

EMISSION AND EXTINCTION OF GROUND AND VAPOR-CONDENSED SILICATES FROM 4 TO 14 MICRONS AND THE 10 MICRON SILICATE FEATURE

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ABSTRACT

Emission and absorption spectra from 4 to 14 μm of ground and laser-vaporized olivine and enstatite silicates are compared with the 10 μm emission feature of the Orion Trapezium. The agreement in band center and shape between the amorphous laser-vaporized olivine sample and the Trapezium feature suggests that amorphous silicate grains of approximately olivine composition may be a major constituent of interstellar dust. Differences between the emission and absorption spectral profiles (absorption plus scattering) show characteristics which could be used as a sensitive probe of the morphology of interstellar grain systems, when high signal-to-noise ratio (30-100) observational spectra become available.

Subject headings: infrared: spectra — interstellar: molecules — laboratory spectra

I. INTRODUCTION

The broad emission and absorption features seen in many astronomical spectra near 10 μm are widely believed to be due to the stretching mode of the Si-O bond in micron- and submicron-sized silicate grains (Ney 1977). The nature of the silicate material causing this feature, which occurs with nearly the same band center and width in H II regions (Wynn-Williams and Becklin 1974), oxygen-rich late-type stars and protostellar objects (Merrill and Stein 1976*a, b, c*), the tails of comets (Ney 1974), and in absorption (e.g., toward the galactic center [Woolf 1975]), is subject to debate. Intrinsic to the problem of characterizing the natural silicate dust is producing, in the laboratory, samples whose physical characteristics and hence optical behavior are analogous to those of cosmic grains, thus rendering valid detailed comparisons between the astronomical and laboratory spectra. A number of workers have taken infrared spectra of both hydrous and anhydrous silicate materials and meteorite samples embedded in KBr pellets, which show strong absorption features in the region of 10 μm (e.g., Lyons 1963; Day 1974; Zaikowski, Knacke, and Porco 1975; Zaikowski and Knacke 1975). However, Mie calculations by Dorschner, Friedemann, and Gürtler (1978) indicate that dispersing 0.1 μm silicate spheres in KBr can cause the silicate band center to shift up to 0.3 μm toward shorter wavelengths relative to spectra taken in a vacuum. Hunt and Logan (1972) obtained emission spectra of various ground silicate samples prepared as single particle layers on mirrored substrates, avoiding possible spectral shifts. The spectra of neither crystalline quartz nor olivine showed a good match to the astronomical feature, however. Day and Donn

(1978) have recently produced amorphous magnesium silicate condensates of widely varying composition. Their condensates, scraped from optically thick particle layers and dispersed in KBr, exhibited a broad absorption feature near 10 μm with the band center depending on the condensate Mg/Si ratio, the peak shifting to shorter wavelengths with decreasing Mg/Si ratio.

We present here emission and absorption spectra of optically thin layers of both crystalline olivine and enstatite (a magnesium-rich orthopyroxene) and silicate condensates nominally of olivine and enstatite composition. The spectra are compared with the emission spectrum of the Orion Trapezium region (Forrest 1974). These spectra are forerunners of a catalog of grain emissivities currently in preparation (Russell *et al.* 1979).

II. EXPERIMENTAL

The samples were prepared from natural olivine and enstatite minerals. Microprobe analyses of polished sections yielded the formulae $(\text{Fe}_{0.07} \text{Mg}_{0.93})_2 \text{SiO}_4$ for the olivine and $(\text{Ca}_{0.01} \text{Fe}_{0.11} \text{Mg}_{0.88}) \text{SiO}_3$ for the enstatite, with other elements constituting less than 1% of the minerals. X-ray diffraction studies revealed a small component of a hydrous alteration product after enstatite (possibly serpentine) in the enstatite sample, while the olivine sample showed only a pure olivine diffraction pattern.

