RECONSIDERING THE ORIGIN OF THE 21 MICRON FEATURE: OXIDES IN CARBON-RICH PROTOPLANETARY NEBULAE?1

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Received 2004 April 7; accepted 2004 August 16

ABSTRACT

The origin of the so-called 21 μm feature that is especially prominent in the spectra of some carbon-rich protoplanetary nebulae (PPNs) is the matter of a lively debate. A large number of potential band carriers have been presented and discarded within the past decade. This paper gives an overview of the problems related to the hitherto proposed feature identifications, including the recently suggested candidate carrier silicon carbide. We also discuss the case for spectroscopically promising oxides. SiC is shown to produce a strong resonance band at 20–21 μm if coated by a layer of silicon dioxide. At low temperatures, core-mantle particles composed of SiC and amorphous SiO2 indeed have their strongest spectral signature at a position of 20.1 μm, which coincides with the position of the 21 μm emission band. The optical constants of another candidate carrier that has been relatively neglected so far—iron monoxide—are proven to permit a fairly accurate reproduction of the 21 μm feature profile as well, especially when low-temperature measurements of the infrared properties of FeO are taken into account.

As candidate carrier of the 21 μm emission band, FeO has the advantage of being stable against further oxidation and reduction only in a narrow range of chemical and physical conditions, coinciding with the fact that this feature, too, is detected in a small group of objects only. However, it is unclear how FeO would form or survive, particularly in carbon-rich PPNs.

Subject headings: circumstellar matter — infrared: stars — methods: laboratory — stars: AGB and post-AGB — stars: atmospheres

1. INTRODUCTION

Kwok et al. (1989) reported the discovery of a strong emission band, centered (as it then seemed) at 21 μm, in the spectra of four carbon-rich protoplanetary nebulae (PPNs) taken by the Infrared Astronomical Satellite (IRAS). The feature was not resolved well with the Low Resolution Spectrometer (LRS), but nevertheless, it was already evident from the LRS observations that it has a considerable strength in some objects (especially IRAS 07134+1005) and is too broad (FWHM >2 μm) to originate from any atomic transition. The pioneering work by Kwok et al. also highlighted the fact that the 21 μm feature only occurs in a short transitional phase of stellar evolution, i.e., in a very limited range of physical and chemical conditions. Any identification of the 21 μm feature has to deal with this fact.

Observations of selected PPNs with the Infrared Space Observatory (ISO) by Hrivnak et al. (2000) brought substantial progress, especially concerning the position and width of the feature, which was shown to be 20.1 μm instead of 21 μm (nevertheless, the feature is still being referred to as the “21 μm band, a tradition to which we stick in this paper). Hrivnak et al. (2000) analyzed ISO observations at 2–45 μm for seven PPNs and two other carbon-rich objects. Six of the sources exhibit emission features at 21 and 30 μm. The authors resolved the 30 μm band into a broad feature peaking at 27.2 μm (the “30 μm feature) and a narrower feature at 25.5 μm (the “26 μm feature). The observations suggest that the sources with the 21 μm feature also show the 30 μm feature. The 26 μm feature appears to be present in a broader range of objects—carbon stars, PPNs, and possibly planetary nebulae (PNs)—than does the 21 μm feature.

The candidate carriers have long been the subject of discussion since the discovery of the 21 μm band. Cox (1990) presented IRAS LRS spectra of 10 H II regions that showed a peak close to 21 μm. He associated this peak with iron oxides with the stoichiometries γ-Fe2O3 and Fe3O4. In the late 1990s, some of these H II regions have also been observed with ISO; in the ISO spectra; however, we do not find any traces of a broad 21 or 20 μm emission band (in accordance with Oudmaijer & de Winter 1995, who had already cast doubt on Cox’s observations).

Goebel (1993), still on the basis of IRAS spectra, assigned the 21 μm feature to silicon disulfide (SiS2), which has indeed an intense vibrational band in the 20 μm spectral range (but, unfortunately, a second one that is not observed; see §4). From a chemical point of view, other sulfur compounds such as S8, OCS, S2, and CS2 were also taken into account by Goebel as potential emitters in the 20 μm region, even though mainly as mantles of other grains.

1 Based on observations with ISO, an ESA project with instruments funded by ESA Member States (especially the PI countries: France, Germany, the Netherlands, and the United Kingdom) and with the participation of ISAS and NASA.
Webster (1995) brought fulleranes as potential carriers of the 21 μm feature into the discussion. Having studied the IR bands of terrestrial nitrogen-doped and neutron-irradiated diamonds, Hill et al. (1998) showed that defects in diamond structures can cause an emission band at 20–22 μm and even stronger bands in the 8–10 μm region. However, there is a significant discrepancy between the position of 21–22 μm and the actual position of the 21 μm band as determined by recent observations.

Papoular (2000) calculated synthetic spectra of carbonaceous macromolecules containing OH, oxygen, sulfur, nitrogen, or a combination of them and found that it is possible to reproduce not only the 21 μm feature but also the 3.3, 11.3, 12+, 26, and 30 μm bands by emissions of such molecules. According to this scenario, the 21 μm feature would arise from out-of-plane vibrations of oxygen or nitrogen atoms in five-membered carbon rings. Papoular’s approach seems promising because it aims at an identification of all the major features detected in the sources of the 21 μm band on the basis of one unified dust model. But at the time being, substantial problems remain, such as the unsatisfactory reproduction of the observed 26–35 μm band profile.

There are various other papers discussing carbonaceous materials as carriers of the 21 μm feature but without any detailed fits of its average profile. Sorousseau et al. (1992) suggested amides, especially urea, as potential carriers, Buss et al. (1990) and Justtanont et al. (1996) suggested polycyclic aromatic hydrocarbon molecules, and Grishko et al. (2001) suggested hydrogenated amorphous carbon.

von Helden et al. (2000) came up with another suggestion, attributing the 20.1 μm feature to titanium carbide clusters (made of 27–125 atoms). Spectra of bulk titanium carbide and TiC particles, such as those subsequently published by Henning & Mutschke (2001) and Kimura & Kaito (2003), show no band in the respective wavelength region but rather weak bands at 9.5, 12.5 (Kimura & Kaito 2003), and 19 μm (Henning & Mutschke 2001; see also Speck & Hofmeister 2004). This does not contradict the measurements by von Helden et al. (2000), however, since clusters are likely to have electronic and vibrational properties deviating from those of bulk material even if composition and crystal structure are similar.

