SILICON NANOPARTICLES: SOURCE OF EXTENDED RED EMISSION?

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ABSTRACT

We have reviewed the characteristics of the extended red emission (ERE) as observed in many dusty astronomical environments, in particular, the diffuse interstellar medium of the Galaxy. The spectral nature and the photon conversion efficiency of the ERE identify the underlying process as highly efficient photoluminescence by an abundant component of interstellar dust. We have compared the photoluminescence properties of a variety of carbon- and silicon-based materials proposed as sources for the ERE with the observationally established constraints. We found that silicon nanoparticles provide the best match to the spectrum and to the efficiency requirement of the ERE. If present in interstellar space with an abundance sufficient to explain the intensity of the ERE, silicon nanoparticles will also contribute to the interstellar 9.7 μm Si—O stretch feature in absorption, to the near- and mid-IR nonequilibrium thermal background radiation, and to the continuum extinction in the near- and far-UV. About 36% of the interstellar silicon that is depleted into the dust phase would be needed in the form of silicon nanoparticles, amounting to less than 5% of the interstellar dust mass. We propose that silicon nanoparticles form through the nucleation of SiO in oxygen-rich stellar mass outflows and that they represent an important small-grain component of the interstellar dust spectrum.

Subject headings: dust, extinction — radiation mechanisms: nonthermal

1. INTRODUCTION

The recent detection of extended red emission (ERE) in the diffuse interstellar medium (ISM) of the Galaxy by Gordon, Witt, & Friedmann (1998) and the spectroscopic confirmation of its luminescence-band nature by Szomoru & Guhathakurta (1998) fundamentally changed our perception of the ERE as an interstellar process in several ways. First, the ERE is no longer seen as a phenomenon limited to localized special environments, such as reflection and planetary nebulae. As a Galaxy-wide process, its characteristics must now be imposed as an additional observational constraint on models for interstellar dust in the diffuse ISM. Second, by correlating the ERE intensity with the H i column density in the diffuse ISM at intermediate and high Galactic latitudes, and thus with the dust column density, it has become possible to determine the efficiency with which UV/visible photons of the interstellar radiation field, absorbed by interstellar dust, are converted into ERE photons. An ERE photon conversion efficiency of 10% ± 3% (Gordon et al. 1998; Szomoru & Guhathakurta 1998) was derived by assuming that the ERE agent consumes all photons absorbed by dust in the 91.2–550 nm wavelength range. To the extent that we know of the existence of other dust components that are not expected to contribute to the ERE, this assumption is false. The ERE agent, most likely, is not responsible for the absorption of all absorbed UV/visible photons. Thus, the derived efficiency is only a lower limit to the true, intrinsic, efficiency of the photoluminescence (PL) process seen as ERE. However, even if the intrinsic efficiency is as high as 50%, a reasonable upper limit for naturally occurring PL, the ERE agent still needs to absorb about 20% of all absorbed UV/visible photons in the diffuse ISM. This can only happen if the ERE agent consists of cosmically abundant material that is capable of highly efficient PL. It appears that only carbon- or silicon-based materials fit these criteria. In this Letter, we present the case for silicon nanoparticles being the component of the ISM that is responsible for the ERE.

2. CHARACTERISTICS OF THE ERE AND THE IMPLIED PROPERTIES OF ITS CARRIER

We briefly summarize the observed characteristics of the ERE and refer to the original sources for the details of the observations:

1. ERE manifests itself through a broad, featureless emission band of 60 < FWHM < 100 nm, with a peak appearing in the general wavelength range 610 < λp < 820 nm. The presence of ERE has been established spectroscopically in many dusty astronomical environments, e.g., the diffuse ISM (Szomoru & Guhathakurta 1998), reflection nebulae (Witt & Boroson 1990), planetary nebulae (Furton & Witt 1990, 1992), the Orion Nebula (Perrin & Sivan 1992), the high-b dark nebula L1780 (Chlewicki & Laureijs 1987; Mattila 1979), and the starburst galaxy M82 (Perrin, Darbon, & Sivan 1995). The ERE was first recognized clearly in the peculiar reflection nebula called the Red Rectangle by Schmidt, Cohen, & Margon (1980).

