Materials Research.

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[a] Present address: Exxon Research and Engineering, Linden, N. J. 07036.

[1] R. Ludeke and A. Koma, Phys. Rev. Lett. 34, 1170 (1975).

[2] P. Pianetta, I. Lindau, C. M. Garner, and W. E. Spicer, Phys. Rev. Lett. 35, 1356 (1975).

[3] K. C. Pandey, T. Sakurai, and H. D. Hagstrum, Phys. Rev. Lett. 35, 1728 (1975).

[4] J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 34, 806 (1975).

[5] M. Schlüter, J. E. Rowe, G. Margaritondo, K. M. Ho, and M. L. Cohen, Phys. Rev. Lett. 37, 1632 (1976).

[6] J. Stöhr, R. S. Bauer, J. C. McMenamin, L. I. Johansson, and S. Brennan, J. Vac. Sci. Technol. 16, 1195 (1979).

[7] P. H. Citrin, P. Eisenberger, and R. C. Hewitt, Phys. Rev. Lett. 41, 309 (1978), and 45, 1948 (1980).

[8] These patterns have also been referred to as 1×1; see Ref. 5.

[9] For details of data analysis, see Ref. 7 and P. A. Lee, P. H. Citrin, P. Eisenberger, and B. M. Kincaid, Rev. Mod. Phys. 53, 769 (1981).

[10] Differences between raw and first-nn filtered data in Fig. 2(a), particularly at low k, are due to additional SEXAFS from second-nn atoms (a filter from 2.4 to 4.4 Å is used for its analysis).

[11] H. N. Rexroad, D. W. Howgate, R. C. Gunton, and J. F. Ollom, J. Chem. Phys. 24, 625 (1956).

[12] Because the $(p \rightarrow s)(p \rightarrow d)$ cross term in the L_{III}-edge SEXAFS amplitude function is nonzero for anisotropic absorbers, N_S is modified from $\frac{3}{2}\sum_i(\frac{1}{3}+|\vec{\epsilon}\cdot\vec{r}_i|^2)$ (cf. Ref. 7) to $\frac{3}{2}\sum_i(1.4/3+0.6|\vec{\epsilon}\cdot\vec{r}_i|^2)$ [cf. P. H. Citrin, P. Eisenberger, and R. C. Hewitt, Phys. Rev. Lett. 47, 1567 (1981)]. The factor of $\frac{3}{2}$ is included here to account for appropriate normalization (cf. Lee *et al.*, Ref. 9).

[13] This weighting ignores differences between first- and second-nn atom Debye-Waller and inelastic loss terms, both of which could reduce the second-nn contribution.

[14] The I-Ge bond length in $\mathrm{GeI_4}$ vapor is 2.50 ± 0.03 Å; M. W. Lister and L. E. Sutton, Trans. Faraday Soc. 37, 393 (1941).

[15] This was verified theoretically from calculated values (cf. Lee *et al.*, Ref. 9) and empirically using $\mathrm{Cu_2Te}$ bulk EXAFS data.

[16] Although the second-nn atom amplitudes could contribute less than calculated here (see Ref. 13), it is unlikely that they would not contribute at all. For example, our adsorption site determination for Te/Si{111} would remain valid even if only 20% of our calculated contribution applied.

[17] L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, New York, 1960), 3rd ed., p. 246.

[18] For example, see F. Jona, J. Phys. C 11, 4271 (1978), and references therein.

[19] Assuming $R_1 = 2.45$ Å, we calculate average distances $R(35°) = 2.74$ Å and $R(90°) = 2.69$ Å, compared with observed values $R(35°) = 2.74 \pm 0.04$ Å and $R(90°) = 2.66 \pm 0.04$ Å.

Low-Frequency and Low-Temperature Raman Scattering in Silica Fibers

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The Raman scattering spectrum of silica was measured to low temperature and very small frequency shifts. Strain-free cooling of a long silica-core fiber allowed us to investigate Raman scattering of the two-level tunneling systems to 1.5 K. A considerable central line broadening from relaxation of two-level tunneling systems is evident, although the predicted strong scattering contribution from resonant two-level tunneling centers at very low temperature and small frequency shift was not observed.

