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TRANSPARENT SILICA AEROGELS FOR WINDOW INSULATION

Michael Rubin and Carl M. Lampert

June 1982

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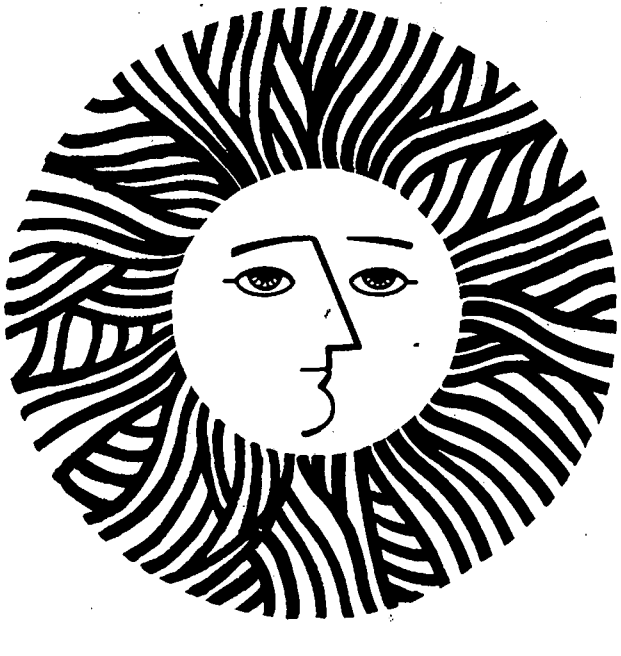

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ABSTRACT

Supercritically drying a colloidal gel of silica produces a porous material called an aerogel. These aerogels not only are excellent thermal insulators, but also can be highly transparent. We investigate the microstructure and optical properties of transparent silica aerogels and calculate the energy transfer through hypothetical aerogel windows.

The work described in this paper was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Buildings and Community Systems, Buildings Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Supercritically drying a colloidal gel of silica produces a porous material called an aerogel. These aerogels not only are excellent thermal insulators, but also can be highly transparent. We investigate the microstructure and optical properties of transparent silica aerogels, and calculate the energy transfer through hypothetical aerogel windows.

Introduction

Attempts to make a window that is both insulating and highly transparent have met with only limited success, partly because most glazing materials, such as glass, have a thermal conductivity much higher than that of air. A single pane of glass derives most of its insulating value from the boundary layers of slowly moving air. Adding panes of glass traps layers of air, lowering the overall thermal conductance of the window. However, radiation and convection limit the effectiveness of increasing the space between panes. Further dividing the air layer, either vertically or horizontally, reduces transmission of solar heat and daylight and deteriorates outdoor view.

Conventional insulating materials, having many internal reflecting surfaces, are opaque even when made from transparent substances. The insulating aerogels discussed in this paper, however, are transparent because they consist of silica particles much smaller than a wavelength

of visible light. Also, the thermal conductivity of aerogels can be lower than that of still air because they contain as much as 97% air by volume in pores smaller than the mean free path of air molecules.

Originally produced by Kistler [1,2], silica aerogels have been used as insulators and, because of their high porosity, as fillers, adsorbents, and catalytic substrates [3,4]. Aerogels composed of other inorganic oxides have also been produced [1,2,5]. Improvements to Kistler's method by Nicolaon and Teichner [6,7] and by Cantin et al. [8] led to the production of large blocks of clear, uniform aerogel [9]. Because such aerogel has an index of refraction lower than that of any other solid, they are used to replace pressurized gases in Cherenkov radiation detectors [8-14]. Recently, a prototype aerogel window was made by forming transparent aerogel between protective panes of glass [15].

In this paper, we examine the microstructure of transparent silica aerogels and measure their visible and infrared optical properties. We investigate the scattering process at short wavelengths and identify some of the impurities in aerogel from the infrared absorptions. We then calculate the solar and thermal properties of hypothetical windows incorporating aerogels.