2. The ERE peak wavelength varies from one environment to another, and even within a given object, the peak shifts with distance from the illuminating source. The density and hardness of the incident radiation field appear to be the determining factors. The shortest peak wavelength is seen for the ERE in the diffuse ISM (∼610 nm) in the case of the relatively weak interstellar radiation field; the longest (∼820 nm) is found on the Orion Nebula bar adjacent to the Trapezium stars, where the radiation density is several orders of magnitude higher.

3. The photon conversion efficiency of the ERE, calculated on the basis that all photons absorbed by dust in the 91.2–550 nm range
The absorption of one UV/VIS photon leading to the emission of at most one ERE photon, has been determined to be near 10% ± 3% in the diffuse ISM (Gordon et al. 1998; Sizomor & Guhathakurta 1998), and it is at least this high in the Red Rectangle and not much lower in the Orion Nebula and a number of reflection nebulae. This implies that the ERE agent must absorb a significant fraction of the UV/VIS photons in the diffuse ISM and, simultaneously, possess an exceedingly high intrinsic PL efficiency, >10%. Since only part of the energy of an absorbed photon is converted into ERE, the energy conversion efficiency of the ERE agent is only about 4% ± 1%.

4. No ERE is seen shortward of the wavelength of 540 nm. A sensitive search for PL by dust in several reflection nebulae in the 400–500 nm range, carried out by Rush & Witt (1975), produced a null result. While found in many dusty environments, ERE is essentially absent in some, e.g., the Merope reflection nebula. The absence of ERE in an otherwise normal dusty interstellar environment has not been explained.

5. Among planetary nebulae, ERE was detected only in objects currently thought to be carbon rich, in the sense that C/O > 1 (Furton & Witt 1992). This was thought to be a strong argument in favor of the carbonaceous nature of the ERE carrier. This argument can no longer be maintained in light of the Infrared Space Observatory (ISO) observations of C-rich planetary (Waters et al. 1998a), which show the presence of strong spectral features of crystalline silicates in the mid-IR wavelength region. In these planetary, the oxygen-rich dust appears to be present in the outer parts of the envelopes where material resides from earlier mass-loss episodes. In NGC 7027, the only planetary in which spatially resolved ERE observations have been made, the ERE is found most strongly enhanced in the outermost envelopes (Furton & Witt 1990). In a similar way, ISO observations of the Red Rectangle by Waters et al. (1998b), showing the presence of oxygen-rich dust there as well, have greatly diminished the argument that the currently C-rich stellar mass outflow implies a carbonaceous nature for the ERE carrier in that object. One important aspect of the ERE in planetary nebulae is that the ERE band is seen superposed on the atomic continuum only; i.e., there is no evidence of a scattered light component. This would indicate that the dust particles in these objects are sufficiently small to be in the Rayleigh limit, where scattering becomes inefficient. ERE observations in planetary nebulae therefore imply that the origin of ERE is connected with very small grains.