Ground samples were prepared by passing each roughly ground mineral through a Trost Gem T Fluid Energy Mill grinder and allowing the exhaust gas-particle stream to blow directly onto a polished copper block for emission analysis, or onto KBr disks for

absorption studies. Silicate condensates were prepared by vaporizing in an oxygen atmosphere a portion of each mineral by a series of laser pulses from a solid-state laser operating in the normal (non-Q-switched) mode. Power densities of $\sim 10^6 \text{ W cm}^{-2}$ were obtained by focusing the beam onto the target. The resulting condensate smoke was allowed to settle out onto a copper block or KBr disk (Stephens and Kothari 1978, 1979).

The emission spectra were taken in a specially fabricated vacuum chamber. Radiation from the copper block and sample, heated to 350 K, was modulated by a rotating polished aluminium chopper wheel and directed by a mirror into a continuous variable filter-wheel spectrometer normally used for astronomical observations (see Russell 1978 and references therein). Spectra of the bare copper block ($\epsilon \sim 0.02$) and copper block painted with 3M Black Velvet paint were used in conjunction with the sample spectra to obtain sample emissivities. Separate spectrometers were used for the 4–8 and 8–14 μm ranges, the normalization being carried out by matching the sample emissivities in the overlapping channels. The emissivities between the two systems agreed within 20%. Due to the small masses of material used in these experiments (< 2 micrograms cm^{-2}), mass absorption coefficients were not obtainable.

III. RESULTS

Scanning (SEM) and transmission (TEM) electron micrographs of the ground and condensed silicate samples are shown in Figure 1 (Plate 6). The ground samples occur as single particle layers with particle diameters predominantly less than 5 μm (5000 nm). The condensed silicate samples were prepared as $\sim 10 \mu\text{m}$ deep, optically thin ($\sim 10\%$ absorbing) layers on the substrates. The sample of olivine condensate used for emission (Fig. 1c) showed a substantially lower surface coverage than the other condensate samples. In high magnification, TEM electron micrographs ($40,000\times$ —Fig. 1d and 1g) the condensate strands are resolved as strings of spherical submicron grains, which have a median diameter of 15–30 nm. Electron diffraction and X-ray diffraction traces of ground and condensed samples are shown in Figure 2. The amorphous condensate samples show only broad peaks which are similar to the electron diffraction pattern of SiO_2 glass produced by this technique, while the ground samples are highly crystalline and show sharp

diffraction lines. Electron microprobe analysis of the condensates showed the (Fe + Mg)/Si ratios to be within 30% of their respective targets and ground samples (Stephens and Kothari 1978). The elemental composition of the olivine and enstatite condensates were clearly distinguishable.

An emissivity curve for each of the samples is shown in Figure 3, together with the emissivity of the Orion Trapezium region derived from the data of Forrest (1974). The corresponding absorption curve of each sample, inverted and normalized to the peak and minimum of the emission curve, is shown in Fig. 4, superposed on the emission data. By plotting the absorption in this way, an increase in absorption by the sample corresponds to a rise in the curves shown in Figure 4. The noise in the spectra is indicated by the point-to-point scatter in the curves. The emissivity curves show a scatter of less than 5%, while the absorption curves show considerably more scatter, particularly at $\lambda < 7.25 \mu\text{m}$ where strong water absorption occurs, making the correction for the KBr difficult. Table 1 shows the maximum emissivity and absorption for each spectrum. The enstatite spectra show larger emissivities than the olivine spectra due to the greater amount of enstatite present (Fig. 1).

Emission and absorption spectra of ground olivine show a strong double-peaked feature at 10.15 and 11.25 μm , with the peaks occurring within 0.05 μm of the peak positions for ground olivine embedded in KBr pellets (Lyons 1963; Zaikowski, Knacke, and Porco 1975). The feature is considerably wider in absorption than in emission, with a larger signal both shortward and longward of the absorption peak. A predominant minimum occurs at 8.9 μm . In contrast, the spectrum of the olivine condensate shows a single broad peak centered at 9.75 μm in both emission and absorption, with the absorption curve higher (more absorbing) than the emission curve at wavelengths longward of the peak. Absorption analyses of several olivine condensate samples showed a spread in band center of $\pm 0.05 \mu\text{m}$. A minimum, just above the noise level, occurs at 8.35 μm .