Nevertheless, in 2003, three papers with substantial arguments doubting the “TiC-cluster identification” came out, all based essentially on arguments concerning the abundance of titanium (Hony et al. 2003; Chigai et al. 2003; Li 2003). Hony et al. (2003) argue that TiC, like any kind of dust, can only emit if unrealistic large amounts of TiC are predicted to form in cool dusty environments, i.e., environments with dust temperatures below 250 K. Among them are the aforementioned C-rich PPNs (about half of them show the feature), two planetary nebulae (Hony et al. 2001) with central stars of the Wolf-Rayet type, and according to Volk et al. (2000), two extreme carbon stars (IRAS 21318+5631 and IRAS 06582+1507). Reanalyzing the ISO spectrum of IRAS 21318+5631, however, Clément et al. (2004) find no evidence for a feature at 20 μm, and in the case of IRAS 06582+1507, Volk et al. (2000) also remark that its reality is doubtful.

It should be noted that an emission band with a position and width quite comparable to the 21 μm band is detected in the spectra of stars on the early asymptotic giant branch (AGB), i.e., at the very opposite end of AGB evolution: the 19.5 μm feature (Posch et al. 2002). Its peak position amounts to 19.4–19.6 μm, its profile is symmetric, and its FWHM is close to 3 μm. The dust shells of the mostly semiregular variable stars in which this feature is observed are generally assumed to consist of refractory oxides but not at all of carbonaceous dust grains. A solid solution of FeO and MgO has been proposed as feature carrier in this case (see also Ferrarotti & Gail 2003).

Coming back to the PPNs exhibiting the 21 μm band in its “canonical” form, let us consider the spectrum and the derived properties of its best-known source, IRAS 07134+1005 (=SAO 96709 or HD 56126; see Fig. 1). The F5 I central star of this PPN has a surface temperature of about 7000 K according to Hrivnak et al. (2000); other PPN sources of the same feature have comparable effective temperatures (5500–8000 K). The circumstellar envelopes of these objects are all optically thin at infrared wavelengths. As for unusual properties of the central stars, van Winckel & Reyniers (2000) found them to be enriched in s-process elements and metal-poor. Apart from the peak due to the radiation of the central star at visual wavelengths, several infrared bands arising from dust grains are present in the spectrum of HD 56126, namely, at 8, 11.3, 12.1, and 30 μm. They are partly unidentified and partly attributed to SiC (11.3, broad component), PAHs (11.3, narrow component, 12+ plateau emission), and magnesium sulfide (30 μm), respectively. No silicate features are seen in any of the sources of the 21 μm band.
We derived the profile of the 21 μm band using the polynomial subtraction method that has been applied by Posch et al. (1999) for the derivation of the 13 μm band profile. The residual emission of HD 56126, based on an ISO-SWS spectrum reduced with the ISO Spectral Analysis Package (ISAP), is shown at the bottom of Figure 1. For comparison, the scaled residual emission of SAO 34504—calculated by the same method—is shown in the bottom part of Figure 1 as well (open triangles). The close coincidence of the two emission profiles is noteworthy; together with the result by Volk et al. (1999) that the feature profile is pretty much the same in all sources, this implies that the spectrum of HD 56126 can be considered representative and will be so considered in the following. The most conspicuous properties of the feature profile are a steep rise in its blue wing, a maximum position of 20.1 μm, and a long "tail" extending to 23—24 μm.

In contrast to stars on the early AGB, bright PPNs have spatial extensions large enough to resolve them even at infrared wavelengths. Kwok et al. (2002) and Miyata et al. (2003) tried to answer the question whether the different broad infrared features of PPNs have their origin in different or coincident regions on the basis of imaging through broad filters. They tried to answer the question whether the different broad infrared bands (e.g., at 667 cm\(^{-1}\) [15 μm] and 580 cm\(^{-1}\) [17.2 μm]) are not seen in the sources of the astronomical 21 μm feature. Moreover, the whole series of nitrogen-induced secondary features of SiC is weaker than the SiC main feature by at least a factor of 1000. Therefore, very low temperatures (below 80 K) would be necessary to reverse this ratio of band strengths. According to Hrivnak et al. (2000), the dust temperatures at the outer radii of the dust shells of the 21 μm sources are between 165 and 220 K; because of the relatively small ratio between the outer and inner shell radius, the average temperature of the dust grains producing the 21 μm will hardly be below 80 K, even for very transparent dust species (see Fig. 11).

As for C-doped SiC, there is presently too little information at hand about its potential secondary bands. As long as no studies on analytically well-characterized SiC samples with carbon impurities are available, it remains unclear whether the properties of N-doped SiC can be extrapolated to C-doped SiC.

Interestingly, there is yet another possibility for producing an 11 plus a 21 μm band: by, so to speak, "SiC plus something," namely, by coating SiC grains with SiO\(_2\). Recently performed experiments (Clément et al. 2003) demonstrate that pure SiC nanoparticles, under the influence of the laboratory atmosphere, are quite easily oxidized at their surfaces. This effect is shown in Figure 2, where we compare the transmittance of SiO\(_2\) grains with the transmittance of partially oxidized SiC nanoparticles (both embedded in KBr). The method for the production of SiC nanoparticles by laser pyrolysis and the infrared spectra of these grains have been discussed extensively by Clément et al. (2003). They also report the detection of an amorphous silicon oxide mantle by means of transmission electron microscopy (see Fig. 3). The large surface-to-volume ratio of the SiC core favors the formation and growth of a silicon oxide mantle, which can be a few nanometers thick and thus reach a considerable volume fraction of the particulate. Further evidence for the formation of SiO\(_2\) on SiC surfaces, has been delivered—albeit for significantly higher temperatures—by Mendybaev et al. (2002) and Tang & Bando (2003).

Depending on the particle size and shape as well as agglomeration effects, SiC nanoparticles show one strong IR resonance band, located at 10.8—12.4 μm. However, if partially oxidized at their surfaces, the SiC nanogranules produce additional infrared bands at 9 and 21—22 μm. These bands can be assigned to stretching and bending vibrations of the SiO\(_2\) tetrahedra. The minor 12.5 μm band of SiO\(_2\) is not detected in the spectrum of partially oxidized SiC nanoparticles, since it almost coincides with the SiC main band shifted to longer wavelengths by shape effects.

