field dependent and appears to characterize an equilibrium state. Energy considerations ($\mu_{\rm cl}H_s \sim kT$) imply that populations of at least ~ 10^5 spins cooperatively respond to the presence of a weak magnetic field, and in this sense there are long-range correlations. The small value of H_s suggests that dipolar fields play an important role in this cooperative response.

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Intrinsic-Defect Photoluminescence in Amorphous SiO_2

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The first observation of photoluminescence (PL) originating from intrinsic defects in annealed and neutron-irradiated amorphous (a-)SiO_2 is reported. The PL is compared with that for a-As_2S_3. The PL spectra scale with energy band gap and the temperature dependence of the PL quantum efficiencies scale with glass transition temperature. This strongly suggests that defects in a-SiO_2 and semiconducting chalcogenide glasses are similar.

Defects in amorphous (a-)SiO_2 are thought to give rise to deleterious optical and electronic effects.[1] Therefore, a better understanding of defects in this technologically prominent material is important. Present models[2-4] for defects in chalcogenide glasses have been successful in explaining Fermi-level pinning in the diamagnetic ground state and a wide variety of excited-state properties in narrow–band-gap chalcogenide glasses (such as As_2S_3 and As_2Se_3). In particular, photoluminescence (PL) was instrumental in the development of the models because the large Stokes shift demonstrated the strong electron-phonon coupling at the defects. The valence-alternation model[4] of Kastner, Adler, and Fritzsche (KAF) which is based on chemical bonding in glasses predicts that oxide glasses should have defects similar to those found in sulfides, selenides, and tellurides. In addition, Mott[5] proposed that the model[3] of charged dangling bonds might apply to SiO_2.

Recently, Lucovsky showed[6] that a valence-alternation pair (VAP, threefold-coordinated and onefold-coordinated oxygen) can account for intrinsic-defect infrared absorption and Raman scattering in a-SiO_2. Utilizing transport results,[6] he further argued that VAP's must be close together spatially (intimate pairs). However, the extension of the KAF model to oxide glasses has not yet been universally accepted since a major consequence of VAP's, intrinsic photoluminescence, had not been observed in oxide glasses. Demonstrating that the important defects in a-SiO_2 are similar to those in narrower gap glasses would establish a-SiO_2 as a member of the chalcogenide glass family.

In this Letter we report the first observation of intrinsic photoluminescence in a-SiO_2. Although some features of the PL are different from those in sulfide and selenide glasses, these differences are quantitative rather than qualitative. Indeed, we find a remarkable scaling in the PL spectra, photoluminescence excitation (PLE) spectra, and even the temperature dependence of the PL quantum efficiences of a-SiO_2 and narrower–band-gap glasses. This strongly suggests that the luminescence centers in a-SiO_2 are similar to those in narrower–band-gap chalcogenide glasses. Establishment of this link will help in the understanding of the PL mechanism in *all* the glasses.

Polished samples of pure fused silica (Suprasil and Suprasil W)[7] were cooled on the tip of a liquid He cold finger. The sample chamber was evacuated to 10^{-8} Torr using a completely oil-free pumping system. A gold (0.7% Fe)-Chromel thermocouple soldered directly to the sample showed that radiational heating limited the temperature of the sample to $T \geqslant 15$ K. The PL was excited with light from a modified[8] Hinteregger hydrogen discharge lamp and 0.3-m vacuum monochromator. Excitation was continuous. LiF windows isolated the sample chamber from the excitation monochromator and from the PL detection system. The detection system consisted of a 0.25-m grating monochromator and photomultiplier tube.

The luminescence and excitation spectra[9] of Suprasil are displayed in Fig. 1. The spectra for Suprasil W are identical to those for Suprasil. The results after neutron irradiation ($\sim 10^{19}$ cm^{-2} fast neutrons) are also shown in Fig. 1. It is clear that the major effect of the irradiation is to increase the PL intensity by a factor ~20. After neutron damage, the linewidth of the PL is narrower and is shifted slightly to higher energy. The PL is probably not composed of two unresolved peaks since the PL does not change as the excitation energy is varied.[10] In addition, a shoulder appears on the low-energy side of the PLE spectrum.