The ground enstatite sample shows in emission a single, sharp peak at 9.90 μm with shoulders at 9.2 and 11 μm and small peaks at 12.75 and 14.1 μm . The absorption curve is similar in the strongly absorbing region, but shows a higher signal level between 4 and 8 μm a sharp minimum centered on 8.3 μm , and a small sharp peak at 12.0 μm (not seen in the emission curve) riding on a moderately strong continuum which

TABLE 1
OPTICAL THICKNESS OF LABORATORY SAMPLES AND ASTRONOMICAL OBSERVATIONS

MATERIAL	EMISSION		ABSORPTION	
	Emissivity Max.	Emissivity/Division	Absorption Max.	Absorption/Division
Ground enstatite.....	0.68	0.1	0.17	0.025
Enstatite condensate.....	0.19	0.04	0.07	0.016
Ground olivine.....	0.022	0.004	0.21	0.038
Olivine condensate.....	0.013	0.002	0.05	0.008
Orion Trapezium.....	1	0.2

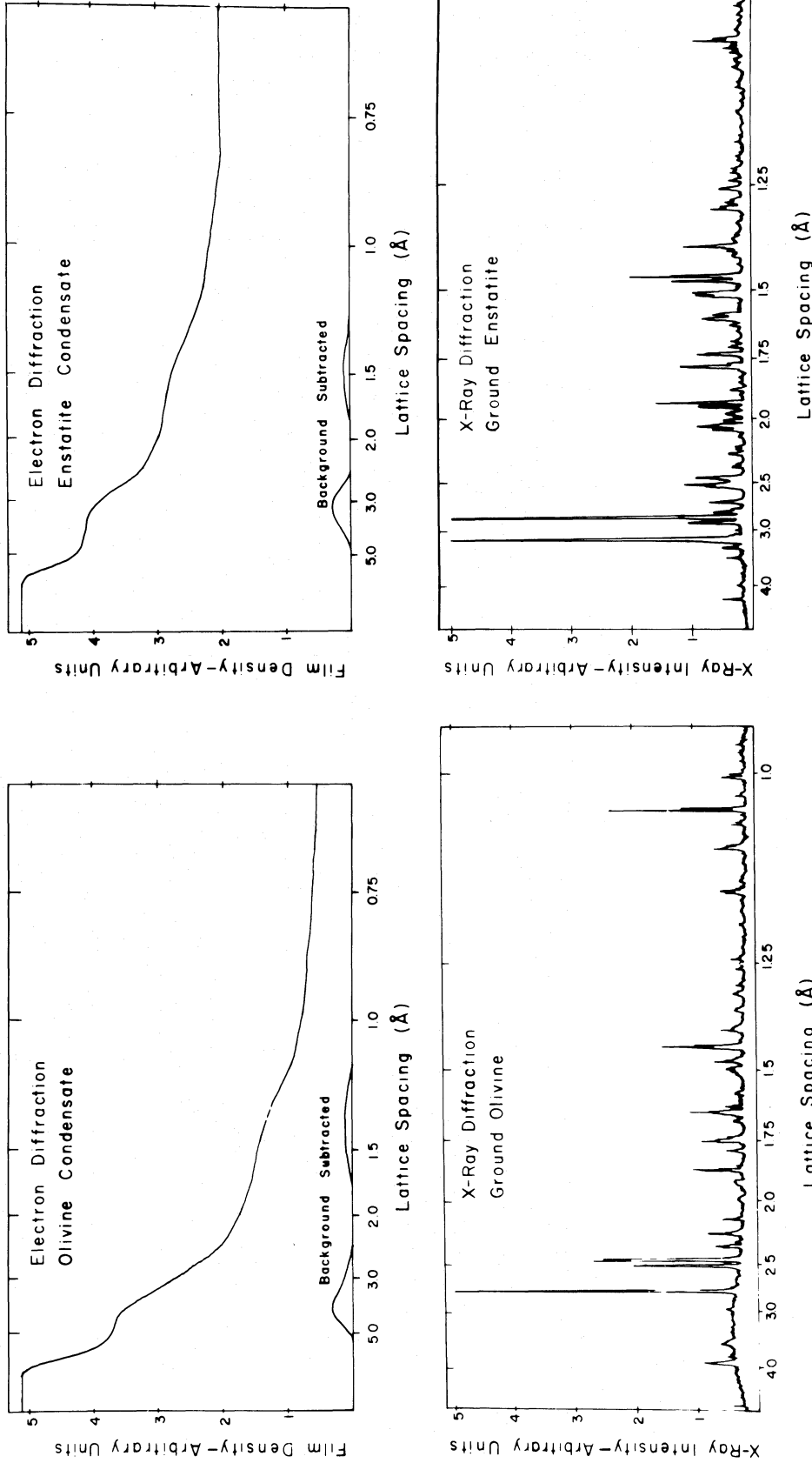


FIG. 2.—X-ray and electron diffraction traces for both the ground and condensed samples. In the background-subtracted curves, the inelasticity scattered components have been removed.