An additional proof for the oxidation of SiC is delivered by treating the oxidized grains with HF, which quickly reduces

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![Figure 1](https://example.com/fig1.png)  
**Fig. 1.**—ISO-SWS spectrum of the PPN IRAS 07134+1005 at a resolution λ/Δλ = 600. The profile of the 21 μm band is shown at the bottom, both as derived from the ISO-SWS spectrum HD 56126 (solid line) and from an ISO-SWS spectrum of SAO 34504 (open triangles) by subtraction of a polynomial (dotted line overplotted to the ISO spectrum at the top).
the oxidized grains, leaving only the pure silicon carbide cores. The spectroscopic result of this process is depicted in Figure 4.

Absorption spectra with the principal structure of those shown in Figures 2 and 4 can be derived not only experimentally, but also by calculating the absorption efficiency of core-mantle particles composed of SiC and amorphous SiO$_2$. For this purpose, the optical constants of amorphous SiO$_2$ compiled in the first volume of Palik (1985–1998) have been used. We performed a Lorentz fit to these optical constants in order to analyze the underlying oscillator parameters. The damping constants of the SiC oscillator have been set to 50 cm$^{-1}$ and those of the 456 cm$^{-1}$ oscillator of SiO$_2$ to 42 (instead of 27), assuming that the nanocrystalline structure is comparable to that of defect-bearing polycrystalline films (see Mutschke et al. 1999, § 2.3). As for the 456 cm$^{-1}$ SiO$_2$ oscillator, a larger damping constant than that corresponding to the Palik data is justifiable also on the basis of the spectra published by Lehmann et al. (1984). These authors studied the transmittance of thin SiO$_2$ films (with $x < 2$) and found a strong broadening of the 20–21 $\mu$m band with decreasing $x$. This result is of potential relevance for the coating of SiC by silicon oxide in carbon-rich circumstellar shells, since in these environments, the formation of oxygen-deficient SiO$_2$ is very well conceivable. For a summary of all Lorentz parameters used, see Table 1.
Figure 5 shows the absorption efficiency factor $Q_{\text{abs}}/a$ of spherical core-mantle particles composed of SiC and amorphous SiO$_2$ with core volume fractions ranging from 40% to 60%. Three prominent maxima of $Q_{\text{abs}}$ are discernible: a peak at 8.3 μm, which originates from the SiO$_2$ mantle, the sharp 11 μm SiC resonance, and finally a 20 μm peak, with a main peak and a shoulder at the long-wavelength side, originating again from the SiO$_2$ mantle. Peak splitting is typical for bands of mantle materials. It arises from the existence of two interfaces with core and ambient medium. All the bands are sharper than those of the transmission spectrum of partially oxidized SiC shown in Figure 2. This difference in the bandwidth is primarily due to shape effects.

Looking at Figure 5, one may assume that the depicted pattern of $C_{\text{abs}}/V$ maxima is incompatible with the spectra of astronomical objects such as HD 56126, since the 20 μm band in this figure is only a minor peak compared to those at 8.2 and 11 μm. However, such a conclusion would be premature, given that the dust in the sources of the 21 μm feature is rather cold, as has been highlighted in § 2. For dust particles with temperatures below 150 K, all features at wavelengths smaller than ~20 μm are strongly attenuated, because they tend to be located in the Wien regime of the corresponding Planck functions. This effect, which was already noted by Speck & Hofmeister (2004), is illustrated in Figure 6.

It is evident from this figure that cold core-mantle particles composed of SiC and amorphous SiO$_2$ do produce a strong 20 μm feature. There is a rather good agreement between the observed and the calculated band positions (see also Table 3 for a quantitative assessment), and the weakness of the observed 11 μm feature can be explained by dust temperatures significantly lower than 160 K, on average. There remains a problem, however, with the width and shape of the 20 μm band produced by SiO$_2$. For spherical particles, the FWHM of the 20 μm SiO$_2$ emissivity maximum amounts to 1.9 μm, compared to an observed FWHM of 2.2–2.3 μm. Furthermore, the shoulder at the “red” wing of the 20 μm SiO$_2$ feature has not been seen in the astronomical 21 μm band. The bandwidth discrepancy can be overcome by a continuous distribution of ellipsoids (CDE); the shoulder at the red wing of the band, however, does not vanish in the CDE case (see Fig. 7), nor does it vanish by any particular (realistic) choice of the dust temperature or dust temperature distribution.

### 3.2. Oxidized Silicon Grains

Instead of growing on top of silicon carbide grains, SiO$_2$ can equally well form mantles on top of pure silicon particles. Li & Draine (2002) were the first to examine the spectra emerging from silicon grains with oxide coatings, focusing on the case of stochastically heated nanoparticles. Smith & Witt (2002) proposed silicon nanoparticles as carriers of the so-called extended red emission observed in circumstellar environments; however, this identification is still a matter of debate.

The principal structure of the IR spectrum of Si-SiO$_2$ core-mantle grains is similar to that of SiC-SiO$_2$ core-mantle grains, except for the absence of the 11 μm band. In addition to the 8.2 and 20 μm peaks, a rather strong 12.5 μm band appears in the SiO$_2$ absorption efficiency spectrum. The exact position $\lambda_{20}$ of the 20 μm resonance depends on the volume fraction $f$ of the Si core. Here $\lambda_{20}$ increases from 19.7 to 19.8 μm as $f$ decreases from 0.6 to 0.4.

Following the procedure explained in § 3.1, we folded the absorption efficiency of a Si-SiO$_2$ core-mantle grain with $f = 0.5$ with two different Planck curves $B_\nu(T_d)$. For the dust temperature, the two values $T_d = 100$ and 160 K have been chosen. As for the 20 μm band, the result—plotted in Figure 8—strongly resembles the case of SiC cores, which is not surprising, since the optical constants of the core have only a limited influence on the structure of those bands that are due primarily to the mantle.

