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Formation of SiC grains and the 11.3µm feature in circumstellar envelopes of carbon stars

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Abstract. We propose that the so–called 11.3µm emission features observed toward carbon stars can be attributed to small spherical core–mantle type grains consisting of a SiC core and a carbon mantle or small carbon grains containing SiC as an impurity. Based on the optical constants measured from bulk α–SiC, we show that as the volume fraction of the carbon mantle increases, the peak wavelength of the absorption shifts towards longer wavelengths, the strength decreases, and the band width becomes wider; the emission peak appears at 11.3µm for a volume fraction of 0.4. This behaviour would explain a variety of SiC features observed toward infrared carbon stars.

The possibility for the formation of the proposed core–mantle dust grains in circumstellar envelopes of carbon stars has been investigated by applying a theory of homogeneous nucleation and grain growth. Using a simple model for circumstellar envelopes, we demonstrate that the nucleation of SiC grains always precedes that of carbon grains when the non–LTE effect, i.e. the difference between the temperatures of gas and small clusters, is taken into account. In the case of mass loss rates $|\dot{M}| \lesssim 1.5 \times 10^{-5} M_\odot$/yr, the SiC grains are gradually coated by carbon and show a distinctive emission feature around 11.3µm. Otherwise, the condensation of SiC and carbon simultaneously occurs after an avalanche of the formation of SiC nuclei and the emission feature is almost suppressed for $|\dot{M}| \gtrsim 1.5 \times 10^{-5} M_\odot$/yr.

The radiation pressure force acting on these dust grains is sufficient to drive the mass loss of carbon stars when the volume fraction of carbon is larger than 0.1. The profile of the 11.3µm feature can be a diagnostic mean of the formation process of dust grains prevailing in circumstellar envelopes of carbon stars and well reflects the differences in the mass loss rate and the evolutionary stage.

Key words: carbon stars – circumstellar matter – dust – infrared: stars

1. Introduction

Almost all carbon stars show an emission feature around 11.3µm. It is well–established that the so–called 11.3µm features is due to SiC grains condensed in circumstellar envelopes of carbon stars. Historically, SiC grains in the atmospheres of carbon stars have been predicted based on chemical equilibrium calculations (Gilman 1969; Friedemann 1969). The 11.3µm feature was discovered by Hackwell (1972). Treffers & Cohen (1974) analyzed the shape of the feature. Goebel et al. (1980) identified the observed feature with that of SiC grains comparing the laboratory spectra of the powder samples measured by Dorschner et al. (1977). Isotopic anomalies of presolar SiC grains discovered in carbonaceous meteorites strongly support the formation of SiC grains in carbon–rich AGB stars (Tang et al. 1989, Virag et al. 1992, Lewis et al. 1994).

Little–Marĕnin (1986) analyzed the spectra of bright stars in the IRAS LRS class 4n and showed a striking uniformity of the emission feature due to SiC grains peaking at about 11.15µm in comparison to the great variations of the silicate features of the stars in class 2n. On the other hand, the statistical analysis of the stars in LRS class 4n and 1n by Baron et al. (1987) and Papoular (1988) revealed some more variety of the emission features. They classified the stars according to the strength of the emission feature and suggested that the emission features of some sub–classes are in good agreement with the mass absorption spectra of pure or polluted α–SiC powders measured by Borghesi et al. (1985). The emission feature is very weak or absent in the spectra of extreme carbon stars with optically very thick circumstellar envelopes. From radiative transfer calculations using the optical constants derived from the measurement of α–SiC powders, Lorenz–Martins & Lefèvre (1993, 1994) have claimed a correlation of the number ratio of SiC to amorphous carbon grains with the optical depth of circumstellar envelopes as well as with the mass loss rate of carbon stars.

Although the 11.3µm feature is attributed to α–SiC grains based on the comparison with the laboratory measurement of the powder samples, it should be kept in mind that the peak wavelength, the shape and the width of the spectra are sensitive

to the preparation procedure of the samples as already noted by Dorschner et al. (1977) and Borghesi et al. (1985). The optical constants tabulated by Choyke & Palik (1985) based on the measurement of the bulk α–SiC samples (Spitzer et al. 1959) are completely different from those derived from the measurements of the powder samples (Pégourié 1988). As discussed in the textbook by Bohren & Huffman (1983), the appearance of the resonance features of small SiC grains is very sensitive to the size, the morphology, and the chemical composition of impurities as well as the surrounding medium. This fact strongly suggests that the variety of emission features assigned to SiC grains is closely related with the formation process of the dust grains in the circumstellar envelopes of carbon stars, reflecting the difference in the physical and chemical conditions.

The aim of this paper is to elucidate the nature of the so-called 11.3μm feature in relation to the formation process of SiC grains in the circumstellar envelopes of carbon stars. We shall show in Sect. 2 that a single–peaked and smooth spectral feature similar to the observed 11.3μm features can be realized by small spherical SiC grains coated by carbon, using the optical constants obtained from the measurements of the bulk α–SiC sample. In Sect. 3, we consider the formation process of SiC grains taking into account a non–LTE effect, i.e. the difference between the temperatures of the gas and small clusters. This investigation is based on a theory of homogeneous nucleation and grain growth with a simple model for circumstellar envelopes of carbon stars. It is shown that the nucleation of SiC grains always precedes that of carbon grains and leads to the formation of dust grains consisting of a SiC core and a carbon mantle or carbon grains containing SiC as an impurity according to the mass loss rate. The concluding remarks are presented in Sect. 4.