6. In clumpy reflection nebulae (e.g., NGC 2023 and NGC 7023), ERE appears strongly enhanced in filamentary structures, coincident with surfaces of clumps seen in projection (Witt & Malin 1989). It was suggested that the ERE in these filaments becomes activated by the exposure of carbonaceous materials to warm atomic hydrogen and UV radiation in molecular hydrogen photodissociation zones (Furton & Witt 1993). However, high spatial resolution observations of H$_2$ vibrational fluorescence in NGC 2023 by Field et al. (1994, 1998) show that the correlation between ERE and H$_2$ structures is not strong. In addition to some clearly correlated structures, there are ERE filaments without corresponding H$_2$ filaments. This lack of correlation is not explainable by optical depth effects, as is the also observed case of H$_2$ filaments without ERE filaments. An analogous result was found when high-resolution H$_2$ observations of NGC 7023 were compared with ERE structures in that nebula (Lemaire et al. 1996). Frequently, interstellar environments exhibiting ERE also emit the unidentified infrared (UIR) bands attributed to large aromatic molecules, e.g., polycyclic aromatic hydrocarbons (PAHs). Often (e.g., in NGC 2023, 7023, 7027, and the Orion Nebula) both emission phenomena are seen in photodissociation zones, but their intensities are poorly correlated. In particular, in the Orion bar, where both ERE and UIR bands have been observed, there is no correlation between their respective intensities (Perrin & Sivan 1992). There is therefore little support to connect the emitters of the ERE and of the UIR bands, except that they both occupy the same general environments and that they respond to stellar UV illumination.

3. PROBLEMS WITH PREVIOUSLY PROPOSED ERE CANDIDATES

Published models for materials causing the ERE have relied on carbon-based substances, either solid-state carbonaceous solids or carbon-based molecules. The former include hydrogenated amorphous carbon (HAC) (Duley 1985), a quenched carbonaceous composite (QCC) (Sakata et al. 1992), and coal (Papoular et al. 1996); the latter category includes PAH molecules (D’Hendecourt et al. 1986) and C$_6$O (Webster 1993). A common problem is the failure to match the observed ERE spectra with the required PL efficiency.

The most widely advocated model involves HAC (Duley, Searah, & Williams 1997; Furton & Witt 1993); it relies on amorphous carbon, which is already a component of several interstellar dust models. The HAC PL peak varies in wavelength in response to the conditions of production and subsequent treatment; the absorption spectrum in the blue and UV is smooth and does not introduce troublesome absorption features unobserved in the ISM. It also explains the 3.4 $\mu$m C–H stretch feature observed in absorption along lines of sight in the diffuse ISM. The QCC model is similar in all of these respects. Recent detailed laboratory studies of HAC (Robertson 1996, Rusli, Robertson, & Amaratunga 1996, and references therein), however, have led to quantitative results that cast doubts on HAC as the ERE carrier. HAC is a highly efficient photoluminescing material when its band gap is large, near 4.4 eV. When illuminated by UV radiation, this HAC luminesces strongly in the blue region of the spectrum, which makes it unsuitable as an ERE analog. Narrowing the band gap, e.g., by dehydrogenation, reduces the PL efficiency of HAC exponentially, so that the HAC PL efficiency drops to a few 10$^{-5}$ of its maximum value when the band gap is small enough to yield PL emission in the wavelength region where ERE is observed. HAC’s principal problem, therefore, is its inability to meet the spectral characteristics and the efficiency of the ERE simultaneously.

The PAH model (D’Hendecourt et al. 1986) was a competing early suggestion, which attributed the ERE in the Red Rectangle to luminescence by large PAH molecules. However, even a large PAH like the 13 ring hexabenzocoronene exhibits a sharply structured PL spectrum peaking near 500 nm wavelength, and smaller PAHs luminesce generally at still shorter wavelengths. To obtain a broad, unstructured band as observed in the ERE, D’Hendecourt et al. rely upon a poorly studied process of intramolecular vibrational energy randomization. The fact that ERE is seen with peaks only in the 610–820 nm wavelength range would require substantially larger PAHs than hexabenzocoronene, with a total absence of smaller PAHs. A further problem with all organic luminescing materials is that their absorption spectra are highly structured as well, which should lead to observable absorption bands in the blue and UV spectral regions of highly reddened stars, which so far remain...
undetected. On the other hand, the PAH model has had considerable success in explaining the near-IR emission bands at 3.3, 6.2, 7.7, 8.6, and 11.3 μm.