Preparation and Microstructure

Schmitt gives a detailed description of the equipment and method used to prepare silica aerogel [15]. This method substitutes tetraethyl orthosilicate for the highly toxic tetramethyl orthosilicate used by Cantin [8] and Henning [9]. Briefly, the procedure is as follows: col-

loidal silica is prepared by hydrolizing tetraethyl orthosilicate in ethanol, catalyzed by HCl and HF, yielding monosilicic acid:

$$Si(CH_3CH_2O)_4 + 4H_2O \xrightarrow{\text{catalyst}} Si(OH)_4 + 4CH_3CH_2OH \ . \qquad (1)$$

The monosilicic acid condenses to produce colloidal silica,

$$n \cdot Si(OH)_4 \longrightarrow n \cdot SiO_2 + 2n \cdot H_2O \ . \qquad (2)$$

The ethanol is then removed by supercritical drying. Above the critical point of ethanol no liquid/vapor interface forms to create surface tension that would collapse the pores. The resulting aerogel has a low density, ρ, and high porosity (volume fraction of air), ϵ. The most transparent aerogel produced by the above process has $\rho = 0.141$ g/cm^3 and $\epsilon = 0.937$. Two serious drawbacks associated with these properties are fragility and a tendency to adsorb water.

We made transmission electron micrographs of aerogel using a Phillips 400 STEM, operating at 100 kV. Samples were microsectioned from the bulk material and coated with carbon to increase conductivity. The sample decomposes rapidly in the beam. Figure 1 shows approximately spherical particles having a mean diameter of 104 A. Although distinct, the spheres display some necking and interparticle bonding, similar to ceramic particles during the early stages of sintering. This picture supports Iler's hypothesis that the particles in the gel are joined by siloxane bonds to form an open network of short chains [4]. Based on measured density and particle size, the particles pack with a coordination number slightly less than 3 and have a center-to-center spacing of about 2 diameters. This estimate of particle separation agrees with the value of 98 A for pore radius obtained by nitrogen adsorption on similar

aerogels [16,17].

Optical Properties

The size of the individual particles easily satisfies the criterion for Rayleigh scattering in the visible. However, aerogel is far too densely packed to behave as a collection of independent particles. Nevertheless, the aerogel exhibits some of the characteristic features of Rayleigh scattering, as shown below.

An isolated spherical particle behaves as a Rayleigh scatterer if its radius, a, is much less than $\lambda/2\pi n$, where λ is the vacuum wavelength of incident and scattered light and n is the index of refraction of the particle. For incident light of unit intensity the scattered intensity from this particle is

$$I = \frac{8\pi^4 a^6}{r^2 \lambda^4} \left[\frac{n^2 - 1}{n^2 + 2}\right]^2 (1 + \cos^2\theta) , \tag{3}$$

where the scattering angle, θ, is measured from the forward beam direction, and r is the distance from the particle.

Integrating (3) over a large spherical surface gives the total cross section for scattering, and dividing by the geometrical cross section gives the dimensionless efficiency for scattering,

$$Q_s = \frac{1}{\pi a^2} \iint I(r,\theta) r^2 \sin\theta \, d\theta \, d\phi = \frac{8}{3} \left[\frac{2\pi a}{\lambda}\right]^4 \left[\frac{n^2 - 1}{n^2 + 2}\right]^2 . \tag{4}$$

To test the applicability of Rayleigh scattering, we measured the normal-normal spectral transmittance, $T_n(\lambda)$. We shielded the detector from scattered light reflected by the walls of the sample chamber,

estimating that the detector intercepts less than 0.5% of the forward-scattered light. Multiple scattering in optically thick samples will alter the angular distribution of scattered light given by (3). However, if little scattered light reenters the beam (4) still yields the correct result for the volumetric coefficient of scattering:

$$\sigma(\lambda) = N\pi a^2 Q_s(\lambda) = (1 - \epsilon)\,\frac{32a^3\pi^4}{\lambda^4}\left[\frac{n^2 - 1}{n^2 + 2}\right]^2 , \qquad (5)$$

where N is the number of particles per unit volume. Figure 2 shows that T_n increases rapidly with wavelength in the visible and generally decreases in the infrared, exhibiting a number of absorption bands. Silica absorbs only slightly in the visible and near-ultraviolet, so most of the attenuation of the beam results from scattering. No correction for surface reflection will be required in the calculations that follow because the index of refraction of an aerogel is small, between 1.01 and 1.1 depending on density [8-10].