2. The spectral feature of SiC grains

Silicon carbide is an ionic crystal and shows a variety of crystalline forms because of a large number of hexagonal and rhombohedral modifications. The absorption spectra of the powder samples of α–SiC (hexagonal form) and β–SiC (cubic form) have been usually measured in relation to the 11.3μm emission feature observed toward carbon stars (Dorschner et al. 1977; Stephens 1980; Borghesi et al. 1985). The optical constants of α–SiC around 11μm derived from the measurements of absorption spectra of the powder samples (Pégourié 1988) are completely different from those obtained from the measurement of the bulk sample (Spitzer et al. 1959). Friedemann et al. (1981) pointed out that the optical constants derived from the bulk sample cannot reproduce the absorption spectrum of the powder samples. The reason for that difference must be related to shape and clustering effects which have to be considered in either case, in the derivation of optical constants from absorption spectra of powder samples as well as in reproducing their absorption spectra with bulk optical constants. The inclusion of shape and clustering effects is especially important in resonant regions for the optical constants (Stognienko et al. 1995).

The bulk α–SiC has a lattice longitudinal vibration mode at $\lambda_L = 10.3$μm and a lattice transverse vibration mode at
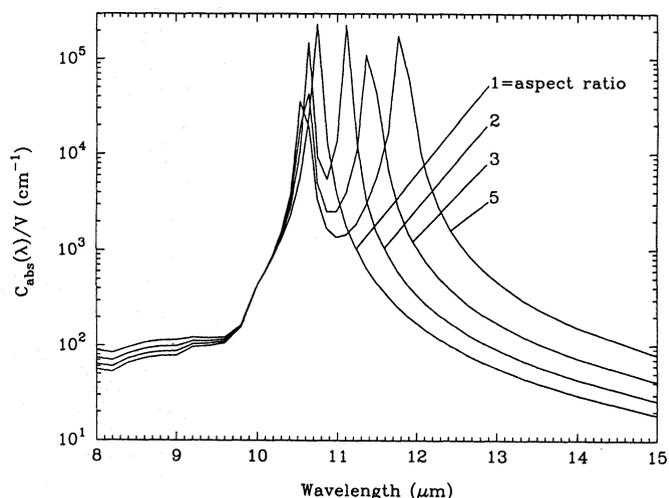

Fig. 1. Absorption cross sections per unit volume of prolate SiC grains in the Rayleigh limit with the aspect ratios of the main axes ranging from 1 to 5

$\lambda_T = 12.6$μm. As discussed by Bohren & Huffman (1983), small SiC grains show characteristic absorption spectra called Fröhlich bands arising from surface modes at wavelengths falling between λ_L and λ_T; as an example, a small spherical α–SiC grain shows a very sharp and strong absorption feature at 10.75μm but not at 11.3μm if we use the optical constants tabulated by Choyke & Palik (1985). The shape and strength as well as the number and position of the bands are very sensitive to the shape and the size of dust grains, and are also strongly affected by the chemical composition of impurities as well as the surrounding medium. Referring to those facts, Borghesi et al. (1985) discussed the variation of the absorption spectra from a powder sample to another.

The variety of the 11.3μm features revealed by the statistical analysis of IRAS LRS class 4n and 1n stars (Baron et al. 1987; Papoular 1988) may be closely related to the sensitivity of the spectral feature arising from the surface mode of SiC grains as described above. Here we shall demonstrate what kind of SiC grains exhibits a spectral feature similar to the observed 11.3μm feature, by changing the shape of dust grains and their chemical composition. We use the optical constants of α–SiC tabulated by Choyke & Palik (1985) and of glassy carbon measured by Edoh (1983, see the table in Hanner 1988). Considering the formation of SiC grains in circumstellar envelopes of carbon stars, we can imagine that the shape may be different from the shape of a sphere, and that SiC condenses on carbon grains or SiC grains are coated by carbon.