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The Raman spectrum of silica at low temperatures and small frequency shifts is of particular interest because of the possibility of observing two-level tunneling systems which are characteristic of the amorphous state.[1-4] The two-level systems have been observed directly by ultrasonic absorption[3] but their density of states can only be inferred from heat-capacity measurements.[4] In this respect, a spectroscopic technique such as far-infrared absorption or Raman scattering would be highly desirable. Two-level systems have been seen by far-infrared absorption between 2 and 12 $\mathrm{cm^{-1}}$ in silica[5] and silicate glasses.[5,6] The relevant absorption is much stronger in the mixed glasses than in silica but, even there, difficulties with other absorption processes prevent the extraction of a reliable density of states.[6] Relaxation processes associated with the two-

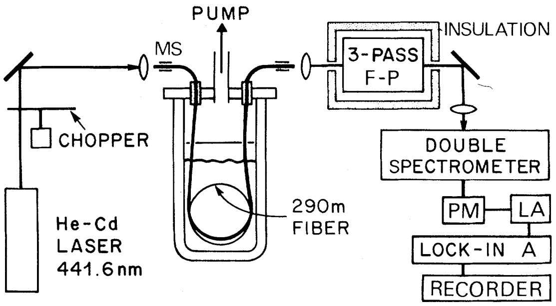

FIG. 1. Experimental arrangement. MS, mode-stripper; F-P, Fabry-Perot interferometer; PM, photomultiplier; LA, low-noise preamplifier. Temperatures from 1.5 to 450 K were attainable in the double insulated stainless-steel Dewar.

level systems have been observed by Raman scattering in silica and borosilicate glass[7] and one might expect to see the scattering from their direct excitation at frequency shifts of 5 cm^{-1} and temperatures of 1.5 K.[8] Unfortunately, under just these conditions, the Raman spectrum of silica is extremely weak.

A fiber provides a conveniently cooled sample where light is gathered from its entire length. By using a 290-m fiber, we have measured the Raman spectrum of silica at frequencies as low as 2 cm^{-1} and temperatures to 1.5 K. To analyze the spectrum we used a triple-pass Fabry-Perot interferometer followed by a double-grating spectrometer which provided an unambiguous separation of inelastic and elastic scattering. The results clearly show the Raman scattering from the relaxation process but we do not observe direct scattering from the two-level systems.

The basic features of the experimental apparatus are illustrated in Fig. 1. Raman scattering from an optical fiber is analyzed with a triple-pass Fabry-Perot interferometer[9] followed by a double-grating spectrometer. The signal is detected with a photomultiplier, processed with a lock-in amplifier, and displayed on a chart recorder. The fiber is mounted strain-free in a Dewar and immersed in liquid nitrogen or helium.

The fiber has been demonstrated to be a useful medium for Raman scattering inasmuch as all the Raman light emitted in a solid angle corresponding to the numerical aperture is collected from the entire fiber.[10] For forward scattering, the price to be paid is the presence of the exciting line along with the Raman light. The Raman spectrum of silica is fairly weak—especially at small frequency shifts. Separation of the spectrum from wings of the exciting line is already a serious problem in the 90° scattering geometry from bulk samples.[7,11] For a long fiber, the enhanced Raman signal permits additional filtering which more than overcomes the disadvantages from the strong exciting light.

The spectral output from the fiber is a continuum which is sampled by the Fabry-Perot channel spectrum providing discrete points on the Stokes and anti-Stokes Raman spectrum. An example of such a scan is given in Fig. 2. A convenient free spectral range is 2–5 cm^{-1}. The resolution of the double spectrometer has to be sufficient to separate the peaks passed by the interferometer.

There are two important features of the series Fabry-Perot double-spectrometer arrangement. First, the contrast ratio of the triple-pass Fabry-Perot is extremely high. The interferometer mirror reflectivity at 441.6 nm (He-Cd) was 0.86 so the contrast between maxima and minima[9] can be as high as 2×10^7. The plate spacing was adjusted with piezoelectric transducers so that the laser line fell on a transmission minimum. Higher contrast ratios are possible with higher reflectivities but in our case this increased the sensitiv-

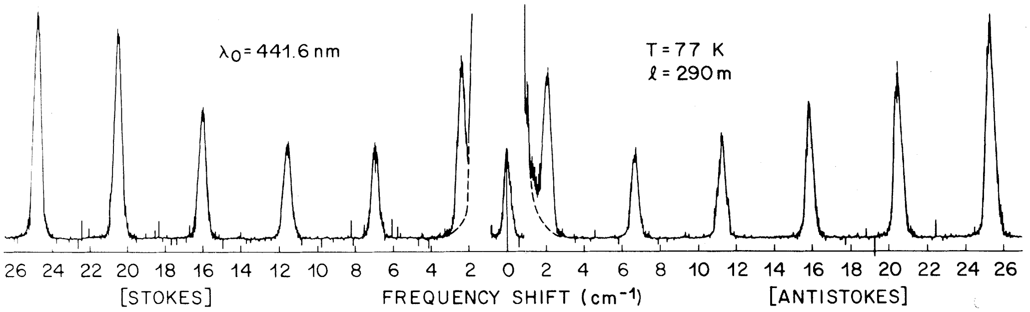

FIG. 2. Raman spectrum of silica-core fiber obtained with the experimental arrangement shown in Fig. 1.