Spectral scattering coefficients calculated from measurements of T_n in the visible agree moderately well with the λ^{-4} dependence specified by Rayleigh's theory. A least-squares fit of this function to the data for specimens of various thicknesses yields an average value of 124 A for the particle diameter. From the micrographs we obtained a mean particle size of 104 A. This discrepancy could be caused by groups of particles behaving as a single scattering unit.

Aerogel appears slightly yellow when viewed against a bright background, such as the sky or a white wall, because the blue light is scattered most efficiently. Against a dark background, the aerogel appears milky blue because the light is backscattered from the aerogel itself.

For a single scattering medium, (3) predicts symmetrical scattering about the plane of the sample. Measurements of the normal-hemispherical transmittance, T_h, are in rough agreement with this prediction. Due to multiple scattering and the poor condition of the integrating sphere, we probably underestimated the forward component. A larger forward component would undermine the hypothesis of Rayleigh scattering and favor scattering from large-scale inhomogeneities such as might be described by Rayleigh-Debye or similar theories.

The aerogel specimen of Figure 2 was exposed to moist air and as expected absorbed some water vapor. The breadth and position of the strong absorption at 3 μm indicates the presence of liquid water as well as SiOH. The absorption bands near 1.2, 1.4, and 1.9 μm are also seen in liquid water [18], and the 2.2 and 2.6 μm bands have been identified as combinations of O-H and Si-O fundamentals [19]. There is a small shoulder at 4.45 μm, which may be the first overtone of the Si-O stretching vibration. Beyond about 5 μm, both silica and water are very absorbing, and no band structure can be observed in the thick samples used.

Aerogel Windows

Aerogel must be protected from moisture, shock, and handling. Although it can be fractured quite easily, aerogel is surprisingly strong in compression. Thus it can be protected by rigid glass panes on either side and should be sealed at the edges. Schmitt has produced such a window by forming aerogel between panes of glass and drying through the edges. Even a large window can be dried by this method because the aerogel has a high permeability for ethanol under

supercritical conditions. Other methods for protecting the aerogel should be investigated.

The thickness of glass in an ordinary window is determined by the size of the unsupported area. The sandwich structure of an aerogel window undoubtedly will permit thinner glass based on structural requirements alone. However, tests are needed to determine the thickness of glass required to protect the aerogel from damage. This thickness may prove to be greater than that required for standard windows unless transparent spacers are used.

We have used the procedures of [20] together with the optical measurements of the previous section to calculate T_h for aerogel windows. Figure 3 shows the effect of aerogel thickness on T_h, averaged over the air-mass-2 solar spectrum. Aerogel by itself, despite scattering losses in the visible and O-H absorption in the infrared, has a higher transmittance than does window glass of equal thickness. The transmittance of an aerogel window made with low-iron glass and an aerogel thickness of 6 mm equals that of double glass. Doubling the thickness of aerogel reduces T_h to about 0.6, equal to triple glass. Increasing aerogel thickness reduces transmittance but also lowers the thermal conductance, U, of the aerogel window, while U for the double-glass window rapidly reaches a limiting value.

Using the measured thermal conductivity of aerogel [15], 0.019 $Wm^{-1}K^{-1}$, and the methods of [21], we can predict the heat transfer through an aerogel window. Figure 4 compares the thermal conductance of aerogel windows to that of ordinary double-glass windows as a function of the space between panes, D. At D = 0 the panes of glass touch,

effectively becoming a single sheet of glass having U only slightly lower than for a single glass pane. For low D, heat flows only by conduction and radiation. However, the radiative term in U is much larger for the double-glass window because the air is transparent to infrared radiation. As D increases further, convection heat transfer increases in the double-glass window but not in the aerogel window, so the overall conductance of the aerogel window continues to drop. Kistler [22-24] measured the thermal conductivity of aerogel at reduced pressures and in CO_2 and CCl_2F_2 atmospheres. He achieved the lowest value, 0.011 $Wm^{-1}K^{-1}$, with CCl_2F_2. For this value, an window with 20 mm of aerogel would have a thermal conductance less than 0.5 $Wm^{-2}K^{-1}$.

In principle, we could increase the thickness of the aerogel until reaching the desired conductance, but unless scattering can be reduced, the solar transmittance and optical quality degrade to unacceptable levels for thicknesses greater than a few centimeters. In any case, it may not be possible to make layers thicker than a few centimeters by the process described above; experiments with tall columns of aerogel produced defects at the base of the column. The optimum thickness will depend on climate, building type, and window orientation.