Figure 1 shows the absorption cross sections per unit volume around the resonance features of prolate SiC grains with different aspect ratios in the Rayleigh limit. As the shape departs from sphericity, a single absorption feature peaking at 10.75μm splits into a double feature. With increasing aspect ratio, the peak positions approach λ_T and λ_L, and the strength decreases. We can easily see from Fig. 1 that the spectral feature tends to be rectangular when we apply the continuous distribution of el-
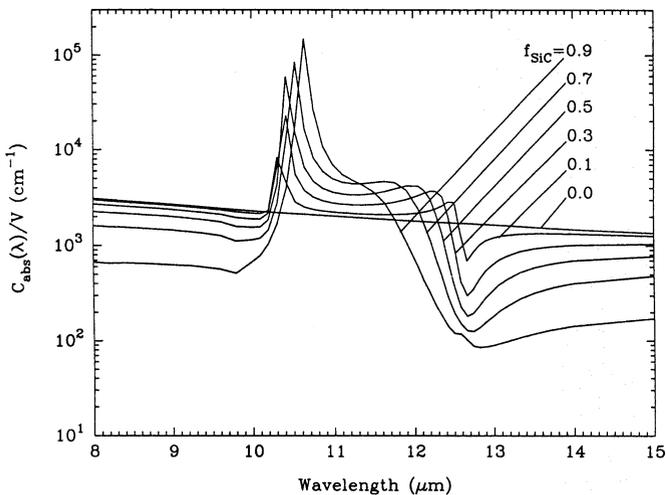
Fig. 2. Absorption cross sections per unit volume of core–mantle type grains consisting of a carbon core of radius 0.01μm and a SiC mantle whose volume fractions range from 0.1 to 0.9

lipsoidal shapes (CDE) (see Bohren & Huffman 1983). Though Cohen (1984) has suggested the rectangular emission features in the spectra of optically identified carbon stars, the prolate SiC grains cannot reproduce the single and smooth emission features obtained from the analysis of IRAS LRS data (Little–Marenin 1986; Baron et al. 1987). Of course, we cannot exclude the possibility that a shape distribution can be found that reproduces a single and smooth absorption feature similar to the observed feature as demonstrated by Treffers & Cohen (1974).

Chemical equilibrium calculations predict that the condensation of carbon grains precedes that of SiC grains in a gas with the ratio C/O $\gtrsim$ 1. (see Gilman 1969 for example). In this case, it is possible for carbon grains to act as condensation sites for SiC. This results in the formation of core–mantle type grains consisting of a carbon core and a SiC mantle. The absorption cross sections per unit volume are presented in Fig. 2 for the volume fractions f_{SiC} of the SiC mantle ranging from 0.1 to 0.9, where the radius of the carbon core is 0.01μm. As the volume fraction of the SiC mantle increases, an absorption peak and a dip appear around λ_L and λ_T, respectively, and the absorption feature shifts towards longer wavelengths up to 10.75μm with increasing strength. In the circumstellar envelopes of carbon stars with C/O = 1.5, the volume fraction of the SiC mantles is to be less than 0.05 under the assumptions that all silicon atoms are locked into SiC and the remaining carbon atoms which are not locked into CO molecules are available for the formation of carbon grains. Thus, the emission feature arising from this type of grains is very weak. The features appear only around the wavelengths corresponding to the lattice vibration modes, and are completely different from the emission features observed toward carbon stars.

Contrary to the prediction of chemical equilibrium calculations, however, Lefèvre (1979) and McCabe (1982) have claimed that SiC grains condense close to stellar photospheres due to the inverse greenhouse effect and carbon grains con-

dense in the outer regions due to the greenhouse effect. Also a recent laboratory experiment of condensation of SiC grains from a mixture of molecular gases has shown that the formation of SiC grains occurs at a very high temperature (Frenklach et al. 1989), although the experimental conditions are very far from the conditions in circumstellar envelopes of carbon stars. If this scheme is correct, we can expect the formation of core–mantle type grains consisting of a SiC core and a carbon mantle. Figures 3a and 3b show the absorption cross sections per unit volume of the core–mantle type grains calculated by changing the volume fraction f_C of the carbon mantle from 0.1 to 0.9; the radius of the SiC core is 0.01μm in Fig. 3a and 0.1μm in Fig. 3b. This core–mantle type grain is characterized by a single absorption peak. A small satellite feature appears at the wavelength of the lattice transverse vibration mode of bulk SiC if the radius of the SiC core is larger than 0.05μm, which is, however, completely depressed as the volume fraction of the carbon mantle increases. With increasing volume fraction of the carbon mantle, the peak wavelength shifts towards the longer wavelengths, the peak strength decreases and the bandwidth becomes wider.

Anyway, the core–mantle type grains consisting of a SiC core and a carbon mantle can show a single–peaked and smooth feature around 11.3μm similar to the feature observed toward carbon stars. The absorption peaks around λ_p = 11.2μm for a volume fraction of the carbon mantle f_C = 0.3 and around 11.4μm for f_C = 0.5. It should be noted that the absorption cross section of core–mantle type grains in the Rayleigh limit is equivalent to that of composite grains containing the core material as an impurity, which can be calculated by applying the Maxwell–Garnett theory (see Bohren & Huffman 1983). Therefore, the results of calculations presented in Figs. 3 are true for small carbon grains containing SiC as an impurity if the volume fraction of carbon is much larger than that of SiC.