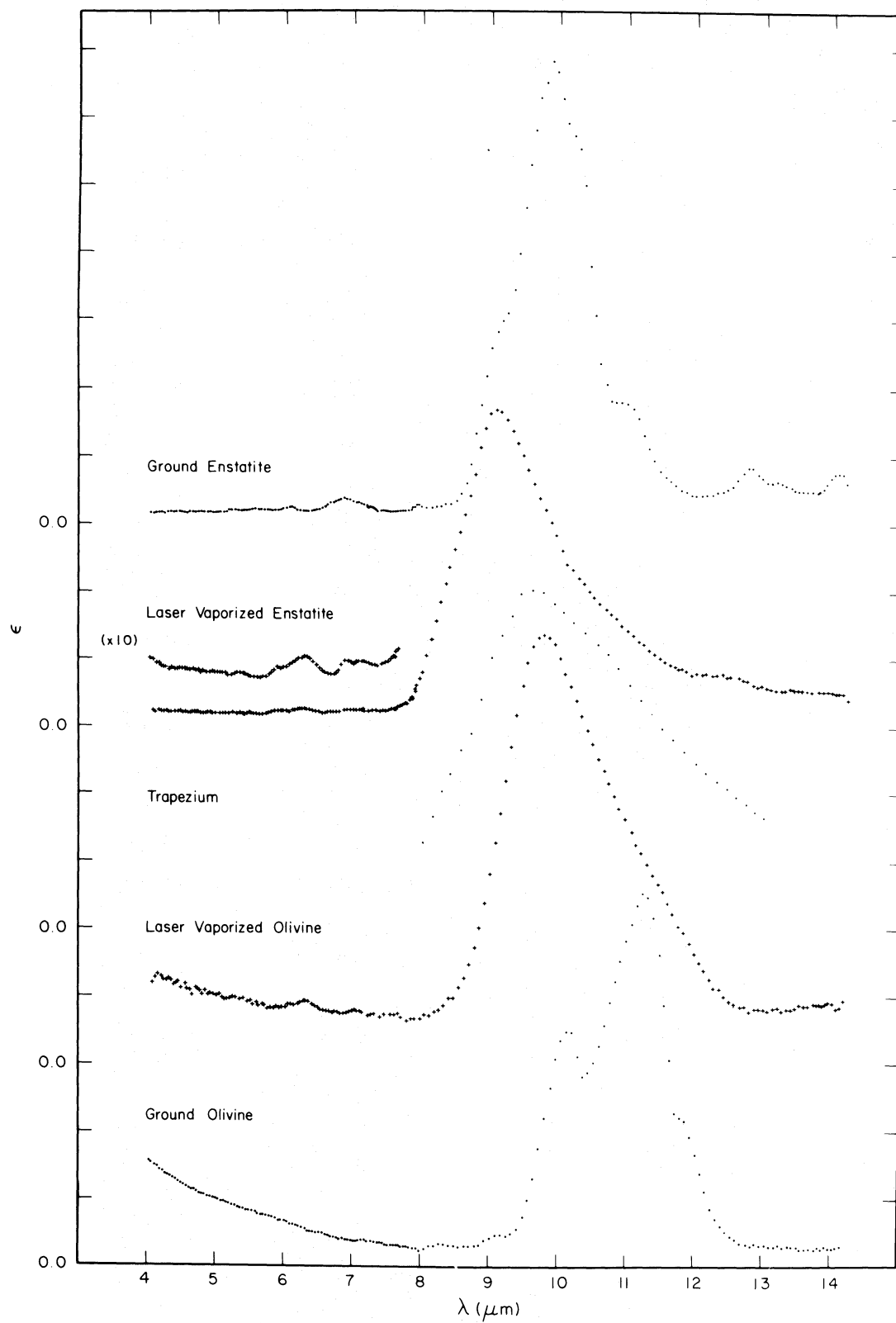


FIG. 3.—Emissivities of the various samples, as discussed in the text. The measured values for each spectrum can be derived by using the values in Table 1. A temperature of 250 K (Gillett *et al.* 1975) was used to derive the Trapezium emissivity.