It must be stressed, however, that core-mantle particles composed of Si and SiO$_2$ are more unlikely to be the carrier of the 21 μm band than those composed of SiC and SiO$_2$, since it is questionable whether silicon grains can be formed in carbon-rich PPNs at all.

### Table 1

| Dust Species     | $\omega_0$ (cm$^{-1}$) | $\Omega_0$ (cm$^{-1}$) | $\gamma_0$ (cm$^{-1}$) |
|------------------|------------------------|------------------------|------------------------|
| SiC              | 796                    | 1423                   | 50                     |
| SiO$_2$          | 456                    | 417                    | 42                     |
|                  | 798                    | 150                    | 30                     |
|                  | 1080                   | 866                    | 60                     |
|                  | 1194                   | 257                    | 100                    |
|                  | 1479                   | 200                    | 80                     |

*Note.—We adopted the values $\epsilon_\infty = 6.49$ for SiC and $\epsilon_\infty = 2.2$ for amorphous SiO$_2$.*
3.3. Cold FeO (Wustite)

As mentioned in § 1, various authors have already considered iron oxides as carriers of bands in the 20–21 μm region. It seems clear, however, that none of the "higher" iron oxides like Fe$_2$O$_3$ or Fe$_3$O$_4$ can survive in a reducing environment. Iron monoxide (FeO, also called wustite), by contrast, may survive in a carbon-rich circumstellar shell.

According to Duley (1980), the oxidation of metallic iron is a very efficient process provided that enough O$_2$ molecules are present. The degree to which iron particles are oxidized depends on the physical conditions, inter alia on the temperature. The higher iron oxides Fe$_2$O$_3$ or Fe$_3$O$_4$ become stable at higher temperatures (see, e.g., Gail & Sedlmayr 1998). By contrast, as Roberts (1961) and Fehlner & Mott (1970) pointed out, several monolayers of iron monoxide form very quickly on top of Fe surfaces, even at low temperatures, since this process requires a negligible activation energy. In order to end up with dust grains composed essentially of FeO (instead of a large metallic iron core and a tiny FeO mantle), i.e., grains composed of $10^3$ atoms at maximum. Only such small iron grains—their diameters amounting to ~2 nm—could be fully converted into FeO by the process mentioned above. The oxidation of iron grains consisting of less than $10^3$ atoms is to some extent an artificial assumption, less artificial, however, than the constraint that the TiC clusters—which were previously considered to be carriers of the 21 μm band—should consist of no more than 125 atoms to efficiently produce the TiC cluster signature.

Why would FeO, according to our suggestion, not exist in the vast majority of the PNs, at least not with high number densities? A plausible explanation is that in PNs with their large fractional ionization and high UV photon densities, iron oxides will be reduced to metallic iron. While the nondetection of the 21 μm band in PNs spectra can thus be accounted for, its nondetection in the spectra of most of the oxygen-rich as well as carbon-rich AGB stars is more difficult to understand within the iron grain oxidation scenario for PPNs. If in PPNs, such as HD 56126, FeO forms by oxidation of iron, why does the same process not take place in C-stars, S-stars, and in the vast majority of M-AGB stars? This may be due to the fact that the dust around these stars is, on average, much hotter than dust in PPNs and that the sticking probability of oxygen on iron decreases as the temperature increases. The Mg-Fe-oxide formation around some M-stars, postulated by Posch et al. (2002), must involve an entirely different mechanism than the low-temperature oxidation of iron in PPNs.

Strictly speaking, wustite is the terrestrial form of iron monoxide and has the chemical composition Fe$_{1-x}$O with $x = 0.05 \ldots 0.16$. 

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governed by oxygen availability and that the iron abundance is therefore only crucial if there is enough free oxygen.

While knowledge of the Fe-Mg oxide formation in circumstellar environments is still scarce, quite detailed spectroscopic information on Mg-Fe oxides is available. The optical constants of Fe$_x$Mg$_{1-x}$O samples ($x$ amounting to 0.4 to 1.0) with magnesiowustite structure have been measured at room temperature by Henning et al. (1995). Subsequently, Henning & Mutschke (1997) published low-temperature data for various cosmic dust analogs, i.e., their indices of refraction $n(k)$ and absorption $k(k)$ for $T = 10, 100, 200,$ and $300$ K. A major change of the infrared spectrum of Fe$_x$Mg$_{1-x}$O is observed as the samples are cooled, namely, a sharpening of the vibration band located at 18–20 µm (depending on $x$). Figure 9 shows this effect for $x = 1.0$, i.e., for pure FeO. (The case $T = 10$ K has been omitted, since it does not significantly differ from $T = 100$ K.)

The FWHM of the 20 µm FeO band decreases from 3.6 µm at room temperature to 2.4 µm at $T = 100$ K, while the band position is shifted from $\lambda_{\text{max}} = 19.9$ to 20.1 µm. The latter effect is exclusively due to the multiplication with the Planck functions $B_{\nu}(T)$, which have maxima positions of 17, 25.5, and 51 µm for $T = 300, 200,$ and $100$ K, respectively. The rather large width of the 20 µm band produced by FeO, in combination with the fact that for $T = 200$ and $100$ K the peak position is located at the “blue” wing of the corresponding Planck curve, leads to an asymmetric profile of the $C_{\text{abs}}B_{\nu}(T)$ curves—the same kind of asymmetry that is found for the astronomical 21 µm band.

Iron monoxide has a rather high absorption efficiency in the visual range of the spectrum. Therefore, it is comparatively strongly heated in the radiation field of an F or G star. An equilibrium temperature of less than 100 K is reached only at distances from the central star larger than 2.1 $\times$ 10$^4$ stellar radii. This can be shown by calculating the energy balance for the case of an equilibrium between the radiation field of the central star and the dust grains in its circumstellar according to the scheme summarized in the Appendix.

According to Kwok et al. (2002), the inner radius $R_{\text{in}}$ of the dust shell of IRAS 07134+1005 is located at 1.72 from the central star, corresponding to 1.2 (1.8) $\times$ 10$^{-2}$ pc for an assumed distance of 2 (3) kpc (Kwok et al. 2002 assume a distance of 2 kpc, while Meixner et al. 2003 assume 3 kpc). In terms of the stellar radius corresponding to a luminosity of 1400 $L_\odot$ kpc$^{-2}$ (Hrivnak et al. 2000) and a temperature of 7000 K, this amounts to 9760 or 6490 stellar radii for $d = 2$ (3) kpc, respectively.