The behaviour of the absorption feature as a function of the volume fraction of the carbon mantle seems to be consistent with the variation of the emission features derived from the statistical analysis of carbon stars in the IRAS LRS class 4n by Baron et al. (1987) and Papoular (1988): They divided the carbon stars in class 4n into 6 sub–classes according to the strength of the emission feature at 11.3μm. Except for the sub–class 6, we can see from Fig. 9 in Papoular (1988) that the peak wavelength shifts toward 11.7μm as the strength of the 11.3μm decreases. The decrease of the strength at 11.3μm accompanies the increase of a feature at 8.8μm which are considered to be attributed to a–C:H, while they claimed that the 11.7μm feature is a sub–feature whose origin is the same as that for the 8.8μm feature. Otherwise, they suggested that the behaviour of the 11.3μm feature is closely related with dust grains producing the underlying continuum. Furthermore the variation of emission features of MS and S stars obtained from the analysis of IRAS LRS (Little–Marenin & Little 1988) could be interpreted in terms of the difference of the volume fraction of the carbon mantle reflecting the difference in the C/O ratios of these stars. The strong S stars have a spectral feature around 10.8μm, although the variation of the features of MS and S stars is con-
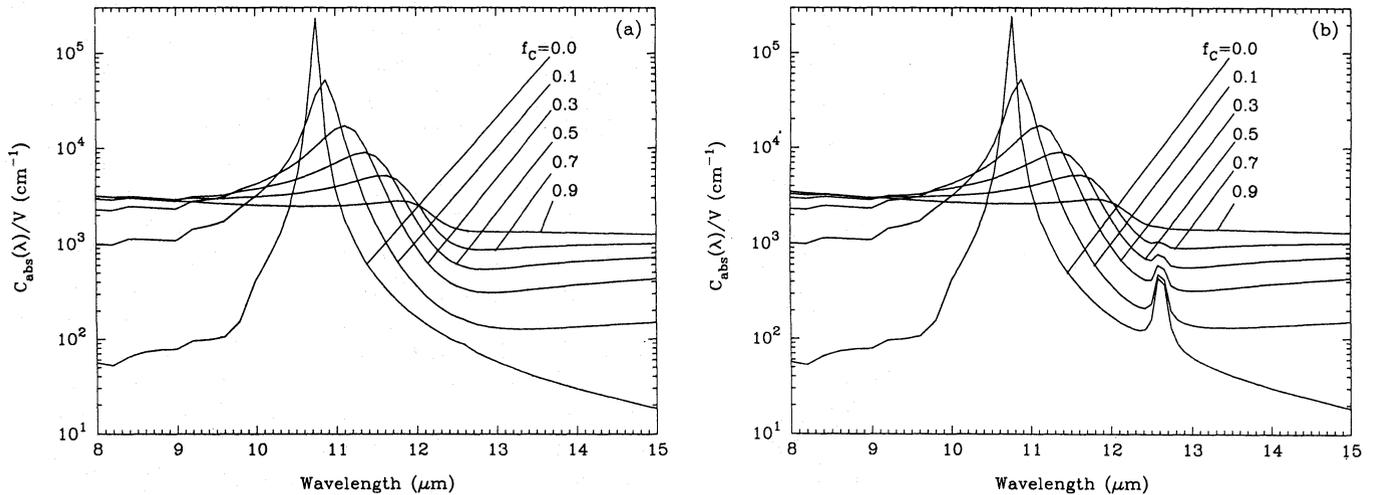
Fig. 3a and b. Absorption cross sections per unit volume of the core–mantle type grains consisting of a SiC core and carbon mantles whose volume fractions range from 0.1 to 0.9. The radius is of SiC core is **a** 0.01μm and **b** 0.1μm

sidered to be reproduced by a simple mixture of silicate and SiC features.

We propose that the core–mantle grains consisting of a SiC core and a carbon mantle are the most plausible candidate to reproduce the 11.3μm feature observed towards infrared carbon stars. If this model is correct, we must be careful to derive the emission feature by subtracting the underlying continuum because both components have the same origin. This aspect should be investigated by radiative transfer calculations using the core–mantle type grains. Also the possibility of the formation of such dust grains should be explored for circumstellar envelopes of related stars. In the next section we will investigate the formation of dust grains in circumstellar envelopes of carbon stars.

3. Formation of SiC grains

So far the dust formation in circumstellar envelopes around carbon stars has been extensively studied by the German group in a series of papers following Gail & Sedlmayr (1984); see Sedlmayr (1994) for the references of the papers. However, they did not treat the formation of SiC grains because it is generally assumed that SiC grains themselves have only a minor influence on the dynamical structure of circumstellar envelopes as well as the emergent flux. On the other hand, being closely related with the behaviour of the 11.3μm feature, the understanding of the formation process of SiC grains is very important not only to reveal the physical conditions prevailing in the circumstellar envelopes, but also to get insight into the nucleation process which is still a controversial subject.

Chemical equilibrium calculations predict that the condensation of SiC follows after carbon grain condensation in an environment where the C/O ratio is larger than 1. However, taking into account the inverse greenhouse effect for SiC grains, Lefèvre (1979) and McCabe (1982) have claimed that SiC grains condense close to stellar photospheres and then carbon grains condense. However, it should be noted that their conclusion is

only based on a necessary condition for the formation of SiC grains; even if the supersaturation ratio is greater than 1, dust grains do not always condense. We must consider the nucleation process taking into account the non–LTE effects, i.e. the difference between the temperatures of gas and small clusters.