Conclusions

Silica aerogels consist of a bonded network of silica spheres having a coordination number of 3 or less. The closely packed silica particles scatter light dependently and cannot be treated as a collection of isolated Rayleigh scattering centers. Reducing silica particle size or improving homogeneity theoretically could increase the transmittance to nearly 100%. An aerogel window could have a substantially lower

thermal conductance than an ordinary multiple-glass window of equal transmittance. This conductance could be lowered still further by evacuating and sealing the aerogel in the window or by filling with a gas having a low thermal conductivity. Remaining problems include (1) lack of adequate protection and sealing in an architectural environment; (2) difficulty in producing uniform, monolithic specimens of window size; and (3) long processing time.

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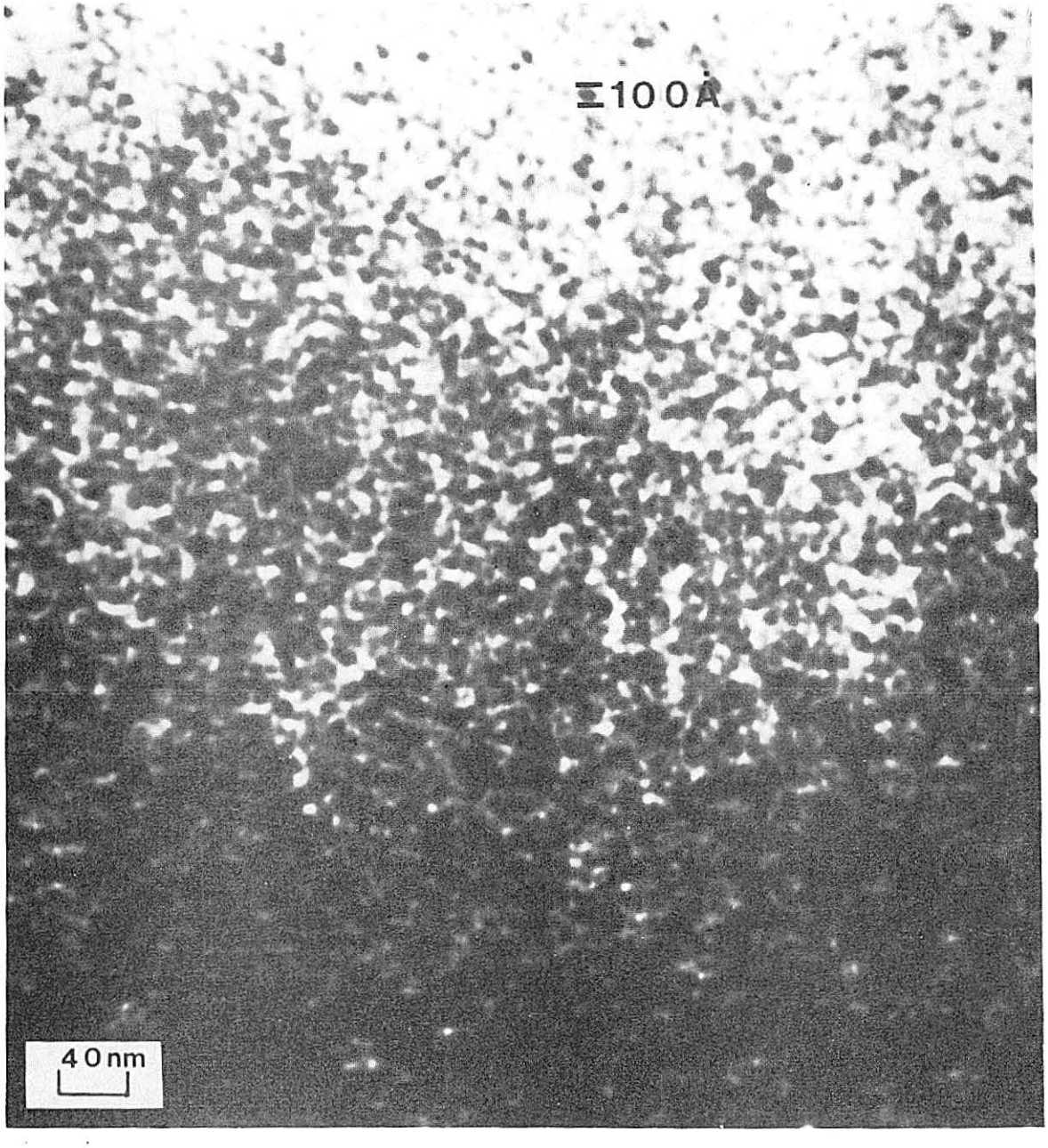

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Figure 1. Bright-field transmission electron micrograph of a wedge-shaped sample of silica aerogel (magnification 240,000x).