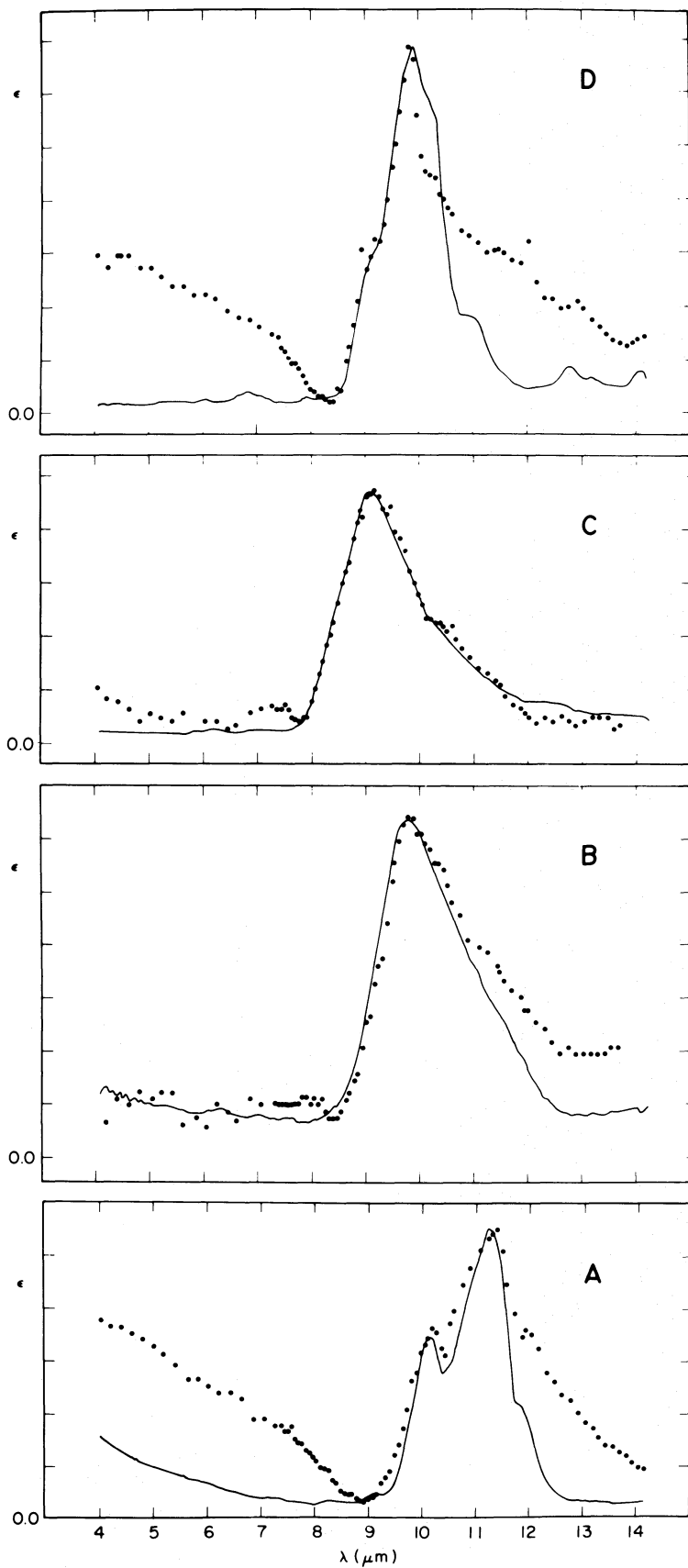


Figure 4.—Absorption (extinction) spectra (dots) of A: ground olivine; B: olivine condensate; C: enstatite condensate; and D: ground enstatite, superposed on the corresponding emissivity data (solid lines) from Fig. 3.

FIG. 4.—Absorption (extinction) spectra (dots) of A: ground olivine; B: olivine condensate; C: enstatite condensate; and D: ground enstatite, superposed on the corresponding emissivity data (solid lines) from Fig. 3.

decreases in strength toward longer wavelengths. The enstatite condensate spectrum exhibits a single broad feature peaking at $9.1 \mu\text{m}$. The emission and absorption spectra of this condensate are substantially the same except for a barely discernible minimum at $7.75 \mu\text{m}$ in the absorption curve.

IV. DISCUSSION

Neither ground olivine nor ground enstatite exhibits a band center which matches the Trapezium's $9.7 \mu\text{m}$ feature (Fig. 3) (Lyons 1963; Zaikowski and Knacke 1975). The peak in the spectrum of the enstatite condensate occurs at too short a wavelength ($9.1 \mu\text{m}$) to match the astronomical feature. The band center of the olivine condensate occurs at $9.75 \mu\text{m}$, however, and is a good match to the Trapezium silicate feature. The band center of our olivine occurs at a wavelength similar to the high-magnesium amorphous condensates by Day and Donn (1978) and the peak in the absorption curve of carbonaceous chondrite meteorites investigated by Zaikowski and Knacke (1975). Both the emission and absorption spectra of olivine condensate are slightly too narrow (FWHM = $2.2 \mu\text{m}$) to match the Trapezium emission (FWHM = $3.5 \mu\text{m}$). Variations in chemical composition of cosmic grains are easily a significant enough effect to broaden the feature, however, as are temperature gradients in the sources (Puetter *et al.* 1979). Glassy silicates of approximately olivine composition appear to be good candidates for the interstellar grain population in addition to or in place of phyllosilicate materials investigated by Zaikowski and Knacke (1975). Such glassy silicates could form as direct condensation products, or as a result of radiation damage to well-crystallized minerals. (For an example of the effect of radiation damage on the $10 \mu\text{m}$ signature of a mineral, see Rose 1977.) Both astronomical and laboratory spectra over the wavelength range $2\text{--}25 \mu\text{m}$, where phyllosilicates and anhydrous silicate condensates show considerable spectral structure, are needed to determine the relative contribution of various silicates to the cosmic grain population.