In this section, we formulate a theory of nucleation and grain growth taking into account the non–LTE effect with the assumption that the lattice vibration temperature of small clusters is independent of the cluster size. Then the theory is applied to the formation of carbon and SiC grains in circumstellar envelopes of carbon stars.

3.1. A theory of nucleation and grain growth

The steady–state homogeneous nucleation rate is derived from a master equation describing the growth and decay processes of small molecular clusters. The growth rate $\alpha_{n+1}(T)$ of an n–mer in a gas of temperature T is determined by the collisional frequency of monomer molecules with an n–mer, which is given by

$$\alpha_{n+1}(T) = \alpha_s s_n \left(\frac{kT}{2\pi m} \right)^{\frac{1}{2}} c_1, \tag{1}$$

where α_s is the sticking probability, s_n the surface area of the n–mer, k the Boltzmann constant, m the reduced mass of the monomer m_1 and the n–mer m_n, and c_1 the concentration of monomer molecules. The decay rate of the $(n + 1)$–mer can be related to the growth rate of the n–mer by using the principle of detailed balance. However, it should be kept in mind that the lattice vibration temperature T_{n+1} of the $(n + 1)$–mer, which determines the decay rate, is not always the same as the gas kinetic temperature T, in particular in a radiation field. Using equilibrium concentrations $\overset{\circ}{c}_n$ and $\overset{\circ}{c}_{n+1}$ at the temperature T_{n+1}, the decay rate β_{n+1} of the $(n + 1)$–mer can be written as

$$\beta_{n+1}(T_{n+1}) = \frac{\overset{\circ}{c}_n}{\overset{\circ}{c}_{n+1}} \alpha_{n+1}(T_{n+1}). \tag{2}$$

Under the assumption that the lattice vibration temperature T_v of a small cluster is independent of n, i.e. $T_n = T_v$, but is not equal to the gas temperature, the steady–state homogeneous nucleation rate J is given by

$$J = \left(\sum_{n=1}^{\infty} \frac{\prod_{j=1}^{n} \gamma_{j+1}}{\alpha_{n+1}(T) \mathring{c}_n(T_n)} \right)^{-1}, \tag{3}$$

where

$$\gamma_j = \frac{\alpha_j(T_v)}{\alpha_j(T)}, \quad \text{and} \quad \gamma_1 = 1. \tag{4}$$

The equilibrium concentration $\mathring{c}_n(T_v)$ of the n–mer at the temperature T_v is given by

$$\mathring{c}_n(T_v) = c_1 \exp(-\Delta G_n / kT_v). \tag{5}$$

The change in the Gibbs free energy of formation $\Delta G_n(T_v)$ from the vapor to n–mer under the capillary approximation is expressed by

$$\frac{\Delta G_n(T_v)}{kT_v} = -(n-1)\ln S(T_v) + (n-1)^{\frac{2}{3}} \frac{4\pi a_0^2 \sigma}{kT_v}, \tag{6}$$

where S is the supersaturation ratio at the temperature T_v, a_0 the volume equivalent monomer radius in and σ the surface tension of the condensate. Then the Eq. (3) is reduced to the usual form

$$J = \left(\sum_{n=1}^{\infty} \frac{1}{\alpha_{n+1}(T) c_1} \exp\left[\Delta \tilde{G}_n(T_v, T)/kT_v \right] \right)^{-1}, \tag{7}$$

where

$$\frac{\Delta \tilde{G}_n(T_v, T)}{kT_v} = \frac{\Delta G_n(T_v)}{kT_v} + (n-1)\ln\left(\frac{T_v}{T} \right)^{\frac{1}{2}}. \tag{8}$$

The quantity $\mu = 4\pi a_0^2 \sigma / kT_v$ representing the energy barrier for nucleation and the modified supersaturation ratio $S' = S(T_v)(T/T_v)^{1/2}$ being introduced, the steady–state homogeneous nucleation rate taking into account the non–LTE effect can be written as

$$J = \alpha_s \Omega_0 \left(\frac{2\sigma}{\pi m_1} \right)^{\frac{1}{2}} \left(\frac{T}{T_v} \right)^{\frac{1}{2}} c_1^2 \exp\left[-\frac{4\mu^3}{27(\ln S')^2} \right], \tag{9}$$

where Ω_0 and m_1 are the volume and the mass of a monomer molecule in a condensate, respectively. This formula is almost the same as that for the LTE case, except for the appearance of the term $(T/T_v)^{1/2}$ and the modification of the supersaturation ratio. The extension of the formula to that taking into account chemical reactions at nucleation is also straightforward by considering that the least abundant molecular species, i.e. "the key species", among molecular species related to dust formation controls the kinetics of the nucleation and grain growth as formulated by Kozasa & Hasegawa (1987).

The process of nucleation and grain growth is determined by two equations; the equation of continuity for the key species and the equation of grain growth, which are given by

$$c_1(t)U(t) - c_1(0)U(0) = -\int_0^t U(t') J(t') \frac{4\pi}{3\Omega_0} r^3(t, t') \mathrm{d}t' \tag{10}$$

and

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \alpha_s \Omega_0 \left(\frac{kT}{2\pi m_1} \right)^{\frac{1}{2}} c_1(t) \left(1 - \frac{1}{S'} \right), \tag{11}$$

respectively. Here the specific volume $U(t)$ is defined so that $c_1(t)U(t)$ is conserved if nucleation and growth do not occur. The origin of time is set to a time when the modified supersaturation ratio $S' = 1$. We can approximately solve both equations, noting that the nucleation rate has a maximum due to the depletion of the key species caused by grain growth as the gas cools down.