In Figure 10, the position of $R_{\text{m}}/R_{\text{eff}} = 6490$ has been highlighted by a vertical dotted line. The equilibrium temperature of FeO corresponding to this distance from the central star amounts to 155 K. This is in good agreement with the results of the model calculations by Hrivnak et al. (2000), who derive an inner temperature of the dust shell of 165 K by radiative transfer calculations aimed at a fit of the spectral energy distribution (SED).

In terms of the ratio between outer and inner shell radius, the dust shells of the PPNs showing the 21 µm feature are rather
thin. For IRAS 07134+1005, the observations of Kwok et al. (2002) and Miyata et al. (2003) yield an outer shell radius not much larger than twice the inner shell radius. This implies that the dust temperature range for a $r/r_0^4$-like decrease of $T(r)$ is rather small. For FeO, we derive a dust temperature at $2R_\text{in}$ of 120 K, meaning that $120 \, \text{K} < T_d < 155 \, \text{K}$ (again for $d = 3 \, \text{kpc}$). For other dust species that are generally assumed to be present in carbon-rich PPNs, narrow $T_d$ ranges are found as well. Amorphous carbon is warmer than FeO because of the monotonous increase of its absorption efficiency factor from the IR to the UV; we find $153 \, \text{K} < T_d < 200 \, \text{K}$ under the same conditions as above. Core-mantle particles composed of SiC and SiO$_2$, unless heavily N-doped, remain cooler than FeO ($104 \, \text{K} < T_d < 126 \, \text{K}$; see Fig. 11).

These estimates make it possible to calculate the emission spectrum of an optically thin dust shell with a homogeneous density distribution and a temperature range of $120 \, \text{K} < T_d < 155 \, \text{K}$. If we are only interested in the profile of the emerging SED, we suffice to calculate a mean of blackbody functions $B_\nu(T)$ for $120 \, \text{K} < T_d < 155 \, \text{K}$ and to multiply the result with $C_{\text{abs}}(T_m)$. The resulting normalized spectrum is shown in Figure 12. With respect to both feature position and width, the emission spectrum of FeO calculated for the temperature range indicated above reproduces the observed 21 $\mu$m band profile fairly accurately, even though no ad hoc assumptions concerning the dust temperature have been made.

For a CDE, quite different spectra of FeO emerge. For a CDE according to Ossenkopf et al. (1992, “CDE-Osk”; it is characterized by a maximum probability for particle shapes close to the spherical shape), the position of the FeO absorption efficiency maximum is shifted to $20.7–21 \, \mu$m, and the band-width changes even more dramatically; i.e., it increases to $6.5–7.6 \mu$m (see Fig. 12). For a CDE with equal probability of all particle shapes, the changes in feature position and shape are even more dramatic, but this kind of shape distribution is unlikely to represent the shapes of circumstellar grains. The assumption that nearly spherically symmetric grains dominate in circumstellar dust shells is more reasonable; hence the “truth” should lie between the CDE-Osk case and the case of spherical particles.

Figure 11 may give the impression that FeO dust can produce a feature comparable to the astronomical 21 $\mu$m emission band only under very particular physical conditions, for example, only for $T < 155 \, \text{K}$, while we know from Hrivnak et al. (2000) that the dust temperatures in the sources of the 21 $\mu$m band can reach 220 K. However, as long as $T < 250 \, \text{K}$, $B_\nu(T)$ will always have its maximum at a wavelength larger than 20 $\mu$m, thus shifting the 19.9 $\mu$m emissivity maximum of FeO to a feature position of 20.0–20.1 $\mu$m. And indeed, $T < 250 \, \text{K}$

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Fig. 10.—Radiative equilibrium temperature of FeO in the radiation field of a star with an effective temperature of 7000 K (solid line). For comparison, the radial temperature profile dust with wavelength-independent optical constants is also shown (dashed line; see also the Appendix). Dotted lines delimit the $r$-range of the brightest part of IRAS 07134+1005.

Fig. 11.—Equilibrium temperatures of amorphous carbon, FeO, and core-mantle particles composed of SiC and SiO$_2$ in the radiation field of an F5 star. The domain from which presumably most of the IR emission of IRAS 07134+1005 comes is indicated by dotted lines.

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3 See the Appendix for a comment on the meaning of the $T(r) \propto r^{-0.4}$ decrease.

4 These values refer to a core volume fraction of 0.5; the larger the (rather transparent) SiO$_2$ mantle, the lower the dust temperature will be.
3.4. Remark on the Elemental Abundances Required to Account for the 21 μm Band

Li (2003) made a very useful estimate of the mass of dust that is required to account for the radiative energy contained in the 21 μm band in the case of IRAS 07134+1005. He pointed out that the Kramers-Kronig equation relates the integral over the absorption efficiency of a grain to its volume and the orientational averaged polarizability \( F \). Since for all materials with a static dielectric constant greater than 4 and for moderately elongated grain shapes, the latter quantity has a value between 0.5 and 1 (Purcell 1969, Fig. 1), there is an upper limit to the integrated absorption efficiency per unit volume, which is more or less the same for the dust species considered here. Consequently, there is also a general upper limit to the energy emitted in the 21 μm band per unit particle mass or, vice versa, a minimum total grain volume for a certain total energy emitted through this band. Hence, the minimum mass derived by Li can be adopted to other materials just by scaling with the mass density of the grain material. This leads to the following conclusion concerning the abundance problem: While the amount of titanium is, according to Li (2003), about 100 times too small to account for the 21 μm band by assigning it to TiC, there is 2.5 times more Fe than would be needed to account for the 21 micron band with FeO (Fe is 250 times more abundant than Ti in HD 56126). Sulfur is 312 times more abundant than Ti in the same star, silicon 1225 times, carbon 34,500 times, and oxygen 36,000 times. Hence, compounds of iron, sulfur, silicon, carbon, and oxygen cannot be excluded as carriers of the 21 μm band in HD 56126 and other objects with comparable elemental abundances.

4. DISCARDED FEATURE CARRIERS

For the sake of completeness, two potential carriers of the 21 μm band that were considered promising candidates (but should no longer be considered as such) will be discussed: silicon disulfide and titanium carbide. In the case of TiC, insurmountable problems with the abundance of titanium exist, whereas SiS\(_2\) can be ruled out by spectroscopic arguments.