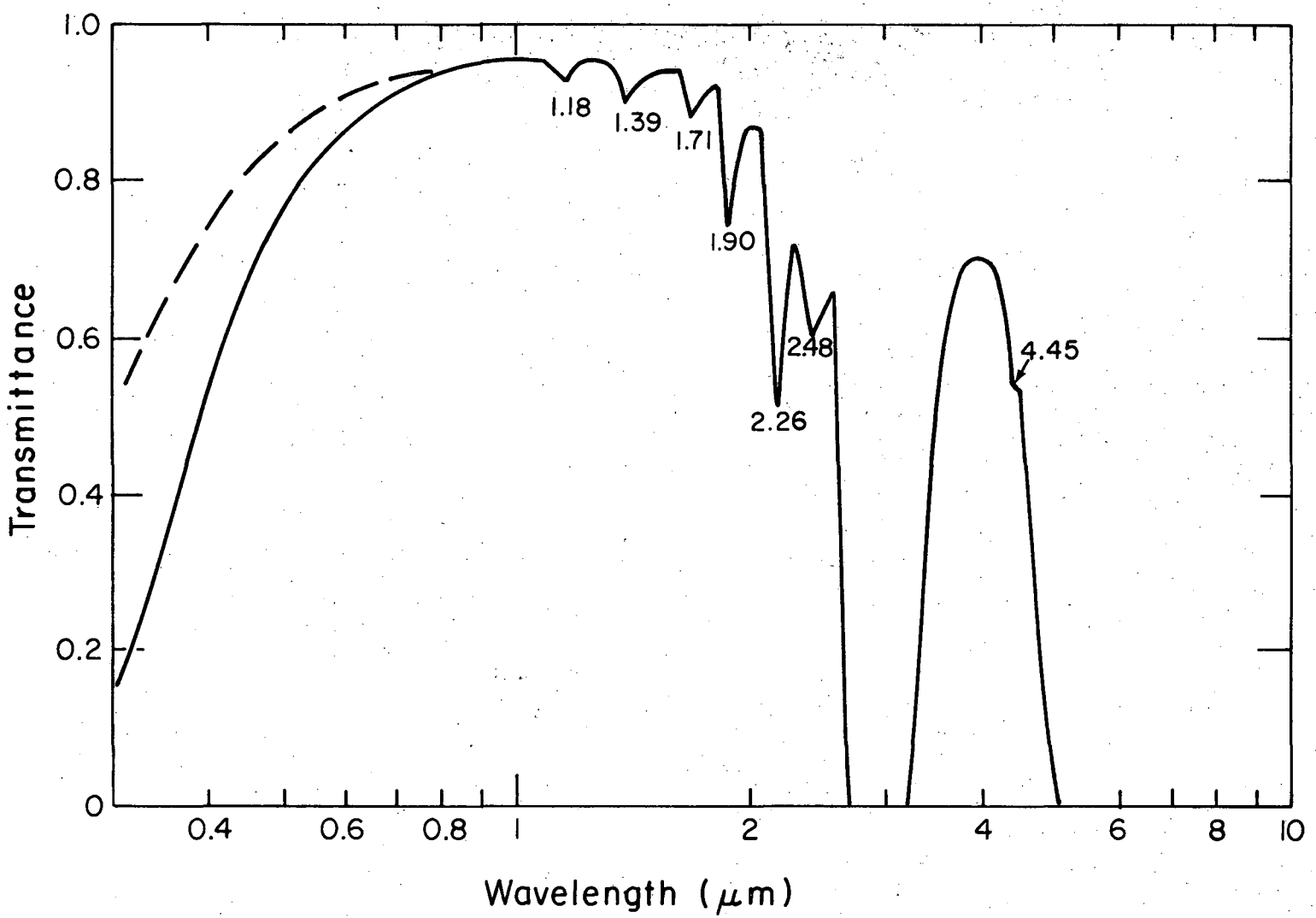

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Figure 2. Spectral normal-normal transmittance (solid line) and spectral normal-hemispherical transmittance (dashed line) of silica aerogel 4 mm thick.