The C$_{60}$ model (Webster 1993) can produce reasonable spectral matches with the observed ERE, especially if mixtures of differently sized fullerenes were used, but its fatal weakness is the measured PL efficiency of 8.5 $\times$ 10^{-4} for the C$_{60}$ fluorescence (Kim et al. 1992). The ERE efficiency requirement is particularly difficult to match for any molecular/organic luminescent material that does not exhibit a broad continuous absorption spectrum covering the 90–550 nm spectral range. The ERE requires the presence of a material with a band gap near 2 eV, which naturally absorbs photons of higher energy and converts part of the absorbed energy of these photons into ERE photons with an efficiency of not less than 10% ± 3%.

4. SILICON NANOPARTICLES AS A POTENTIAL ERE SOURCE

In this section, we shall discuss the PL characteristics of silicon nanoparticles and how these meet the requirements posed by astronomical observations of ERE. In the next section, we will explore whether such particles can form under astrophysical conditions and whether cosmic abundances will permit the existence of sufficient numbers of particles of this type.

In order for materials to be efficient photoluminescent sources, two requirements must be met: the electronic excitation resulting from the absorption of a photon must be confined spatially, and possibilities for nonradiative recombinations must be minimized. In organic luminescent materials such as PAHs, the confining units are individual molecules, and photon yields can be as high as 99% in some instances (Krasovitskii & Bolotin 1988). In the case of HAC, small aromatic islands embedded in a sp$^3$-coordinated amorphous carbon matrix are the absorbing entities. The much higher band gap energy of the surrounding matrix confines the excited electrons to the aromatic islands, where the PL can then occur (Robertson 1992, 1996). The observation of ERE in planetary nebulae, which occurs in the absence of visible scattering, confirms that the luminescing particles are small compared with conventional interstellar grains.

Silicon nanoparticles, which consist of crystalline silicon cores of 1–3 nm diameter, surrounded by a SiO$_2$ mantle, are known to be remarkably efficient PL emitters in the 1.5–2.0 eV energy range (see, e.g., Wilson, Szajowski, & Brus 1993). The quantum confinement in such zero-dimensional crystallites is responsible both for shifting the band gap from a value near 1.1 eV in bulk crystalline silicon to values of 2.0 eV and above (Brus 1986, 1994; Delley & Steigmeier 1993; Delerue, Allan, & Lamoo 1993) and for greatly enhancing the PL efficiency (Efros & Prigodin 1993) to laboratory-measured values as high as 50% at temperatures around 50 K (Wilson et al. 1993). A series of recent investigations using size-selected silicon nanostructures (Schuppler et al. 1994, 1995; Ehrbrecht et al. 1997; Lockwood, Lu, & Baribeau 1996) has established the correlation between the structure size and the wavelength of peak PL emission. According to these studies, silicon nanoparticles in the 1.5–5 nm diameter range luminesce strongly in the 600–850 nm wavelength range. The reported maximum PL efficiencies occurred for sizes near 1.6 nm, corresponding to a 664 nm wavelength, for two-dimensional silicon nanostructures (Lockwood et al. 1996) and for sizes near 3.9 nm, corresponding to 726 nm wavelength, for zero-dimensional nanoparticles (Ehrbrecht et al. 1997), and both studies reported a rapid drop in PL efficiency when going to both larger and smaller size parameters.

We conclude from the published experimental results that silicon nanoparticles luminesce extremely efficiently (up to 50%) in the 600–850 nm range when they occur in a very limited size range from 1.5 to 5.0 nm and not otherwise. The width of the PL band depends on the width of the size distribution present, and the wavelength of maximum PL intensity is determined by the dominant size within the distribution. The published PL spectra of silicon nanoparticles match those observed in ERE sources extremely closely (see Fig. 1). Environmental effects, such as vaporization of the smaller particles in intense radiation fields, will lead to a gradual shift of maximum PL toward longer wavelength, as observed. On the other hand, the diffuse ISM with the lowest radiation densities will allow the existence of the smaller particles as well, with a resultant maximum efficiency and a very broad PL spectrum.