The PLE peak is at 7.6 eV where an absorption band (the E band) has been observed in both annealed glass[11] and neutron-damaged glass.[12] The 7.6 eV absorption band grows from an absorption coefficient $\alpha \sim 10$ cm^{-1} before neutron irradiation, to $\alpha \gtrsim 100$ cm^{-1} after irradiation. Thus, one can safely assume that in the damaged glass, all incident photons are absorbed in the sample. The quantum efficiency η of the PL was determined by replacing the sample with sodium salicylate[13] ($\eta \sim 1$). In this way, one finds $\eta \sim 10^{-3}$ for the irradiated material. In the undamaged glass, α may be too small for all photons to be absorbed

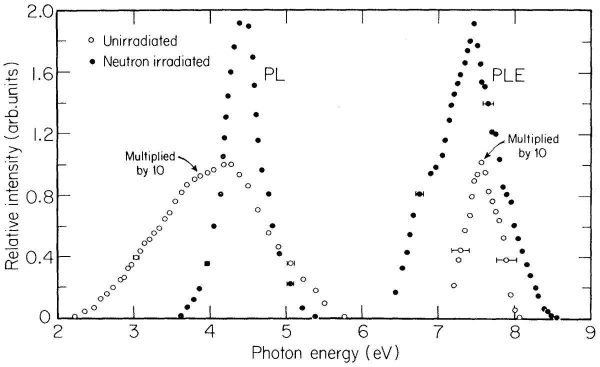

FIG. 1. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of unirradiated (open circles) and neutron-irradiated (solid circles) Suprasil at 15 K. Excitation energy of 7.6 eV was used for measuring the PL spectra. Instrument resolution is given by the horizontal bars.

in our 3-mm sample. In that case, one can only place a limit $\eta \gtrsim 10^{-4}$.

Since Suprasil and Suprasil W have less than $\sim 10^{15}$ cm^{-3} metal impurities[14] whereas the neutron-induced absorption coefficient corresponds to $\gtrsim 10^{18}$ cm^{-3} electrons, the PL and absorption at 7.6 eV is not associated with metal impurities. Since Suprasil contains[14] $\sim 10^{19}$ cm^{-3} OH and Suprasil W contains $\sim 10^{16}$ cm^{-3} OH, whereas the PL quantum efficiencies for these two materials are identical, the PL is not associated with OH. The only impurities which have not been excluded are halogens (present[14] in both glasses at levels of $\sim 10^{18}$ cm^{-3}). On the other hand, because of the scaling with narrower–band-gap glasses discussed below, it is clear that the luminescence is intrinsic.

The scaling with energy band gap of the PL and PLE peak energies of a-SiO$_2$ and a typical chalcogenide glass is clearly demonstrated in Fig. 2. Plotted in the figure are the PL and PLE spectra[15] as well as the absorption spectra[11,16] for unirradiated a-SiO$_2$ and a-As$_2$S$_3$. Photon energy has been normalized to the energy at which $\alpha = 10^4$ cm^{-1}, a rough measure of the band gap. The large Stokes shift of half the band gap observed in most chalcogenide glasses is thought to arise from strong electron-phonon coupling. This same coupling is required to explain the negative effective correlation energy[2] at the defects. The Stokes shift is usually[15] explained with the following simplified model. The total energies of the ground (E_g) and excited (E_e) states of the defect are given by

$$E_g(q) = A_g q^2, \qquad E_e(q) = E^* + A_e q^2 - Bq, \tag{1}$$

where q is a generalized configurational coordinate B, is the electron-phonon coupling strength and A_g (A_e) determines the magnitude of the elastic energy in the ground (excited) state. E^* is the zero-phonon transition energy. The Stokes shift is then given by

$$W = B^2(A_e + A_g)/4A_e^2. \tag{2}$$

A_g and A_e are expected to scale with bond strength since they are proportional to bond-stretching force constants. B should also scale with bond strength since the very large electron-phonon coupling arises from bond rearrangement. Thus, one expects the Stokes shift to scale with bond strength if the luminescence centers in the various glasses are similar. In chalcogenide glasses, the energy band gap also scales[17] with bond strength. Therefore, the scaling of the Stokes shift with band gap seen in Fig. 2 suggests that the PL mechanism in a-SiO$_2$ is similar to that in semiconducting chalcogenide glasses.