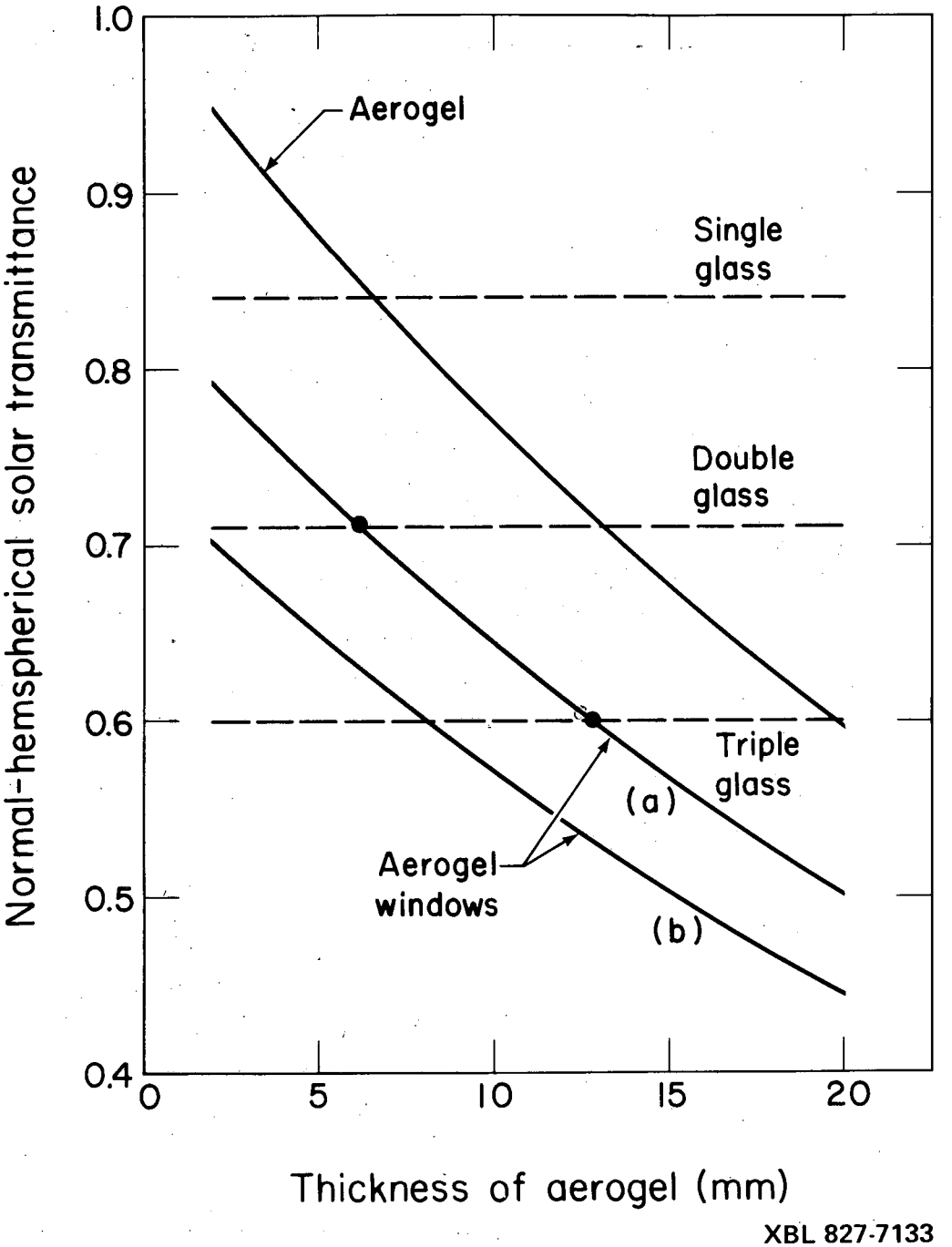

Figure 3. Calculated solar transmittance of aerogel windows vs. aerogel thickness compared to solar transmittance of conventional glass windows. All glass is 3-mm clear float glass except for the 3-mm low-iron glass of aerogel window (a).

