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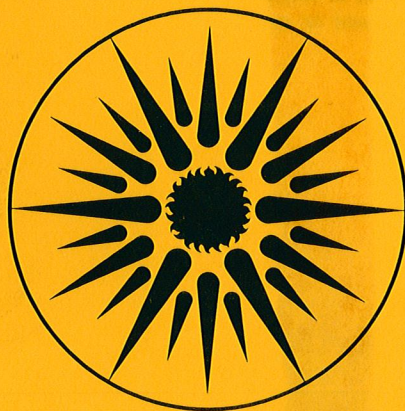
**ENERGY
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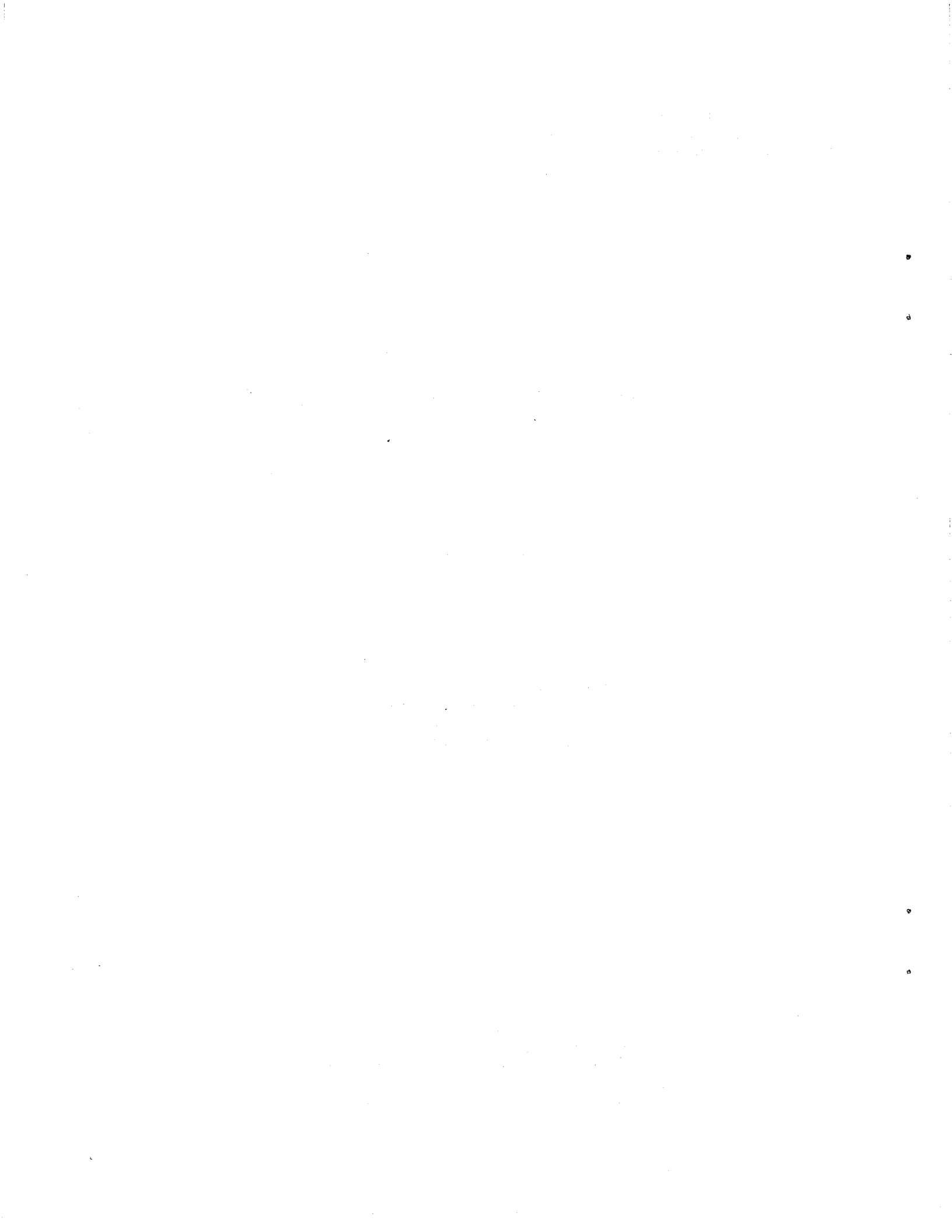University of California
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INTRODUCTION