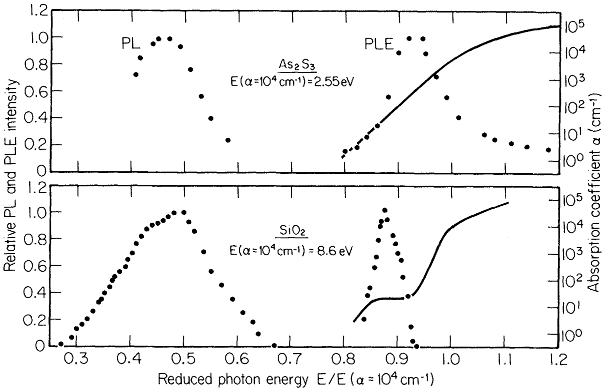

FIG. 2. Scaled PL, PLE, and absorption spectra for unirradiated Suprasil and a-As$_2$S$_3$. Photon energy is normalized to the energy at which the absorption coefficient $\alpha = 10^4$ cm^{-1}. PL and PLE spectra for a-As$_2$S$_3$ are from Ref. 15, absorption spectrum for a-As$_2$S$_3$ from Ref. 16 and for a-SiO$_2$ from Ref. 11.

The simple model of Eqs. (1) and (2) predicts a relationship between the Stokes shift and the PL and PLE linewidths. Relating A_g and A_e to phonon frequencies, linewidths for the PL and PLE are found to be

$$\sigma_{\rm PLE} = [2\hbar\Omega_g W A_g^2 / A_e(A_g + A_e)]^{1/2}, \qquad \sigma_{\rm PL} = (A_g/A_e)^{5/4}\sigma_{\rm PLE}, \tag{3}$$

where Ω_g is the vibrational frequency of the ground state. The ratio of the measured linewidths gives $A_g/A_e \sim 2$ and so indicates that the bonding is stronger in the ground state than in the excited state. Using Eq. (3), the ground-state phonon frequency is found to be ~ 1100 cm^{-1} which is typical for optical phonons in a-SiO$_2$. It has usually been assumed[15] that $A_e = A_g$ for chalcogenide glasses. However, since the PLE in semiconducting chalcogenide glasses is degenerate with continuum excitations, $\sigma_{\rm PLE}$ cannot be accurately measured. It may be, therefore, that these materials, like a-SiO$_2$, have different values of A_e and A_g. It is not understood why the PL linewidth narrows after neutron irradiation. However, it would not be too surprising if the values of A_g and A_e for neutron-induced defects were different from those in the annealed glass.

The scaling apparent in Fig. 2 encourages one to compare the nonradiative process in a-As_2S_3 with that in a-SiO_2. In most chalcogenide glasses,[15, 18] the PL quantum efficiency decreases exponentially with increasing temperature as

$$\eta = \eta_0 \exp(-T/T_1), \tag{4}$$

where η_0 and T_1 are constants. Assuming the nonradiative process is activated, the nonradiative rate ν_{nr} is given by

$$\nu_{nr} = \nu_0 e^{-\Delta/kT}, \tag{5}$$

where[19] $\nu_0 \sim 10^{13}$ Hz and Δ is an activation energy. If a single radiative rate ν_r is assumed, then the PL intensity is

$$I_{PL} = \int [1 + (\nu_0/\nu_r) e^{-\Delta/kT}]^{-1} g(\Delta)\, d\Delta. \tag{6}$$

Since the term multiplying $g(\Delta)\,d\Delta$ is approximately a step function (because $\nu_0 \gg \nu_r$), the temperature dependence of Eq. (4) indicates that

$$g(\Delta) = (kT_0)^{-1} \exp(-\Delta/kT_0), \tag{7}$$

where T_0 is proportional to T_1. It was recently shown[20] that the distribution in activation energies given by Eq. (7) also explains the temperature dependence of the time decay of the PL in a-As_2S_3. Since the distribution $g(\Delta)$ is maximum at $\Delta = 0$, it suggests that most centers are nonradiative. Only those centers with $\Delta > 0$ will be radiative even at zero temperature. We suggest that the spread (kT_0) of activation energies is probably a result of disorder. Since the disorder is frozen in at the glass transition, one expects T_0 to be the same order of magnitude as the glass transition temperature T_g. This was found to be the case[20] in a-As_2S_2.