In our spectra, the signal levels of the emission and absorption curves are in fairly good agreement in the region of strong absorption, but outside this region, particularly for the ground samples, the absorption spectra are considerably higher (more absorbing) than the corresponding emission spectra. Since absorption measurements include absorption and scattering in the extinction, while the emission spectra nominally represent only emission (or pure absorption), the difference between the emission and absorption curves for a given sample represents the scattering contribution to the extinction. A moderate scattering contribution, at wavelengths shortward of an absorption feature, which drops to a very low value just at the onset of strong absorption, followed at wavelengths longer than the peak absorption by a scattering contribution decreasing with wavelength, is characteristic of the spectral behavior of small grains of dielectric materials in Mie scattering calculations (Huffman 1977). Since

scattering is most efficient for grain sizes of the order of the wavelength at the band center, our ground samples show strong scattering contributions, while the condensed samples show only a small scattering contribution to the extinction. The minimum in the extinction just shortward ($\lambda \approx 8.0\text{--}8.5 \mu\text{m}$) of the onset of the strong absorption peak, seen in both the olivine and enstatite condensate spectra, is believed to be due to the decrease in scattering in this region, as mentioned above. This characteristic shape must be due to scattering by the long strands or agglomerates thereof, as the scattering due to the individual particles is much too small (Conel 1969). The contrast of the extinction minimum should depend on the depth and strand density of the condensate sample. Since interstellar grains are also likely to occur as agglomerates which consist of strands of submicron grains (Stephens and Kothari 1978; Millman 1975), extinction by the interstellar medium may show a scattering contribution in the $10 \mu\text{m}$ region, depending on the length of the strands and the chain density of the agglomerate, while emission from regions such as the Orion Trapezium or a hot circumstellar dust shell should not. Thus a comparison of the spectral profile derived from the observations of regions which exhibit silicate absorption to the corresponding profile from regions where silicates are seen in emission might yield information on the morphology of these oxygen-rich cosmic grain systems. Unfortunately, the astronomical spectra of sources such as the galactic center (Woollf 1975) or the H II region W3 (Willner 1977) which show strong silicate absorption do not have sufficient signal-to-noise ratio or wavelength coverage to show the slight minimum in extinction shortward of the absorption peak seen in our data. Moreover, a slight drop in extinction near $8.0 \mu\text{m}$ seen in these sources can as well be fitted by a model of hot emitting dust with intervening absorbing dust along the line of sight (Gillett *et al.* 1975). Evaluating the form of interstellar dust by observations of a dip in extinction shortward of the $10 \mu\text{m}$ absorption feature requires both very high signal-to-noise observational spectra and a source region of unusually well-defined temperature structure.

V. CONCLUSIONS

Measurements of the spectral absorption (extinction) and emission behavior from 4 to $14 \mu\text{m}$ of optically thin layers of ground and vapor-condensed materials have been performed. Silicate condensates nominally of olivine composition show a good match to the band center of the astronomical $10 \mu\text{m}$ feature. While the width of the laboratory feature is somewhat narrower than the astronomical feature, variations in chemical composition or source temperature gradients could easily broaden the feature to match the astronomical data. The production of silicate condensates by laser vaporization allows well-characterized materials to be produced whose size and form are likely to be similar to those of cosmic grains.

Emission studies of optically thin layers of vapor-condensed materials appear to be particularly fruitful in studying the spectral behavior of likely astronomical

grain systems, due to the high signal-to-noise ratio obtainable and low sample surface coverages required. The dip in the extinction curve shortward of the 10 μ m silicate feature discussed herein could serve as a diagnostic tool in the study of the form of interstellar grains if the signal-to-noise ratio of the astronomical spectra and the knowledge of the source characteristics are improved.