4.1. Silicon Disulfide

As mentioned in § 1, the formation of sulfides is very likely in carbon-rich circumstellar environments. Indeed, the 26 μm feature, observed in many sources of the 21 μm feature, is currently ascribed to magnesium sulfide (MgS; Hony et al. 2003).

However, from a spectroscopic point of view, there are problems with ascribing the 20.1 μm band to SiS\(_2\). The main point is that this material has two infrared bands, of which the second, located at 16.8 μm for spherical particles (see Fig. 13), has no counterpart in the astronomical spectra. Furthermore, the position and FWHM of the main SiS\(_2\) band, which amounts to 19.8 and 1.6 μm, respectively, do not agree with the observed characteristics of the 20.1 μm band. For a CDE, this discrepancy becomes smaller, but the problem with the unobserved secondary feature at 16.8 μm becomes even worse, given that the ratio between ~17 and ~20 μm band increases for a CDE. Very low dust temperatures (significantly below 100 K) would be required to make the ~17 μm band negligible in strength compared to the ~20 μm SiS\(_2\) band.

The visual and near-infrared optical constants of SiS\(_2\) have not yet been derived, such that it is not possible to calculate \( T(\tau) \) for SiS\(_2\) based on its radiative energy balance. However, it is hardly conceivable that SiS\(_2\) is so transparent in the visual range as to remain much colder than 100 K over the whole range indicated in Figure 11.

4.2. Titanium Carbide

Even though recent papers by Li (2003) and Chigai et al. (2003) exclude TiC nanoparticles as the carrier of the 21 μm band, we append a discussion of TiC’s infrared properties here, focusing on the relation between bulk TiC and TiC clusters.

Macroscopic TiC has metallic properties, with an absorption index \( k \) that is larger than the refractive index \( n \) throughout the whole infrared range. For \( \lambda > 13 \) μm, both \( n \) and \( k \) are larger than 10. At about 19 μm, a resonance peak occurs, which is rather weak, however, with a relative increase of \( n, k \), and \( C_{\text{abs}} \) by less than 10%.

Small TiC clusters, for example, those composed of \( 4 \times 4 \times 4 \) atoms, behave differently from bulk matter insofar as the
mobility of the cluster electrons is reduced. The lattice resonance is then no longer a small additional term in the dielectric function but the dominant contribution at infrared frequencies. Therefore, a comparatively strong $20 \mu m$ emission band arises from the clusters; its exact position, however, depends on the cluster size. Chigai et al. (2003) derived the following Lorentz oscillator parameters for the small TiC clusters produced by von Helden et al. (2000): a resonance frequency of $488 \text{ cm}^{-1}$, a damping constant of $50.2 \text{ cm}^{-1}$, and an oscillator strength of $187 \text{ cm}^{-1}$. For spherical particles, this translates into a maximum position of the absorption efficiency factor of $20.0 \mu m$ and an FWHM of $2.0 \mu m$. For a CDE, no shift of the band position is found in this case (because of the nonnegative values of the dielectric function of TiC, according to Chigai et al. 2003) but only an increase of the FWHM to $2.2 \mu m$ (for a CDE according to Ossenkopf et al. 1992).

Figure 14 shows the normalized emission of a small TiC cluster (at $T_d = 160$ K), the normalized dust emission arising from macroscopic dust grains (at two different temperatures $T_d = 160$ and $120$ K) and, again for comparison, the profile of the astronomical $21 \mu m$ feature as derived from the ISO spectrum of IRAS 07134+1005. Since the maximum of the absorption efficiency factor of TiC is not evident from Figure 14 as a result of the normalization, it should be added that $C_{\text{abs}}/V$ (TiC) does not exceed $0.6 \mu m^{-1}$. (Depending on the value of $\epsilon_\infty$, $C_{\text{abs}}/V$ may also be substantially smaller). By contrast, the $\sim 20 \mu m$ peak absorption efficiency of cold (100 K) FeO as well as that of amorphous SiO$_2$ amounts to $1.6 \mu m^{-1}$.

5. CONCLUSIONS

Tables 2 and 3 summarize the spectroscopic information on the potential carriers of the $21 \mu m$ feature in two different respects. Table 2 gives an overview of the positions of the absorption efficiency maxima and of the corresponding band-widths. Table 3, on the other hand, refers to normalized dust emission spectra like those shown in Figures 7, 12, 13, and 14 and hence to products of the absorption efficiency with blackbody functions. These products are compared with the repeatedly shown profile of the $21 \mu m$ band; we present the sums (hereafter $\sum \delta^2$) of the squares of the differences between the “profile” and the “dust emission” values, for wavelengths between 17 and 25 $\mu m$ (outside this range, the ISO profile is characterized by comparatively large noise). The “temperature grid” has been chosen so as to cover the range between 160 and 70 K in steps of 10 K. For SiC+SiO$_2$-sp, TiC-sph, and FeO-sph, the minimum of $\sum \delta^2$ occurs at blackbody temperatures between 80 and 90 K. This is due to the asymmetric shape of the profile of the $21 \mu m$ band. On the basis of a symmetric absorption efficiency profile, this asymmetric profile is best reproduced by multiplication with a blackbody of 80–90 K. If, however, the absorption efficiency of the feature carrier has an intrinsically asymmetric profile (as for ellipsoidal SiC+SiO$_2$-core-mantle grains), it is not necessary to assume
such a low dust temperature (120 K are sufficient in this case). The \( \sum \Delta^2 \) values for SiS\(_2\) are particular insofar as they continuously decrease with decreasing temperature, down to less than 70 K. This has a very simple reason: The 16.8 \( \mu \)m secondary band of SiS\(_2\) (see Fig. 13), which has no counterpart in the astronomical spectra, is more suppressed the lower the temperature. As regards the absolute values of \( \sum \Delta^2 \), they are smallest for TiC clusters and second smallest for ellipsoidal SiC+SiO\(_2\) core-mantle grains.

