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Anomalies in the Forced Rayleigh Scattering in Glasses

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Two glasses were investigated between 300 and 6 K, by means of forces Rayleigh scattering. Below approximately 50 K, unexpectedly strong scattering was observed. The source of the excess scattering is in local thermal equilibrium with the phonon bath above 20 K. A crossover to local relaxation is found below.

The properties of amorphous substances are influenced by low-energy states related to structural defects.[1] The widely adopted model of smoothly distributed, quantum-mechanical two-level systems[2] was recently extended to more general two-state systems (TSS).[3] TSS may relax by phonon-assisted tunneling,[2] thermal activation,[4] or a combination of both. This approach allows consideration of both very low- and higher-temperature properties from a unified point of view.

I wish to report here the first-time observation of low-temperature Rayleigh scattering in two glasses using the forced-Rayleigh-scattering technique (FRS).[5] My results indicate an extremely large scattering efficiency which cannot be caused by phonon effects alone. I further find a crossover from thermal diffusion to local relaxation below 20 K. Speculatively, these phenomena can be explained by structural rearrangement with large variations in electronic-level positions (which would be a hint as to the nature of TSS) and a hot TSS population.

The presence of fluctuations, $\delta m(E)$, in the population of TSS (with energy E) has been predicted in the low-frequency scattering of light.[6] If their relaxation times $\tau_m(E)$ are sufficiently short, $\delta m(E)$ stays in local thermal equilibrium with fluctuations $\delta d(T_0)$ in the density of thermal phonons (energy distribution thermalized to the average temperature T_0). $\delta d(T_0)$ is the origin of thermal Rayleigh scattering in simple crystalline solids. $\delta m(E)$ will influence the intensity of the Rayleigh line for small $\tau_m(E)$ but hardly its dynamics.

The relevant time scale is established by the diffusive decay time

$$\tau_d = (Dq^2)^{-1}, \tag{1}$$

where D is the thermal diffusivity, and $q = |\vec{q}|$ the scattering vector.

If (some) TSS with energy E' relax slowly, such that $\tau_m(E') \geq \tau_d$, local thermal equilibrium between $\delta m(E')$ and $\delta d(T_0)$ will not in general exist. The relaxation to be observed in a time-resolved scattering experiment will then consist of a sum over exponentials with decay times τ_d and $\tau_m(E')$. Experimentally, such a sum is difficult to resolve and may resemble a single exponential with decay time $\tau > \tau_d$. (The equivalent in the frequency domain is a Rayleigh line narrower than expected on the basis of thermal diffusion alone.)

Fleury and Lyons[7] studied the low-frequency scattering in several glasses with use of classical Fabry-Perot spectroscopy. Their investigation was restricted to temperatures above 60 K and could not resolve the thermal Rayleigh line because of signal-to-background problems. These can be overcome to a large extent by forced Rayleigh scattering[5] with use of artificially created thermal fluctuations instead of statistical ones.

In the present FRS experiment, intended to explore the scattering at lower temperatures, a thermal grating was set up in the sample by interference and absorption of two intersecting argon-laser beams (488 nm). A chopper provided pulses of 1.2-ms duration and $\leqslant 2\times200$-mW peak power in most of the measurements. The angular separation θ was varied between 3.5 and 10 mrad, resulting in scattering vectors with $|\vec{q}|/2\pi$ between 72 and 206 cm^{-1}.

Optical filter glasses (Schott BG20 and FG18)[8] were chosen as sample material. These glasses provide absorption at 488 nm ($\sim 1\ \text{cm}^{-1}$) while being rather transparent around 632 nm. The samples (cross section $2\times5\ \text{mm}^2$, $l=20$ mm) were mounted on a cool finger for measurements between 25 and 300 K, and inside a pumped ^{4}He cryostat for lower temperatures. In the latter arrangement, the average temperature T_0 of the interaction zone inside the sample was considerably above the bath temperature (1.5 K) because of the finite heat diffusions to the bath. Thus it was difficult to get below ~ 6 K with pulses long enough to establish quasistationary conditions implying a grating amplitude $\delta T \ll T_0$. The temperature rise was calculated numerically for each value of the pump power on the basis of the measured values of the absorption coefficient α, the intensities I_a, I_b of the pump beams, the heat conductivity $K(T)$, and the specific heat $C_p(T)$ (cf. acknowledgment). It is important in view of the following results that T_0 was assigned to the maximum temperature which builds up at the center of the sample. T_0 hence tends to be too large rather than too small. δT typically was of the order 10 mK.