Here, we briefly summarize the method; see Kozasa & Hasegawa (1987) for the details. Under the approximation that in the initial stage the depletion of monomer molecules due to the grain growth is negligible, i.e. $Y = c_1(t)U(t)/c_1(0)/U(0) \sim 1$, we introduce non–dimensional quantities characterizing the process of nucleation and grain growth $X = \ln S'$ and $\Lambda = \tau_{coll}/\tau_{sat}$; the collision time τ_{coll} and the saturation time τ_{sat} are defined by

$$\tau_{coll}^{-1} = \alpha_s 4\pi a_0^2 \left(\frac{kT}{2\pi m_1} \right)^{\frac{1}{2}} c_1(t), \tag{12}$$

and

$$\tau_{sat}^{-1} = \frac{\mathrm{d}\ln S'}{\mathrm{d}t} = \frac{\mathrm{d}X}{\mathrm{d}t}. \tag{13}$$

Then we can determine the condensation time which is defined as the time when the nucleation rate has a maximum, by solving the equation

$$\frac{\delta_2}{108} \Lambda_c^4 \left(\frac{\mu_c}{\pi} \right)^{\frac{1}{2}} \frac{X_c^9}{a_c^6} \exp\left(-\frac{a_c^2}{X_c^2} \right) = \left(1 + \frac{1}{W_c} \right)^{-1}, \tag{14}$$

where the subscript "c" denotes the quantities at the condensation time, and δ_2 is a numerical constant determined by the chemical reaction at nucleation, $a^2 = 4\mu^3/27$, and $W_c = \delta_2 a_c^2 / X_c^3$. The number density of dust grains N_{gr} is given by

$$\frac{N_{gr}}{c_{1c}} = \frac{\delta_2}{3} \Lambda_c \left(\frac{\mu_c}{2} \right)^{\frac{1}{2}} \frac{1}{W_c} \exp\left(-1 - \frac{a_c^2}{X_c^2} \right), \tag{15}$$

where c_{1c} is the concentration of the key species at the condensation time in the case of no depletion due to grain growth. The average final grain radius r_∞ expected in the case that all molecules of the key species are locked into dust grains is given by

$$r_\infty = a_0 \left(\frac{N_{gr}}{c_{1c}} \right)^{\frac{1}{3}}. \tag{16}$$

3.2. A model for circumstellar envelopes

We adopt a simple model for circumstellar envelopes of carbon stars to investigate the formation of dust grains. We assume that the circumstellar envelope is spherically symmetric and the gas flow is in a steady state. For a given stellar luminosity L_*, effective temperature T_* and mass loss rate $|\dot{M}|$, the spatial gas density $\rho(r)$ is given by

$$\rho(r) = 3.644 \times 10^{-13} \left(\frac{T_*}{2500K}\right)^4 \left(\frac{1 \times 10^4 L_\odot}{L_*}\right) \tag{17}$$
$$\times \left(\frac{|\dot{M}|}{1 \times 10^{-5} M_\odot}\right)\left(\frac{1\,Km/sec}{v}\right)\left(\frac{r_*}{r}\right)^2 \quad (g/cm^3),$$

where v is the gas velocity, r the distance from the center of the star and r_* the radius of the photosphere. The gas temperature $T(r)$ at r is assumed to be determined by the dilution of the stellar radiation and is given by

$$T(r) = W(r)^{\frac{1}{4}} T_*, \tag{18}$$

with the geometric dilution factor defined by

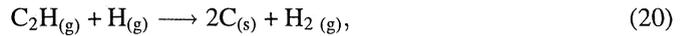$$W(r) = \frac{1}{2}\left(1 - \sqrt{1 - \left(\frac{r_*}{r}\right)^2}\right). \tag{19}$$

The mass loss from carbon stars is considered to be driven by the radiation pressure forces acting on dust grains condensed in the circumstellar envelope. In this case, dust formation occurs at the place close to the so-called sonic point as discussed by Kozasa et al. (1984) and Gail & Sedlmayr (1985, 1987). Thus, for simplicity of the calculation of the dust grain condensation, we assume that the gas velocity is constant and put $v = 2$ km/sec in what follows.
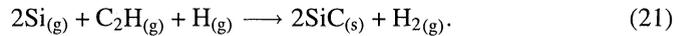
3.3. Condensation of dust grains

We treat here the formation of carbon and SiC grains, using the modified theory of nucleation and grain growth discussed in Sect. 3.1 and a simple model of circumstellar envelopes given in Sect. 3.2. First, we must consider from what kind of gas species the dust grains condense. As shown in chemical equilibrium calculations (e.g. Cherchneff & Barker 1992), gaseous SiC molecules are almost absent, and we must consider a chemical reaction of gas species to realize the formation of SiC grains.