Silica aerogels have been prepared with dried densities in the range of 2–10% of that of bulk silica. If the particle size is very small (e.g., the order of 100 Å or less) and the material has a uniform microstructure, the aerogel is transparent. It is transparent because the characteristic size of the structure is much smaller than the wavelength of light, allowing the material to transmit, rather than strongly scatter visible light. Aerogel is an excellent thermal insulator because of the high ratio of void to volume of solid matrix, combined with its extremely small pore size.

Due to its combination of transparency and low thermal conductivity, aerogel holds considerable promise for use as insulating window materials for residential and commercial applications. Replacement of a conventional double or triple pane window with an aerogel window of similar thickness can result in an increase in thermal resistance and transparency. In addition, aerogel preparation methods may be used to provide optical materials with a wide range of effective indices of refraction, useful for a variety of applications.

In view of these desirable properties, a program to investigate the preparation and properties of transparent aerogels was initiated at LBL. The goal of the work is to improve the optical and physical properties of the material, and explore alternative methods of production compatible with mass production methods.

While aerogels are transparent in the sense that objects may be clearly viewed through several centimeters of material, they exhibit some residual light scattering. The short wavelength end of the visible spectrum is scattered more strongly than longer wavelengths. The scattering results in a slight reddening of transmitted light and a pale bluish appearance of most samples of aerogel.

This paper reports on the preliminary investigation of the optical and scattering properties of silica aerogels. The following section briefly describes the properties of aerogels important for window glazing applications. The optical properties are then described, followed by a discussion of the scattering measurements and their interpretation.

SILICA AEROGELS FOR WINDOW GLAZING MATERIALS

Kistler first prepared transparent silica aerogels over 50 years ago using a process based on colloidal gels[1]. In this process, a colloid is prepared with sufficient density of solid so that the individual colloidal particles link together. After low temperature aging has taken place, the material transforms from a liquid colloidal suspension to an elastic solid or gel. The material is then a semi-solid matrix of linked particles permeated by a liquid.[2] Elimination of the liquid by heating or drying generally causes the collapse of the matrix in such low density gels. The shrinkage occurs because, during drying, both liquid and gaseous states coexist in the matrix. Surface tension effects between gas and liquid are large due to the very small size of the pores and cause the structure to collapse during drying. If the distinction between liquid and gas is eliminated by raising the temperature and pressure of the liquid above its critical point, the resulting fluid can be released from the gel without the surface tension effects that destroy the matrix.

Recently, several investigators have prepared silica aerogels[3,4,5] for applications requiring low density and transparency. The sol preparation methods are based on

hydrolysis of an ester of silicic acid with a catalyst. Henning and Svensson utilized tetramethyl orthosilicate[3] (TMOS) as a starting compound as did Nicolaon[4], and Schmidt used tetraethyl orthosilicate (TEOS).[5] The ester is mixed with ethyl or methyl alcohol and water and catalyzed with a base or combination of acids to form an alcosol. After the gel is formed in a mold, it is placed into an autoclave and dried under supercritical conditions. After drying, the aerogel may be heated in air to 500°C to oxidize the remaining organic compounds.[3]

The final material is a low density, transparent solid composed of almost pure silica and is only sightly absorbing in the terrestrial solar spectrum. Due to their low density and open pore structure, these aerogels are not particularly strong. However, if they are sealed between sheets of conventional glass[5], or if their surface is coated or densified, they have adequate strength for glazing applications.