The probe source is a HeNe laser beam with ~ 1-mW power oriented to meet the Bragg condition with respect to $\vec{q}$. FRS signals, emitted in the complementary Bragg direction, could be readily detected in the whole temperature interval investigated (6–300 K), although patient signal averaging was required at low temperatures. The decay was sufficiently slow in time to be well resolved on the record [similar to Fig. 2(a), upper trace of the first paper of Ref. 5]. As usual, the signals were riding on a strong background of stray light which provided the local oscillator for heterodyne detection.

In the measurements, attention was focused primarily on the variation with temperature of the scattering strength, characterized by the thermo-optic coefficient[9] $(\partial n/\partial T)_{\text{eff}}$ and the decay time τ. Further, the dependence of τ on q was checked carefully at each temperature. In the first part of the investigation, BG20 was studied with particular emphasis on the low-temperature regime. The second series of measurements was made with FG18 under much the same conditions. With this glass, the investigations were facilitated by the appearance of a photochromic effect at low temperatures[10]: The pump radiation produced a visible absorption grating inside the sample which saturated after ~ 20 min and remained stable for a long time. The probe light, deflected from the absorption grating, provides an excellent reference source which is useful for alignment and phase stabilization. For this reason, most quantitative measurements were made with FG18, the results for BG20 being qualitatively the same.

A representative set of experimental decay times is plotted versus T_0 in Fig. 1. τ was determined for four values of q which increase in the proportion of $\sqrt{2}$. The solid curves are the respective diffusive decay times τ_d calculated on the basis of Eq. (1). For this purpose, $D(T_0)$ was determined from the independent stationary measurements of $K(T_0)$ and $C_p(T_0)$ (inset to Fig. 1, solid line).

$(\partial n/\partial T)_{\text{eff}}$, representing the scattering efficiency, is the second important parameter of this FRS experiment (Fig. 2). $(\partial n/\partial T)_{\text{eff}}$ was determined from the signal-to-probe amplitude ratio (E_s/E_t), the sample length l, the probe-light

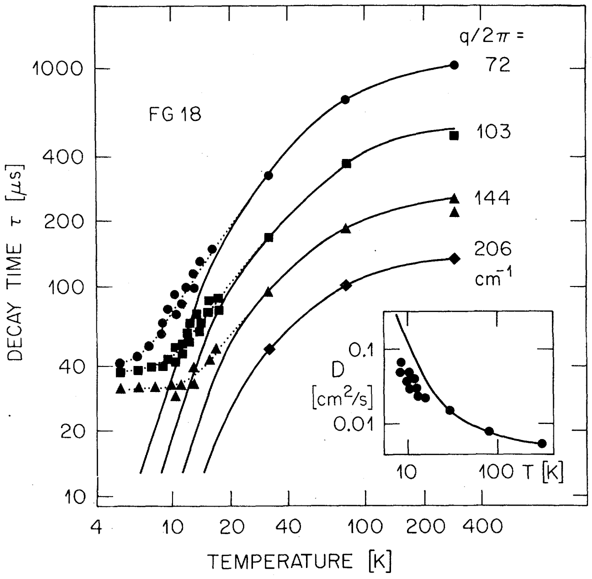

FIG. 1. Decay time and thermal diffusivity vs T. Solid curves are calculated from stationary data.

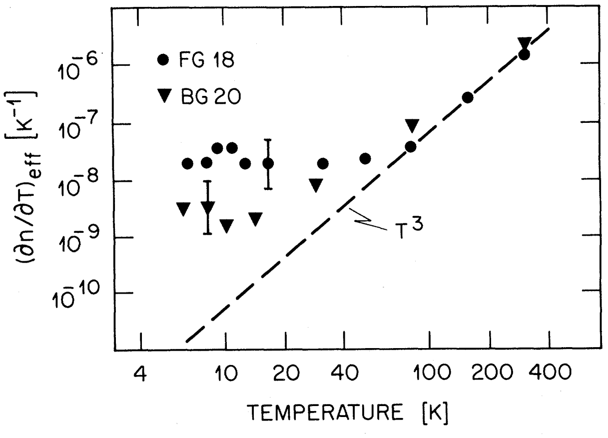

FIG. 2. Experimental thermo-optic coefficients. Error bars and dashed line, see text.

wave vector k_i, and δT,[5]

$$(\partial n/\partial T)_{\rm eff} = E_s/E_i k_i l \delta T, \tag{2}$$

$$\delta T = \alpha (I_a I_b)^{1/2}/q^2 K. \tag{3}$$

The data points in Fig. 2 are the average of several measurements. Since the measured values strongly depend on the precise adjustment, a considerable scatter of data, in particular between different runs, is unavoidable. Within one run, the accuracy is about three times better than indicated by the error bars.