The abundance of molecular species is considered to be in chemical equilibrium close to the stellar photosphere. Figures 4a and 4b show the result of the chemical equilibrium calculation for the radial distribution of the molecular abundances in terms of the fractions of C and Si atoms locked into molecular species, in a gas flow modeled in Sect. 3.1, where $|\dot{M}| = 10^{-5} M_\odot$/yr and the C/O ratio is 1.5; Fig. 4a for C and Fig. 4b for Si. The elemental abundances except for carbon were taken from the table of Anders & Grevesse (1989) and the thermodynamical data from the JANAF tables (Chase et al. 1985), except for the C_2H_2 gas which is taken from a table in Cherchneff et al. (1992). The calculation was performed by the method of the minimization of the Gibbs free energies.

As the gas moves outwards, the molecular abundances depart from those of the chemical equilibrium and are quenched due to the decrease of gas density and temperature. In the circumstellar envelopes of some carbon stars, carbon-bearing molecules such as C_2H, C_2H_2, HCN and Si-bearing molecules such as SiS and SiC_2 are observed (McCabe 1982). Referring to the chemical equilibrium calculations and the observations, we assume that the molecular abundances in circumstellar envelopes are quenched at temperatures ranging from 1800 to 1600 K. In this region, the most abundant C-bearing molecule is C_2H, almost all Si is in atomic form, and the number densities of H and H_2 are almost the same. Then we consider the formation of carbon and SiC grains, respectively, through the following chemical reactions;

$$C_2H_{(g)} + H_{(g)} \longrightarrow 2C_{(s)} + H_{2\,(g)}, \tag{20}$$

and

$$2Si_{(g)} + C_2H_{(g)} + H_{(g)} \longrightarrow 2SiC_{(s)} + H_{2(g)}. \tag{21}$$

The subscripts g and s denote the gas and the solid species, respectively. The above chemical reactions are thermodynamically feasible.

The data necessary for the calculation of nucleation and grain growth are summarized in Table 1. There are no data for the surface tension of SiC available. According to the method developed by Gail & Sedlmayr (1986), the surface tension of bulk SiC is estimated as half of the vaporization energy. The modified supersaturation ratio S' is expressed in the following form excluding the term due to the depletion of the key species;

$$\ln S' = \delta_1 \left(A/T_v + B + \ln P_t\right) + \ln\left(\frac{T}{T_v}\right)^{\frac{1}{2}}, \tag{22}$$

where P_t is the total gas pressure in units of bar at the temperature T_v and δ_1 a numerical constant determined by chemical reaction at nucleation. In the following calculations, the C/O ratio is fixed to $\epsilon = 1.5$, and we also put the sticking probability $\alpha_s = 1$. The abundance γ of the key species is given relative to the sum of the dominant gas species H, H_2 and He.

Figure 5 shows the result of the calculations for the formation of C and SiC grains versus the mass loss rate for the LTE case, where the temperature of the small cluster is equal to the gas temperature. The equilibrium temperature T_e at which the supersaturation ratio $S = 1$ as well as the condensation temperature T_c of carbon grains are much higher than those of SiC. It should be noted that the condensation temperatures of carbon grains obtained in this calculations are a little bit lower than the evaporation temperatures which are determined by taking into account the radiative heating of carbon grains (see Fig. 7a). Thus, being different from the discussion by McCabe (1982), even in the LTE case, the carbon grains condensed are stable against the evaporation when the nucleation and grain growth are taken into account. In this case, the condensation of SiC on the pre-condensed carbon grains is possible.

This will lead to the formation of the core-mantle type grains consisting of a carbon core and a SiC mantle. However, this type
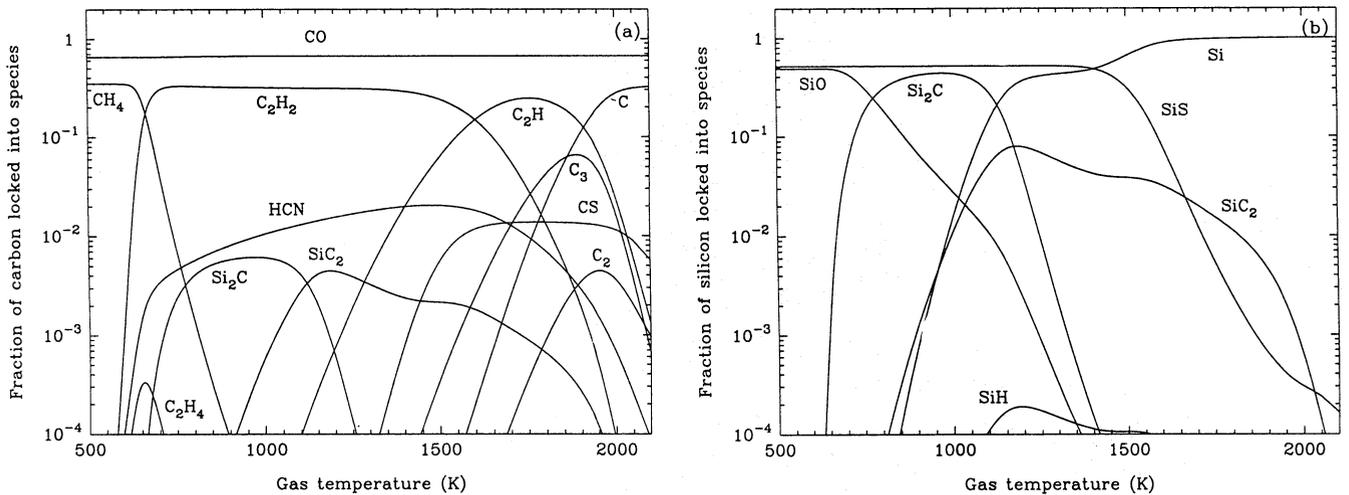
Fig. 4a and b. Fractions of C and Si atoms locked into gas species along a gas flow with v = 2 km/sec, $|\dot{M}| = 10^{-5} M_{\odot}$/yr and a C/O ratio of 1.5; **a** for C and **b** for Si. The cosmic abundances were taken from the table of Anders & Grevesse (1989) and the thermodynamic data from the JANAF tables (Chase et al. 1985), except for C$_2$H$_2$

