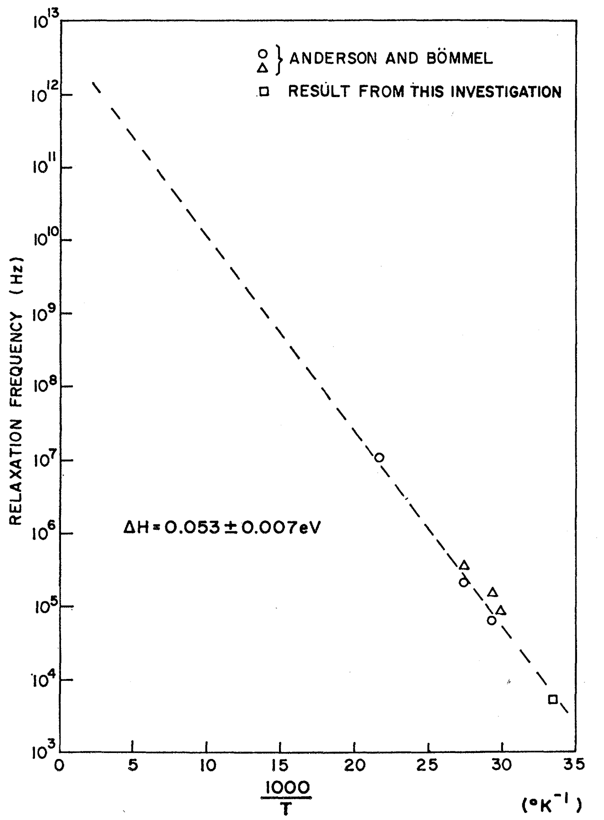

FIG. 8. Experimental $\ln\omega_m$ versus $1/T$ for the high-temperature relaxation indicating an activation energy of 0.053±0.007 eV.

esses were also fitted to the equation $\tau=(\tau_0\theta/T)e^{Q/kT}$, but the standard deviation was greater in both cases. The activation energies for the low- and high-temperature processes, respectively, were 0.0147±0.0019 and 0.0562±0.0117 eV. This indicates that the second case is probably valid at these temperatures and measuring frequencies, i.e., $\hbar\omega_0 \gg kT$.

CONCLUSION

There are several consistencies in the above analysis that are important: (i) The calculated values of the electric susceptibility based on specific-heat measurements and reasonable assumptions agrees well with the measured values, (ii) the calculated values of the anelastic relaxations agree reasonably well with the experimental values, (iii) the phonon-relaxation times measured here are in the same range as those deduced from thermal-conductivity measurements, and (iv) the assumption $\hbar\omega_k \gg kT$ appears valid, in that the experimentally determined values of $\omega_k \approx 1\text{–}5\times10^{13}$ sec^{-1}, which correspond to temperatures ≈100°K. It, thus, appears possible to account for a number of the anomalous properties of vitreous silica based solely on the assumption that excess vibrational modes exist in the material in accord with theoretical normal mode calculations. In this way, a consistant account of the excess low-temperature specific heat and some prominent features of the anelastic and dielectric behavior at low temperatures can be given.

However, it should be pointed out that just as the excess specific heat may be explained by assuming more than just three Einstein modes, by assuming a distribution of Einstein modes, or even by using suitably chosen Schottky specific-heat terms, so also may the anelastic and dielectric relaxations be explained in other ways. Specifically, for example, the relaxations may be due to the field induced inequivalence of an otherwise equivalent two-position defect, the conventional model used in crystalline solids. The merit of the idea developed here lies in the assumption that the simplest theory is also the most acceptable. It is worth noting that similar anelastic relaxations have also been recently observed in polymethyl-methacrylate and polyvinyl acetate,[32] materials which also exhibit excess specific heat.

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