The thermal properties of aerogels are excellent for insulating applications. Room temperature measurements yield thermal conductivity of 0.019 W/M°K.[5] These values compare with the thermal conductivity of stagnant air. A one inch thick aerogel window has an insulating value roughly comparable to a window with five layers of glass.[6]

Silica aerogel is nearly pure silicon dioxide and therefore, not very chemically reactive to most common substances. However, due to the very large surface area it can adsorb gases, and liquids that wet silica will permeate the matrix and cause it to collapse. This further establishes the need to seal aerogel from the environment.

OPTICAL PROPERTIES OF AEROGELS

The visible index of refraction, and the infrared, visible, and ultraviolet transmission of aerogels were studied as well as their scattering properties. Aerogel samples from two sources were examined. Aerogels prepared with TMOS were from the University of Lund and with TEOS were from Schmidt. The specular transmission of the material was consistent with the properties of pure silica in the long wavelength portion of the visible spectrum. The transmission of both samples decreased toward the blue end of the spectrum with a strong wavelength dependence not inconsistent with Rayleigh scattering. The transmission in the ultraviolet, near the beginning of the fundamental absorption edge below 200 nanometers, stopped decreasing.

The reflectance of the samples, as determined from total internal reflectance measurements was extremely low, from 1.022 to 1.035 depending on the sample. The low reflectivity is to be expected from materials with low densities and therefore low average indices of refraction. It has been reported that the index of refraction in excess of unity scales directly with the average density of the aerogel.[3] However, it may be argued that the volume polarizibility rather than the index of refraction should scale with the average density. (This was not tested, as density measurements were not available.) Measurements of the infrared reflectance using a spectrophotometer showed no measurable reflectance.

LIGHT SCATTERING

The results of the light scattering measurements on aerogels are reported in two parts. First, the visual observations will be described, then results from the angular nephelometry measurements will be presented.

A series of scattering observations were performed using both white light and laser light of two wavelengths, 633 and 442 nanometers. These observations were mainly qualitative, but they provided new and valuable information regarding the properties of aerogels. A collimated beam of white light traversing the samples produced a clearly visible path. The scattered light was generally bluish in appearance and the transmitted light became progressively redder with thickness. Observation of the scattered light through a polarizer showed strong polarization of light scattered at an angle of 90°.

When a laser was used as a light source, striking new effects were visible. Along the path of light through the sample, there were regions of varying intensity of the scattered light. The scattered light had the appearance of a string of regularly spaced beads. In the upper drawing in Figure 1, the effect is illustrated as a dashed line with the dashes representing the bright areas. The strength of the effect and spacing of the beads varied with the sample and the direction of propagation of light through the sample. There were strong polarization effects associated with beads.

There are several possible mechanisms to explain this effect. The simplest explanation is that the variation in scattering is due to inhomogeneous regions in the material; more light may be scattered from some regions than others. However, this explanation fails because the beads move as the orientation of the sample is changed.

To understand the situation, refer to the bottom of Figure 1. Light scattered from a medium containing very small particles (Rayleigh scattering) has a minimum intensity at an angle of 90° and is strongly polarized. The bottom of Figure 1 illustrates intensity of scattered light from a dipole as a function of angle for light polarized parallel and perpendicular the scattering plane.[7] The last figure illustrates the effect if the light has equal components parallel and perpendicular the scattering plane.

To understand the observed scattering effects in aerogel, it must be remembered that the laser light was monochromic and polarized before it entered the sample. If the material possesses a strain induced birefringence, the initially linearly polarized light will be broken into components parallel and perpendicular to the strain axis. These components will propagate at different velocities, causing the relative phase between the waves to shift. In regions where the light is circularly polarized, the scattered light will show no dependence on the azimuth angle about the propagation direction. However, in regions where the light is linearly polarized, the scattered light will diminish to nearly zero in the direction of the electric vector. The effect of the aerogel is two fold; it makes light traversing through it visible, and it provides a polarization analyzer because of the scattering.

This effect may be used to provide a convenient technique to study the internal strain in this type of material. Shorter spacing between the beads is indicative of greater strain. By varying the direction of propagation, the strain axis can be located. Thus, the phenomenon offers both novelty and utility.