If the nonradiative processes are the same in a-SiO_2 as in a-As_2S_3, then one would expect the temperature dependence of the PL intensity to be the same for the two materials when temperature is normalized to T_g. In Fig. 3 the temperature dependence[15] is shown for Suprasil and a-As_2S_3. The glass transition temperatures used are published[21] values, 1350 K for a-SiO_2 and 500 K for a-As_2S_3. Thus, *with no arbitrary parameters*, the temperature dependence of the PL is found to scale perfectly. The value of T_1 found[15] for a-Se also scales with its $T_g \sim 330$ K. Clearly the neutron-irradiated sample has a T_1 much larger than that of the annealed glass. This is expected since the neutron-damaged system is much more disordered.

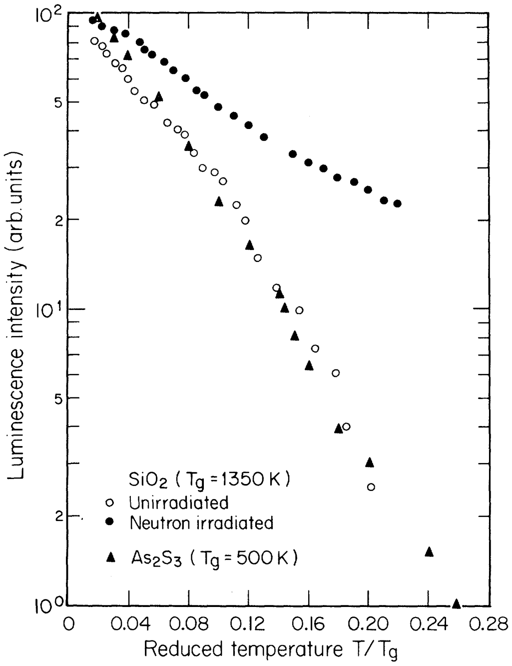

FIG. 3. Scaled temperature dependence of PL intensity for unirradiated (open circles) and irradiated (solid circles) Suprasil and a-As_2S_3 (triangles). Temperature is normalized to the glass transition temperature. The PL was excited by 7.6-eV light. a-As_2S_3 data are from Ref. 15.

The sacling of the PL and PLE peaks with energy band gap and of the temperature dependence of the PL quantum efficiencies with T_g is strong evidence that the PL centers in a-SiO_2 are similar to those in a-As_2S_3. Generally, a-SiO_2 has been assumed to be very different from the semiconducting chalcogenide glasses because its band gap is much larger. However, the scaling shows that despite the large difference of the band gaps, the PL centers are similar. Assuming the PL centers are the same, the results presented give clear evidence that the PL centers in all the glasses arise from intrinsic defects. Previously, the strongest evidence that PL centers are defects was the decrease at high photon energy of the PLE proportional to the inverse of the absorption coefficient.[15] For a-SiO_2 the evidence is much clearer. The PLE is a narrow band, is well separated from the bulk absorption, and is enhanced by neutron irradiation. Furthermore, the luminescence data give more detailed information about the defects. Since the PLE band is separate from the continuum, it cannot be explained by *ionization* of a charged center.[15] The excitation must be local: An electron or hole is promoted to an excited state of a charged or neutral[22] center. The scaling of the temperature dependence over a factor ~4 in T_g (a-Se to a-SiO_2)

implies that the distribution $g(\Delta)$ is a general property of the glasses and that the spread of activation energies is a result of disorder. Finally, the results confirm the prediction of the valence-alternation model that defects similar to those in semiconducting chalcogenide glasses would also be present in oxides.

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Superconductivity in Irradiated Palladium

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Pure palladium films, evaporated between 4.2 and 300 K, can be transformed into superconductors by means of irradiation at low temperatures with He^+ ions. The maximum transition temperature obtained is 3.2 K. It is shown that the presence of a special kind of defects produced during the irradiation is a necessary precondition for the occurrence of superconductivity.

Palladium represents the most strongly exchange-enhanced material among the pure metals. It has a Stoner enhancement factor[1] of $1/[1 - UN(0)] \approx 10$, where U is the exchange parameter and $N(0)$ the electron density of states at the Fermi surface. The occurrence of such strong spin fluctuations is thought to be the reason for the absence of superconductivity[1] above 2 mK.[2] Theoretical calculations[3-5] show that Pd without spin fluctuations should be a superconductor. The calculated values for the corresponding superconducting transition temperatures, T_c, vary between 0.3 (Ref. 5) and 7 K (Ref. 3).

In the present paper it will be shown that Pd