5. SILICON NANOPARTICLES AS A COMPONENT OF INTERSTELLAR DUST

Any interstellar dust component candidate must provide positive answers to two fundamental questions. Can the grains form naturally in an astronomical environment? Is the required total grain mass consistent with the cosmic elemental abundances of the constituents?

Silicon monoxide (SiO) is one of the most abundant and most strongly bonded molecules in the outflows from oxygen-rich stellar sources; virtually all silicon in the gas phase is initially locked up in this form (Gail & Sedlmayr 1986). The nucleation of silicates is thought to be precipitated by the initial formation of SiO clusters (Nuth 1996), a conclusion supported by laboratory evidence regarding the condensation of SiO (Nuth & Donn 1982), which show the condensate to contain elemental silicon plus silicon oxide SiO$_2$ with $x$ ~ 1.5. This can be understood by the fact that SiO$_2$ is the energetically preferred form of silicon oxide in the solid phase, while SiO is preferred in the gas phase. The competition for additional oxygen atoms in the condensing cluster will leave half of the silicon atoms ultimately without a partner, if the change of state can complete itself. Since this condensation occurs in a high-temperature environment (~500–1000 K), we postulate that the resulting annealing of the condensing SiO clusters will lead to a separ-
ration of the elemental silicon into a core and the SiO into a mantle, to form the basic structure of silicon nanocrystals with oxygen passivation (Littau et al. 1993), in which the dangling bonds at the surface of the silicon core are connected to oxygen atoms in the SiO₂ mantle. As we will show, only 5% of the total dust mass needs to remain in the form of silicon nanoparticles; the overwhelming fraction of the condensing particles can therefore remain involved in the condensation of various silicates and metal oxides, as supported by astronomical observations. We conclude, therefore, that silicon nanoparticles are a product of the initial dust formation process occurring in one of several oxygen-rich outflow environments, e.g., M-type supergiants, WN stars, Type II supernovae, and asymptotic giant branch stars. In addition to producing the ERE, these silicon nanoparticles will be subject to temperature fluctuations, resulting from absorptions of individual UV photons, and thus contribute to the near- and mid-IR thermal background radiation received from the diffuse ISM. The temperature increases expected from the absorption of individual 10 eV photons (the absorption peak of the Si cores is near 125 nm) by Si nanoparticles in the 1.5–5 nm size range are 170±60 K (Purcell 1976). These are upper limits because part of the absorbed particles in the 1.5±5 nm size range are 170±60 K (Purcell absorption peak of the Si cores is near 125 nm) by Si nanoparticles. The absorption of individual UV photons (the absorption peak of the Si cores is near 125 nm) by Si nanoparticles in the 1.5–5 nm size range are 170±60 K (Purcell 1976). These are upper limits because part of the absorbed particles in the 1.5±5 nm size range are 170±60 K (Purcell absorption peak of the Si cores is near 125 nm) by Si nanoparticles.

We have examined the observed characteristics of the ERE, a photoluminescence phenomenon associated with interstellar dust and seen in a wide variety of astronomical environments as excess radiation in the 600–850 nm wavelength range. In the diffuse ISM, about 10% of absorbed UV/visible photons contribute to the ERE. The ERE carrier must be a cosmically abundant material exhibiting highly efficient photoluminescence properties. Silicon nanoparticles containing a few hundred silicon atoms each, surrounded by a SiO₂ shell, match the constraints regarding the spectrum and efficiency of the ERE. Interstellar silicon abundances easily suffice to provide the needed material quantities, and the nucleation of SiO in oxygen-rich stellar outflows provides a likely source for their formation. We suggest that silicon nanoparticles are an abundant component of the interstellar dust spectrum.

Note added in manuscript.—After submission of this Letter, we received an advance copy of a paper by Ledoux et al. (1998), which arrives at conclusions similar to ours.

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