Quantitative studies of the intensity of scattered light as a function of angle were performed using the simplified light scattering apparatus[8] diagrammed in Figure 2. The polarization state of the incoming light was fixed by the polarizer. The scattered light was collected by the slit, lens, and filter system diagramed in the figure and detected with a photomultiplier. The results were plotted as function of angle on a x-y plotter. Because of the extremely low index of refraction, no corrections in scattering angles or intensity were needed to compensate for the shape of the sample.

Measurements were made by aligning the polarizer at 45° to the scattering plane and recording the result with no analyzer, and repeated with the analyzer oriented

parallel and perpendicular to the scattering plane. Figure 3 shows the results for the Lund sample made with TMOS. The three curves labeled as I_{tot}, $I_\perp$ and $I_\parallel$ refer respectively to the total intensity of the scattered light, and the intensity for the analyzer set perpendicular and parallel to the scattering plane. The main features of these curves are that they have a minimum near 90° and rise symmetrically on either side. (Note that the I_{tot} curves are plotted to a different scale than $I_\parallel$ and $I_\perp$.)

The curves are very similar to the patterns produced by Rayleigh scattering. The intensity of light scattered from a small spherical particle of radius a is given by the well known result:[7].

$$I_\perp = \frac{a^2 x^4}{2r^2} \left| \frac{m^2-1}{m^2+2} \right|^2 I_o$$

$$I_\parallel = \frac{a^2 x4}{2r^2} \cos^2\theta \left| \frac{m^2-1}{m^2+2} \right|^2 I_o$$

where $x = 2\pi a/\lambda$, λ is the wavelength of light, r is the distance from the scatterer and m is the complex index of refraction of the particle, and I_o the intensity of the incoming beam.

To compare the prediction of the Rayleigh theory with the experimental results, the right hand side of the equations should be divided by the factor $\sin\theta$ to compensate for the increase in illuminated volume with angle incident on the detector system. The circles in Figure 3 are values predicted from a Rayleigh scattering model fit to the relative intensity of the curve. It can be seen that they fit the data rather well. Because of this fit, it is tempting to describe the scattering as originating from small particles or dipoles. However, the material hardly meets the requirements for independent scattering centers upon which the Rayleigh theory is based. The components of the aerogel are spaced much closer than a wavelength of light and be connected together to form a solid.

Figure 4 shows the results from scattering measurements of the sample prepared with TEOS. There is a sharp drop in the forward scattering with a distinct minimum near 15°. The perpendicular component still retains a minimum near 90° but the parallel component shows a rising value at 90° and has a much higher intensity relative to the perpendicular component than in Figure 3. This data obviously can not be fitted by the Rayleigh theory.

The two samples show such distinctly different scattering patterns it seems reasonable to ascribe to them different mechanisms of scattering. A model is tentatively proposed to explain the data. To understand the physical origin of the model, consider the following gedanken experiment. A large collection of silica particles that are small compared to the wavelength of light are randomly positioned in space at distances large compared to the wavelength of light. A light scattering measurement from this ensemble of particles would be properly described by Rayleigh scattering. If the particles are slowly brought together until the spacing becomes less than the wavelength of light but not coalesced, the light will respond to the average between the properties of the particles and empty space. However, with this spacing there may still be significant scattering. If the material is randomly distributed there will be no coherence effects. Because the particles are still separate and small they scatter light like

Rayleigh scatterers. As the particle spacing decreases further, the scattering becomes less and less. In this way, the origin of the scattering is viewed as a remaining vestige of Rayleigh Scattering.

If the particles are brought together as before, but this time with larger but random variation in the average density over lengths comparable to, or larger than a wavelength of light, a different type of scattering may occur. In this case, the scattering is dominated by the larger scale variations in the effective index of refraction. The Rayleigh-Gans theory may be used to describe scattering from isolated particles with larger sizes than allowed by Rayleigh theory. This theory is valid if the relative index of refraction variations are sufficiently small so that phase of the interfering waves that originate from various parts of the scattering body may be determined from the relative path lengths alone, i.e., assuming the medium and the scatterer have nearly the same index of refraction. This approach may be capable of predicting the results shown in Figure 4, but one may have to invoke some rather artificial assumptions about the shape and size of the postulated domains of scattering.