ity to alignment drift. This drift was the major experimental difficulty; signal-to-noise ratio appeared adequate with only 10 mW of laser power. The second advantage of preceding the spectrometer with the interferometer occurs because only the frequency-shifted light appears in the channel spectrum, as illustrated in Fig. 2, and sits on top of the wings of the laser light scattered within the spectrometer.

The fiber diameter is relatively large (150 μm) and the silicone coating is thin (35 μm). Transmission decreased only (1–2)% when the fiber was cooled. Earlier work had shown that uncoated fibers could be cooled[12] but that silicone-coated fibers suffered high scattering loss[13]—probably due to bending losses induced by shrinkage of the coating. Two fibers were pulled from the same preform: one with a small diameter and thick coating and the other with a large diameter and thin coating. When immersed in liquid nitrogen the former fiber suffered high scattering loss while the latter did not.

The fiber was 290 m long and was fed into the top of the Dewar through thin tubes filled with silicone sealant. The total length of fiber outside the Dewar was 90 cm and approximately $\frac{1}{2}$ m of fiber in the Dewar remained at elevated temperatures. The diameter of the step-index silica core was 5.85 μm and the index difference to the borosilicate cladding was 0.0033. At a wavelength of 441.6 nm the fiber supports four modes and almost all the energy is confined to the core. OH content was of the order of 100 ppm.

The Raman spectrum is obtained using information from both the Stokes and anti-Stokes scans. The scattered intensities are first corrected for the spectral response of the entire system which includes the frequency dependence of the fiber loss, photomultiplier sensitivity, and grating efficiency as well as the ω^4 dependence of the Raman cross section. Here, we assume that, over the relatively small region of interest, these effects can be lumped together and treated as a linear correction. The correction factor is obtained by comparing Stokes and anti-Stokes intensities between 20 and 25 cm^{-1}. At these frequencies it is known from earlier Raman[7,11] and infrared[11] measurements that the spectrum can be treated as a distribution of harmonic oscillators.

The major uncertainty comes from the drift in the alignment of the triple-pass Fabry-Perot interferometer. The peak transmission always fell off over the half hour required for a scan. Because of this drift many scans were taken at each temperature and results compared for scans in both directions. While not entirely satisfactory, the procedure permitted identification and rejection of those scans with the worst deviation originating from the drift. Active stabilization of the interferometer would be highly desirable.

At the lowest temperatures (4.2 and 1.5 K) the anti-Stokes intensity did not go to zero at high frequencies. The residual intensity was consistent with the signal from 1.4 m of fiber at room temperature. To obtain the correct low-temperature spectrum this room-temperature contribution was subtracted from the data.

The results are plotted in Fig. 3 as normalized scattered intensity.[7] The Stokes spectrum, after correction for instrumental response, is plotted as $I_{rs}\omega^{-1}[n(\omega,T)+1]^{-1}$ and anti-Stokes as $I_{ra}\omega^{-1} \times n^{-1}(\omega, T)$. The factor of ω is included to be consistent with earlier work[7,8] and $n(\omega,T)$ is the thermal population factor.

The reduced Raman spectrum of Fig. 3 shows a definite increase at the lowest frequencies. The spectrum can be described as a temperature-dependent central line broadening superimposed on a distribution of harmonic oscillator modes. This picture was proposed by Winterling[7] to explain the excess scattering in the 5–20-cm^{-1} region in bulk silica. The present results, extending the range to both lower frequencies and lower temperatures, establish the concept of the central line broadening. A similar broadening has been observed closer to the line center in nonsilicate glasses.[14] The mechanism for the broadening is uncertain although various arguments, based primarily on the depolarization ratio of scattering from bulk