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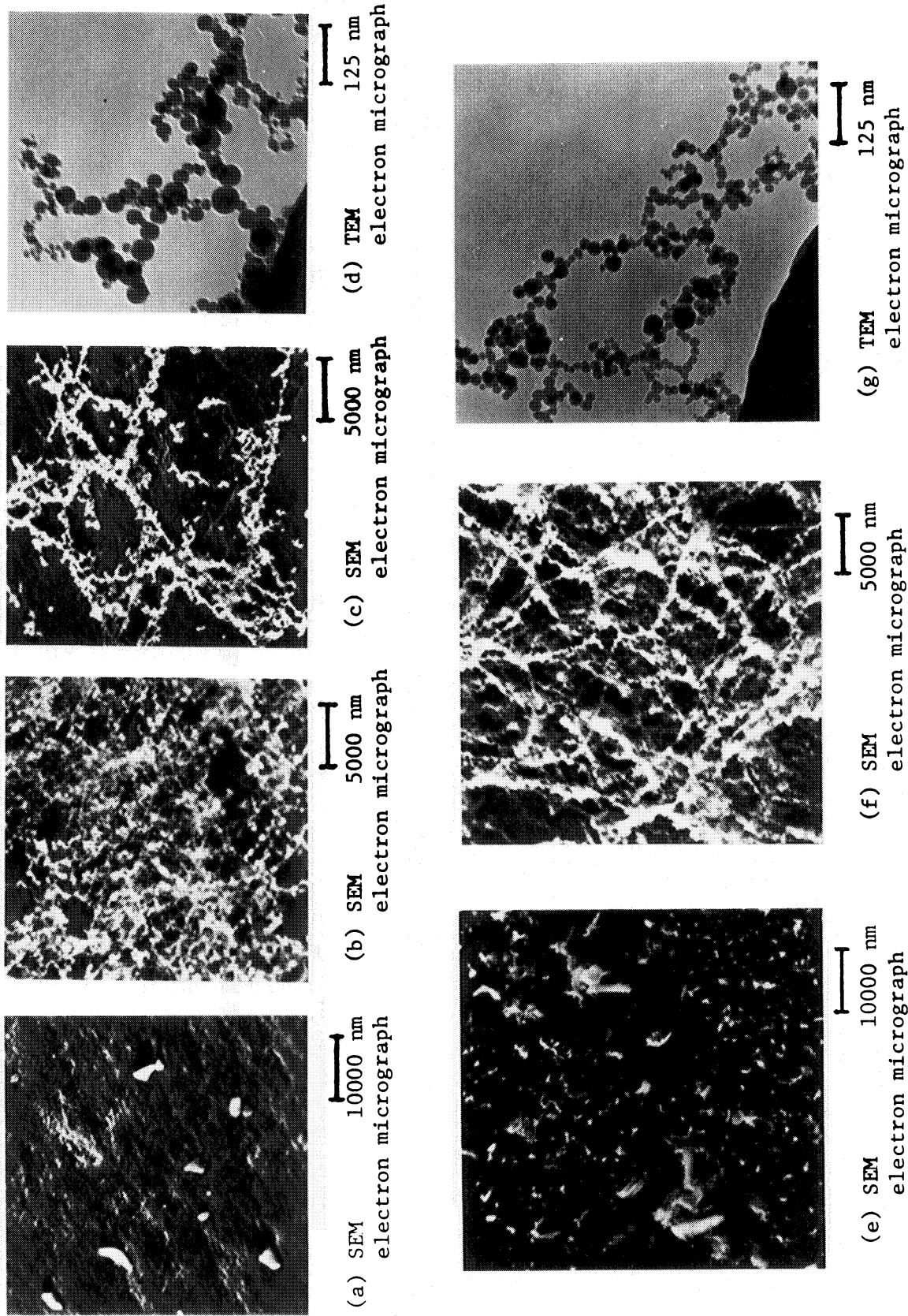


FIG. 1.—Electron micrographs of representative ground and condensed samples. The measurements performed on such samples are given in parentheses in the following list: (a) ground olivine (emission and absorption), (b) olivine condensate (absorption), (c) olivine condensate (absorption), (d) olivine condensate (emission and absorption), (e) ground pyroxene (emission and absorption), (f) pyroxene condensate (emission and absorption), (g) pyroxene condensate (emission and absorption).

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