A better quantitative theory may be based on scattering from statistical fluctuations in the density of the material. The parameters in such a theory that were chosen to fit the experimental data could shed light on the characteristic domain size and variations in index of refraction. One such theory is currently being examined but so far the predictions are not consistent with the experimental results.

Whatever the most quantitatively accurate theory, it seems likely that medium scale variations in the density of the gel are a likely explanation of the scattering data portrayed in Figure 4. Based on the above analysis, it is tentatively concluded that the scattering portrayed in Figure 3 is due to remnants of Rayleigh scattering from a fine grained, but uniform structure. The results in Figure 4 are consistent with a fine grained structure containing small but significant density fluctuations. Our next experimental goal is to determine whether these suppositions regarding the structural details of the aerogels are caused by the differences in starting materials, or are due to the details of the preparation process. We plan to use light scattering as a tool to study the structure from the initial stages of sol formation through the gelling process and to the final product.

CONCLUSIONS

Based on these preliminary studies, light scattering appears to be a useful tool to investigate the structure and uniformity of aerogels. Observations of the light scattering properties arising from stress induced birefringence appear to provide valuable information regarding the residual stresses in the material. The usefulness of the study of the angular dependence of the intensity of scattered light appears to extend to investigations of the sol-gel precursors of the aerogel. If so, light scattering will be an important tool in studying and monitoring formation processes in transparent sols and gels.

ACKNOWLEDGEMENTS

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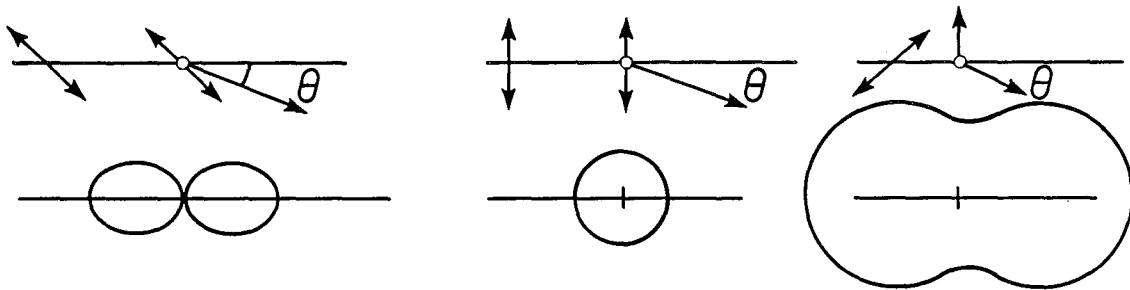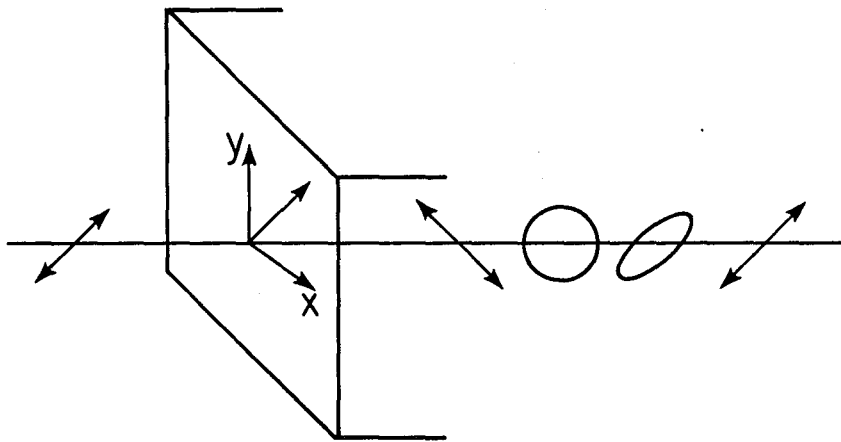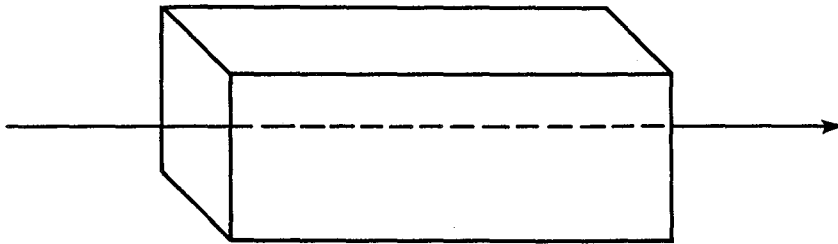
FIGURE CAPTIONS