Despite the good spectroscopic fits obtainable with TiC, cold SiC+SiO\(_2\) and cold FeO, we come to the conclusion, on the basis of the properties of the sources of the 21 \( \mu \)m band, that none of the hitherto discussed candidate carriers is a convincing feature carrier particle in all relevant respects. Even though there are oxides that may appear as likely band carriers from a spectroscopical point of view, it is difficult to conceive of a scenario accounting for their formation in carbon-rich PPNs. On the other hand, dust species that are usually predicted to form in carbon-rich environments, such as carbon, carbides, and sulfides, either do not match the observed 21 \( \mu \)m band profile (e.g., SiS\(_2\)) or else their maximum abundance is too small for emitting the energy contained—at least in some cases—in the 21 \( \mu \)m feature (which rules out TiC).

### Table 2

| Candidate Carrier | Particle Shape | \( \lambda (\text{Abs, max}) \) (\( \mu \)m) | FWHM (20) (\( \mu \)m) |
|-------------------|----------------|----------------------------------------|------------------------|
| SiC+SiO\(_2\)     | sph            | 8.1–8.3, 11.0–11.1, 12.5, 19.7–19.8     | 1.9                    |
|                   | CDE-Osk\(^a\)  | 8.2–8.4, 11.1–11.2, 19.8–20.0           | 2.1–2.6                |
| Si+SiO\(_2\)\(^b\)| sph            | 8.0, 12.5, 19.7–19.8                     | 1.8                    |
| FeO\(^b\)         | sph            | 19.9                                     | 2.3                    |
| SiS\(_2\)         | sph            | 16.8, 19.8                               | 1.6                    |
| TiC clusters      | sph            | 20.0                                     | 2.0                    |
| TiC grains        | sph            | 19.2                                     | –                      |

**Notes.**—The observed position and FWHM of the 21 \( \mu \)m band are 20.1 and 2.3 \( \mu \)m, respectively; “sph” stands for spherical particle shape, while “CDE-Osk” designates a continuous distribution of ellipsoids according to Ossenkopf et al. (1992). The \( \lambda (\text{Abs, max}) \) values do not directly represent feature positions, since these result from the product \( C_{\text{abs}} B(T_d) \); for dust temperatures close to 150 K, this leads to a shift toward the red of 0.1–0.2 \( \mu \)m.

\(^a\) Core-mantle particles with SiC core volume fractions between 0.4 and 0.6.

\(^b\) At an average temperature of \( \sim 140 \) K.

\(^c\) Broad bump, FWHM not defined.

### Table 3

| \( T_d \) (K) | SiC+SiO\(_2\)-sph\(^a\) | SiC+SiO\(_2\)-CDE\(^a\) | FeO-sph | TiC-sph | SiS\(_2\)-sph |
|---------------|--------------------------|------------------------|---------|---------|---------------|
| 160           | 5.98                     | 3.10                   | 6.40    | 3.54    | 18.3          |
| 150           | 5.66                     | 2.92                   | 6.03    | 3.29    | 17.8          |
| 140           | 5.31                     | 2.80                   | 5.62    | 3.02    | 17.4          |
| 130           | 4.94                     | 2.71                   | 5.20    | 2.72    | 16.9          |
| 120           | 4.55                     | 2.67                   | 4.78    | 2.41    | 16.4          |
| 110           | 4.14                     | 2.74                   | 4.37    | 2.08    | 15.8          |
| 100           | 3.76                     | 3.00                   | 4.03    | 1.76    | 15.1          |
| 90            | 3.47                     | 3.63                   | 3.87    | 1.50    | 14.3          |
| 80            | 3.42                     | 4.99                   | 4.13    | 1.40    | 13.4          |
| 70            | 4.02                     | 7.94                   | 5.41    | 1.74    | 12.4          |

**Notes.**—Quality of fits to the profile of the 21 \( \mu \)m band for different mean dust temperatures \( T_d \) (between 130 and 70 K). As an indicator for the quality of an individual fit, the sum \( \sum \chi^2 \) of the squares of the differences of "normalized 21 \( \mu \)m flux" minus \( C_{\text{abs}} B(T_d) \) has been calculated for 17 \( \mu \)m < \( \lambda < 25 \) \( \mu \)m. This sum corresponds to the usual \( \chi^2 \) insofar as the quantities subtracted from each other are already normalized.

\(^a\) Core-mantle particles with a SiC core volume fraction of 0.5.
mantles on top of SiC. Core-mantle particles composed of SiC and SiO$_2$ if colder than 150 K, emit mainly through the lower energy band of SiO$_2$. Thus, they can in principle account for the 21 μm band, even though the reproduction of the feature profile is not as good as in the case of cold FeO.

But there is a major problem with any scenario involving oxides as band carriers, the difficulty of explaining how oxides can form or at least survive in carbon-rich PPNs. It is hardly conceivable that the carrier of the 21 μm band is just a remnant of the oxygen-rich outflow phase of the respective former AGB stars. The interval between the oxygen-rich phase and the carbon-rich PPN phase is too long as to account for a colocation, as proven for HD 56126, of products of the C-rich and the O-rich phase. The remnants of the O-rich phase are expected to be located at least 1 order of magnitude farther out on a radial scale than the products of the C-rich phase. How, then, can either SiC be oxidized or FeO form/survive in C-rich environments? As for the first process, there are several studies showing that complete transformation of SiC to SiO$_2$ occurs at temperatures above 700 K (e.g., Mendybaev et al. 2002; Tang & Bando 2003); provided that large defect surfaces as those of nanograins are available for the reaction, the formation of SiO$_2$ mantles on top of SiC grains also takes place at room temperature as our laboratory experiments indicate (see Fig. 3). But why should this SiO$_2$ mantle formation take place preferentially in PPNs with C/O ratios close to or larger than unity? This question, unfortunately, has to remain open. As for the hypothesis that FeO is the carrier of the 21 μm band, it would require the oxidation of Fe to FeO in cold circumstellar environments. It seems that metal-poor PPNs such as HD 56126—paradoxically, at first glance—provide good conditions for FeO formation, since this process requires the presence of small metallic iron grains. The absence of any feature attributable to FeO in the vast majority of the planetary nebulae, on the other hand, could be accounted for by the fact that FeO can persist in only a narrow range of equilibrium between oxidation (to higher iron oxides) and reduction (to metallic iron). Thus, in PNs, FeO is probably reduced to metallic iron.