The two figures allow three temperature ranges to be distinguished: In the *first* interval, above 70 K in FG18, the scattering dynamics is obviously governed by thermal diffusion, i.e., the dynamics of δd. This is not a matter of course in view of the excitation mechanism involving photon energies more than a hundred times above $k_{\rm B}T_0$ ($k_{\rm B}$ is the Boltzmann constant).

In the discussion of $(\partial n/\partial T)_{\rm eff}$, I first consider the refractive index n in simple crystals where phonons are the only low-energy excitations, and δd the only fluctuations. They influence density and polarizability which essentially are the constituents of n. The first relates $(\partial n/\partial T)_{\rm eff}$ to thermal expansion (α_l). The latter is a function of positions and transition probabilities of the (electronic) levels (Kramers-Kronig relation). These parameters depend, among others, on atomic distances and therefore, also on α_l. As a consequence, $(\partial n/\partial T)_{\rm eff}$ is roughly proportional to α_l (Ref. 11) with a temperature dependence between T^3 (dashed line in Fig. 2; small-T limit) and T^1 ($T \to \infty$). The experimental data in the upper temperature range are consistent with this simple picture giving no evidence of contributions specific for noncrystalline materials.

The *second* temperature interval, starting below 70 K in FG18, is characterized by a practically constant $(\partial n/\partial T)_{\rm eff}$. Such a behavior cannot easily be understood in terms of phonon effects alone. On the other hand, our finding is not unexpected in view of the anomalous thermal expansion of glasses.[12] However, the available experimental $\alpha_l(T)$ are far from being constant at low temperatures, and hence cannot explain the present observations. We therefore assume tentatively the population of states which acts directly on the polarizability. They may, but need not, be the same which cause the anomalies in $\alpha_l(T)$. Their energies must be close to $k_{\rm B}T_0$ above 20 K because of the local thermal equilibrium which manifests itself in the experimental decay times (Fig. 1).

In this context, one may think of structural rearrangement as a possible source of extra scattering. Transitions of the type sketched in Fig. 2 of Hunklinger and Arnold[1] involve considerable changes of atomic distances. Hence, a sizable influence on n may be expected. Similar ideas were developed by Winterling[13] in a discussion of excess Raman scattering. The practically constant value of $(\partial n/\partial T)_{\rm eff}$ below 70 K may be an accidental compensation of parameters, but is not inconsistent with a constant density of states.

The *third* temperature range, starting below 20 K, is characterized by a crossover (not fully completed) from diffusion to local relaxation. Such a behavior could be caused, in principle, by any sufficiently long-lived, nondiffusive excitation of the sample material. We propose, however, that the source of scattering is similar to the one discussed before for the following reasons: (i) The plateau in $(\partial n/\partial T)_{\rm eff}$ continues *smoothly* below 20 K. (ii) When plotted in terms of thermal diffusivity, the present results and their deviation from the stationary $D(T)$ (inset to Fig. 1) agree almost quantitatively with the heat-pulse data of Block, Meissner, and Spitzmann.[14] Such deviations are seen only with pulses of relatively large amplitude.[15-18]

Putting together the heat-pulse experience with the present results, I conclude that the source of anomalous behavior is probably the same in both cases. It cannot be far from $k_{\rm B}T_0$ in energy and relaxes slower than δd. One could speculate further that the pertinent levels, though close to $k_{\rm B}T_0$, might be distinctly above the majority of occupied states in the third temperature interval.

They would scarcely get populated by very weak heat pulses, but might be accessible with more intense ones due to anharmonic interactions. They could also easily become occupied during the cascade of processes following the excitation of electronic levels in FRS. The observed long decay times would be understandable if the relaxation required phonon assistance which is less and less available with decreasing temperature. Although supported by a small body of experimental data only, this speculation has the attractive feature to explain the two independent experimental findings on deviations from stationary behavior, while being consistent with current models on low-energy states in amorphous solids.

This work substantially benefitted from stationary measurements of $K(T)$ performed at the Technical University of Munich with the help of W. Dietsche and H. Kinder, and of $C_p(T)$ which was kindly determined at the Max-Planck Institut für Festkörperphysik in Stuttgart by E. Gmelin. I wish to thank them and their institutions for their support, as well as V. Irniger for competent technical assistance. I am also indebted to S. Hunkliger, J. Jäckle, M. Meissner and his collaborators, and E. Courtens for valuable discussions.

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