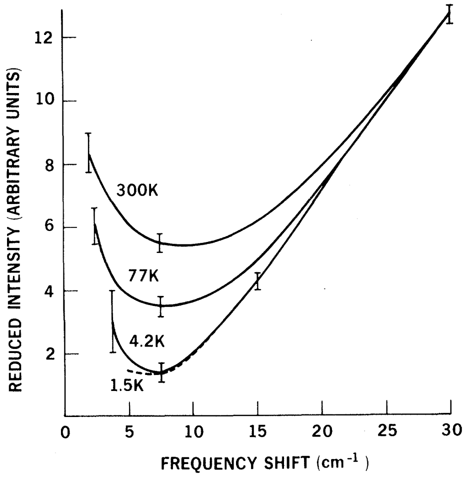

FIG. 3. Normalized Raman scattering intensity of silica for temperatures extending down to 1.5 K.

samples,[7,14] suggest that these are relaxation processes associated with two-level systems. It is not clear just how many relaxation processes are required to describe the broadening adequately though a single process appears insufficient.[7]

Our primary aim in these experiments was to observe the scattering from *direct* excitation of the two-level systems. Estimates of the intensity of this scattering have been made by Theodorakopoulos and Jäckle.[8] The essential feature of the argument is to relate the scattered intensity from direct excitation of the two-level systems to the scattering from structural relaxation of the same centers. Thus, knowing the magnitude of the relaxation scattering, one can estimate the direct scattering. For example, at 5 cm^{-1} it is expected that the direct scattering at 1.5 K should be *comparable* to the relaxation scattering at room temperature. Also, the scattered intensity should *increase* substantially in going from 4.2 to 1.5 K. Instead, we actually observe a further slight decrease of the Raman signal at 1.5 K. It thus appears that the Raman cross section for direct excitation of the two-level systems is more than an order of magnitude weaker than predicted.

In conclusion, we have demonstrated a new technique for Raman spectroscopy of glasses at low frequency and low temperatures. By using an optical fiber as the sample, it is possible to achieve strong Raman signals and to cool the sample to low temperatures. The use of a series Fabry-Perot interferometer and double spectrometer permits resolution of the spectrum at very low frequencies. Measurements with a 290-m silica-core fiber between room temperature and 1.5 K at frequencies down to 2 cm^{-1} clearly verify the presence of a broadened central component in the spectrum. However, we do not observe the expected direct scattering from two-level systems although the experimental signal-to-noise ratio should have been sufficient by more than an order of magnitude.

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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] S. Hunklinger, W. Arnold, S. Stein, R. Nava, and K. Dransfeld, Phys. Lett. 42A, 253 (1972); B. Golding, J. E. Graebner, B. I. Halperin, and R. J. Schutz, Phys. Rev. Lett. 30, 223 (1973).

[4] J. Jäckle, L. Pinché, W. Arnold, and S. Hunklinger, J. Non-Cryst. Solids 20, 365 (1976).

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

[6] M. A. Bösch, Phys. Rev. Lett. 40, 879 (1978); M. A. Bösch and A. J. Sievers, in *Proceedings of the 1977 International Conference on Lattice Dynamics*, edited by M. Balkanski (Flammarion, Paris, 1978).

[7] G. Winterling, Phys. Rev. B 12, 2432 (1975), and in *Phonon Scattering in Solids*, edited by L. J. Challis, V. W. Rampton, and A. F. G. Wyatt (Plenum, New York, 1976), p. 144.

[8] N. Theodorakopoulos and J. Jäckle, Phys. Rev. B 14, 2637 (1976). Other attempts to observe direct excitations have been made at 9.5 cm^{-1} by R. A. Field [Ph. D. thesis, University of Illinois, 1978 (unpublished)].

[9] J. R. Sandercock, in *Proceedings of the Second International Conference on Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1971), p. 9; Burleigh Technical Memo No. FP 18409772, Burleigh Instruments, Inc., East Rochester, N. Y.

[10] G. E. Walrafen and J. Stone, Appl. Spectrosc. 29, 337 (1975); P. O'Connor and J. Tauc, Appl. Opt. 17, 3226 (1979).

[11] R. H. Stolen, Phys. Chem. Glasses 11, 83 (1970).

[12] R. H. Stolen, in *Proceedings of the Third International Conference on Light Scattering of Solids*, edited by M. Balkanski, R. C. Leite, and S. D. S. Porto (Flammarion Sciences, Paris, 1976), p. 656.

[13] E. G. Hanson, Fiber Int. Opt. 3, 113 (1980); Y. Katsuyama, Y. Mitsunaga, Y. Ishida, and K. Ishihara, Appl. Opt. 19, 4200 (1980).

[14] P. A. Fleury and K. B. Lyons, Phys. Rev. Lett. 36, 1188 (1976).