3. Quantum size effects critically influence the optical properties of very small grains and clusters. Phonon modes can shift when the lattice changes from “infinite” to finite size, and conductivity may be reduced. For the TiC grainlets proposed as carriers, this means that a 21 μm band would only occur for clusters and particles in a very narrow size range. This makes it unlikely that there would be a sufficient number of TiC particles in the PPNs to account for the observed band strength, given that the predicted Ti abundance is not large enough and that mantling by amorphous carbon will reduce the band strength even further.

4. Any identification or ruling out of a candidate carrier is strengthened if it has not only one but two or more observable infrared bands. If these bands are separated by ≥10 μm, the secondary bands may be suppressed by temperature effects. This is likely to occur for the 11 μm SiC band expected to arise from the core-mantle particles mentioned above. However, in the case of SiS$_2$, even temperatures on the order of 100 K will not be sufficient to suppress the 16.8 μm secondary emission feature. The multiband identification problem also sets constraints on bands produced by impurities, because the impurity-induced bands are usually much weaker than the phonon bands of the respective matrix materials (which provides a further argument against doped SiC as the carrier of the 21 μm feature).

We thank Gabriele Born, Jena, for preparing our samples. Ingrid Hodous, Vienna, kindly provided us with the ISO spectra of IRAS 07134+1005 and SAO 34504, reduced with the ISO spectral analysis package ISAP. An anonymous referee contributed substantial arguments to the original version of this paper and thereby improved it. T. P. received a DOC grant from the Austrian Academy of Sciences. H. M. acknowledges support by DFG grant Mu 1164/5.

**APPENDIX**

**ON THE TEMPERATURE PROFILE AND SED OF GEOMETRICALLY THIN PPN DUST SHELLS**

In the previous sections, calculations of the radiative equilibrium temperature of the sources of the 21 μm feature have been presented. The temperature profiles in turn have been partly used to calculate model spectra. We append a discussion of the method used for the dust temperature ($T_d$) calculation, as well as of the influence of $T_d$ on the emerging SEDs.

In the radiative equilibrium case and for optically thin shells (where backwarming effects can be neglected), the radial variation of $T_d$ is derived from the following energy balance:

$$
\int_0^\infty 2\pi a^2 Q_{abs}(\lambda) \pi B_s(\lambda, T_{eff}) \frac{R^2}{R(T_d)} d\lambda = \int_0^\infty 4\pi a^2 Q_{abs}(\lambda) \pi B_s(\lambda, T_d) d\lambda.
$$

(A1)

The first term describes the energy absorbed by an individual dust grain with a radius $a$ and an absorption efficiency factor $Q_{abs}(\lambda)$ in a stellar radiation field $B_s(\lambda, T_{eff})$ ($T_{eff}$ denotes the effective stellar temperature); the second term describes the energy emitted by the same dust grain. The parameter $R_{eff}$ is the effective stellar radius, whereas $R(T_d)$ is the distance of the grain with temperature $T_d$ from the star. While the above integral runs from zero to infinity, numerical integration can of course be performed only between a certain lower ($\lambda_{min}$) and a certain upper limit ($\lambda_{max}$). We chose $\lambda_{min} = 0.05$ μm and $\lambda_{max} = 500$ μm. It is difficult, however, to derive the values of $Q_{abs}$ close to $\lambda_{min}$; some of the sets of optical constants have to be extrapolated to UV wavelengths since measurements of the UV properties of cosmic dust analogs are still lacking. For FeO, for example, our measurements extend to 0.2 μm; beyond this wavelength, both $n$ and $k$ were assumed to be constant. Any other assumption, and even the choice $\lambda_{min} = 0.2$ μm, would not significantly change our results.

We recall that simple power-law models for $Q_{abs}(\lambda)$ make it possible to solve equation (A1) analytically for $T(r)$. For $Q_{abs}(\lambda) \propto 1/\lambda$, the case corresponding to small dust particles with wavelength-independent (in practice, weakly wavelength-dependent) optical constants $n$ and $k$, $T(r)$ decreases with $1/r^{0.4}$. This solution to equation (A1) has been plotted in Figure 10. [For the more theoretical case $Q_{abs}(\lambda) = const.$, $T(r)$ decreases with $1/r^{0.5}$]
In the body of our paper, it was shown that the temperature range corresponding to the measured spatial extension of a typical PPN such as HD 56126 is comparatively narrow for all the dust species examined. The ratio between the temperature at the outer and the temperature at the inner dust shell edge (i.e., its dense observable part) is typically on the order of 1.3. This has an important consequence for the calculation of the dust shell’s SED. Again in the optically thin case, the latter is given by

\[ F_d(\lambda) = c \times Q_{abs}(\lambda) \int_{r=1}^{r=R_{\text{out}}/R_{\text{in}}} B_k[\lambda, T_d(r)] \, dr, \]  

(A2)

where \( c \) is a product containing the dust column density, the average geometrical cross section of the dust grains, and the surface of the inner dust shell boundary (e.g., Schutte & Tielens 1989). If \( R_{\text{out}}/R_{\text{in}} \) is indeed on the order of 2 (as for HD 56126 according to the observations of Kwok et al. 2002 and Miyata et al. 2003), the result of the integral on the right-hand side of equation (A2) is surprisingly similar to a single blackbody function for a temperature intermediate between \( T_d(R_{\text{in}}) \) and \( T_d(R_{\text{out}}) \). This effect is shown in Figure 15, where we have set \( c = 1 \) and \( Q_{abs}(\lambda) = 1 \) for simplicity.

It is evident from this figure that the SED calculated for a geometrically thin circumstellar shell (using realistic absorption efficiencies) according to equation (A2) depends much more on the order of magnitude of the dust temperature (i.e., on whether the mean dust temperature amounts to 175 or 125 K) than on actually calculating a weighted average of Planck functions.

On the other hand, even a reasonably good estimation of the mean dust temperature \( T_d(r) \) is difficult without any information on the values of \( Q_{abs}(\lambda) \) in the visual and near-infrared range. For SiS and TiC, for example, no optical constants for wavelengths smaller than 10 \( \mu \)m are available. Hence, the SEDs emerging from dust shells composed of these grain species can only be calculated by arbitrarily assuming mean \( T_d \)-values for them.

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