Figure 1. Observation and interpretation of light scattering effects in aerogels. The upper figure illustrates the appearance of the scattered light as it passes through the sample. The center and lower figures illustrate the effects of birefringence and Rayleigh scattering respectively.

Figure 2. Diagram of the apparatus used for the angular scattering measurements.

Figure 3. Intensity vs. angle profiles of scattered light at 442 nanometers for aerogel samples from the University of Lund. The curves represent scattered light with a polarization parallel and perpendicular to the scattering plane and the total scattered light (the total is plotted to a different scale). The circles represent the angular dependence predicted by the Rayleigh theory with an arbitrary intensity scaling.

Figure 4. Intensity vs. angle profiles of scattered light at 442 nanometers for samples from Schmidt. The curves represent scattered light with a polarization parallel and perpendicular to the scattering plane and the total scattered light (the total is plotted to a different scale).
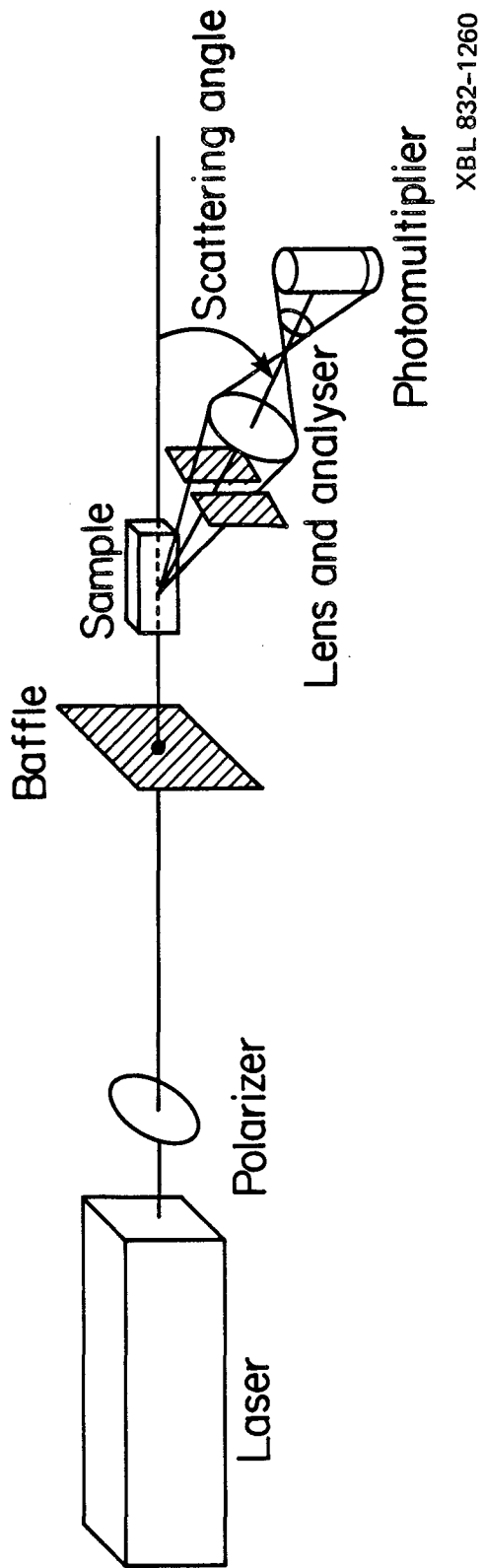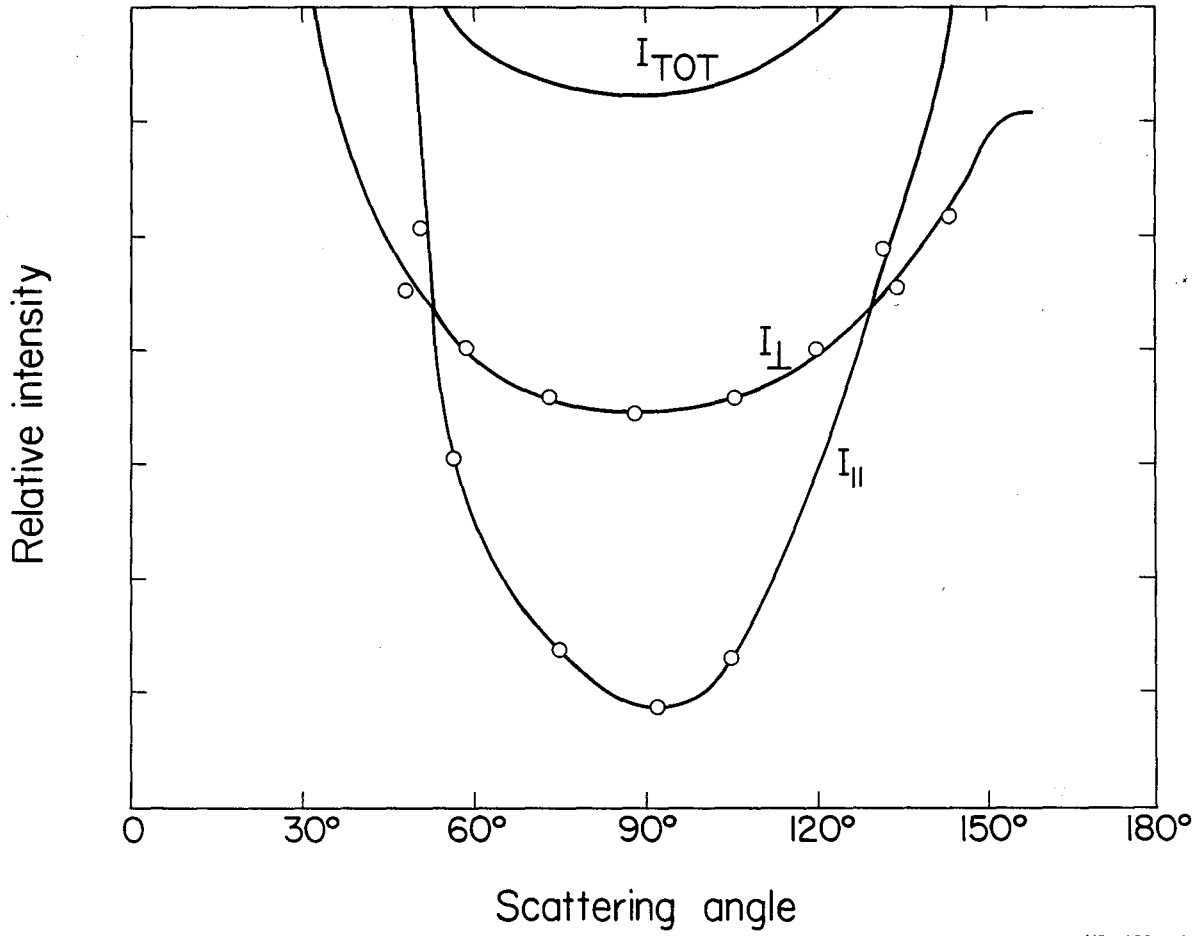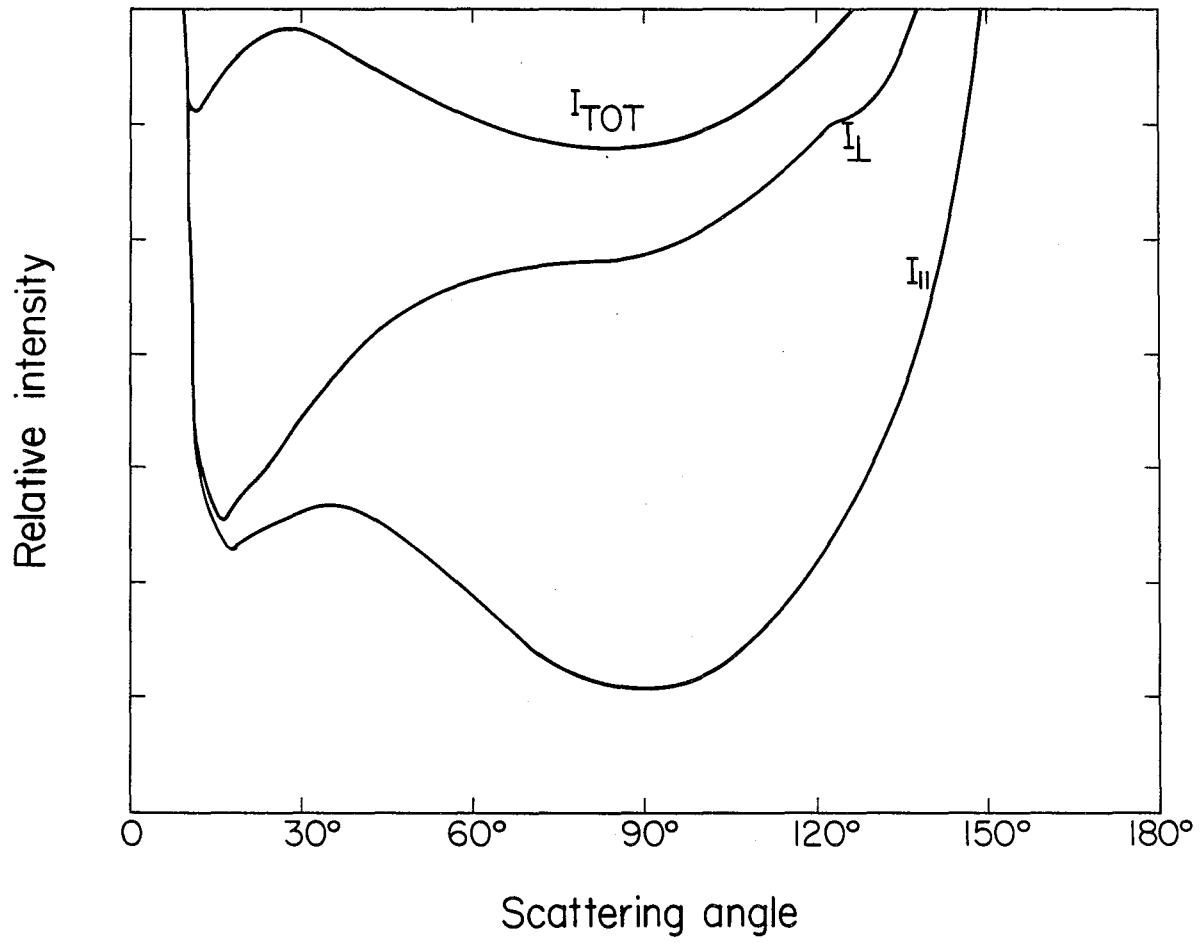
Figure 1

XBL 832-1229

Laser

Polarizer

Baffle

Sample

Scattering angle

Lens and analyser

Photomultiplier

XBL 832-1260

Figure 2

Figure 3

XBL 832-1231

Figure 4

XBL 832-1230