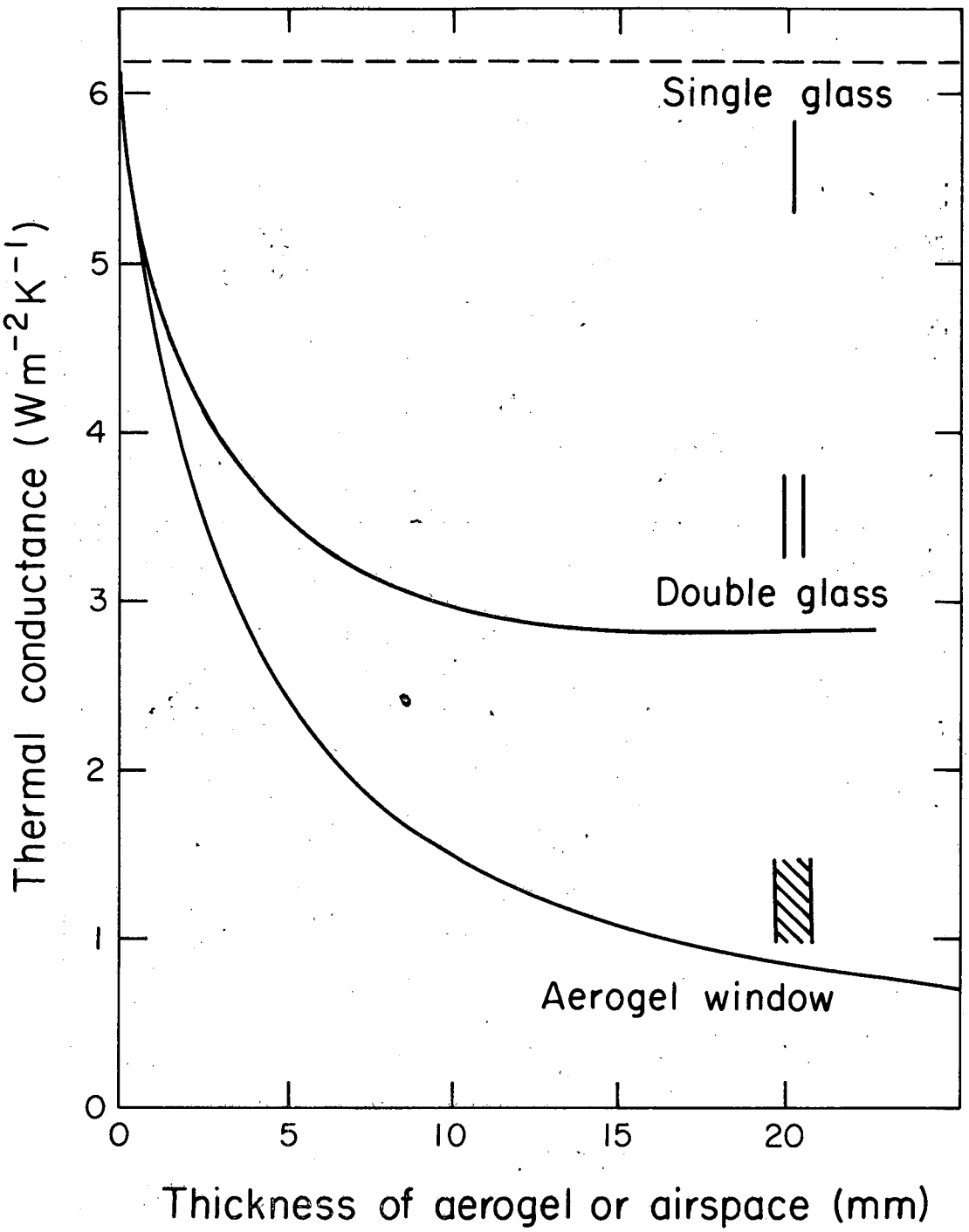

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Figure 4. Calculated thermal conductance of aerogel window and of conventional single- and double-glass windows vs. spacing between glass panes.

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