Table 1. The quantities necessary to calculate the nucleation and grain growth of carbon and SiC grains

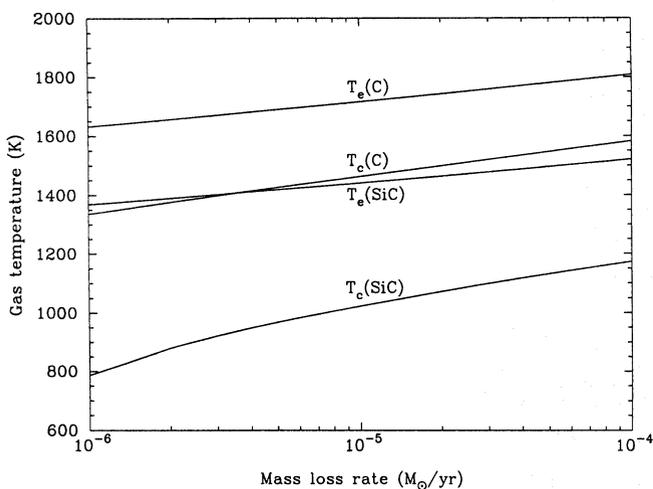| species	key species	a_0 (Å)	$A/10^4$(K)	B	δ_1	δ_2	$\gamma \times 10^4$	σ (erg/cm^2)
C	C$_2$H	1.615	8.3683	$-29.664 + \ln(\epsilon - 1)$	1.	1.	$5.518(\epsilon - 1)$	1400
SiC	Si	1.702	6.9298	$-28.693 + \ln(\epsilon - 1)/3$	1.5	$1 + 0.021/(\epsilon - 1)$	0.469	1800

Fig. 5. Condensation temperatures of carbon and SiC grains versus mass loss rates in the case that the temperature of small clusters is the same as the gas temperature

of grains cannot reproduce the so-called 11.3μm feature as discussed in Sect 2. On the other hand, as pointed out by Lefévre (1979) and McCabe (1982), there is a possibility that the inverse greenhouse effect for SiC grains changes the condensation sequence of SiC and carbon grains.

Next, we shall investigate the non–LTE effect, i.e. the difference between the temperatures of gas and small clusters, on

the formation of carbon and SiC grains. The interaction of small molecular clusters with photons is expected to be different from that of single molecules as well as large dust grains as measured for PAHs by Cherchneff et al. (1991). However, as a matter of fact, at present time there is no comprehensive knowledge about the interaction between small molecular clusters and photons, which determines the vibration temperature of small molecular clusters in a radiation field. According to the discussion by Mc-Cabe (1982), we assume that the optical properties of small molecular clusters are the same as those of very small dust grains with the same chemical composition. In this case, the Planck mean absorption efficiency can be written in the form of $< Q_{abs}(a, T) > = Q_0 a T^{\beta}$. From the least–square fitting of the Planck mean absorption efficiency in the temperature range from T = 800K to 2500 K, we obtain $Q_0 = 5.25 \times 10^{-5}$ and $\beta = 1.43$ for glassy carbon, and $Q_0 = 7.98 \times 10^5$ and $\beta = -2.34$ for SiC, where the radius a is in units of μm.

If the radiative as well as collisional heating and cooling is taken into account, the temperature T_{cl} of small clusters is determined by solving the equation

$$\left(1 - W^{\frac{\beta}{4}} y^{\beta+4}\right) = \left[\sum_{i=1}^{n} \left(\frac{kT}{2\pi m_i}\right)^{\frac{1}{2}} c_i C_{vi} T\right]$$
$$\times \frac{W^{\frac{\beta}{4}}}{a Q_0 \sigma_B T^{\beta+4}} \left(1 - y^{\frac{3}{2}}\right), \qquad (23)$$

where $y = T_{cl}/T$, σ_B the Stefan–Boltzmann constant, m_i the mass, c_i the concentration and C_{vi} the specific heat of the i–th
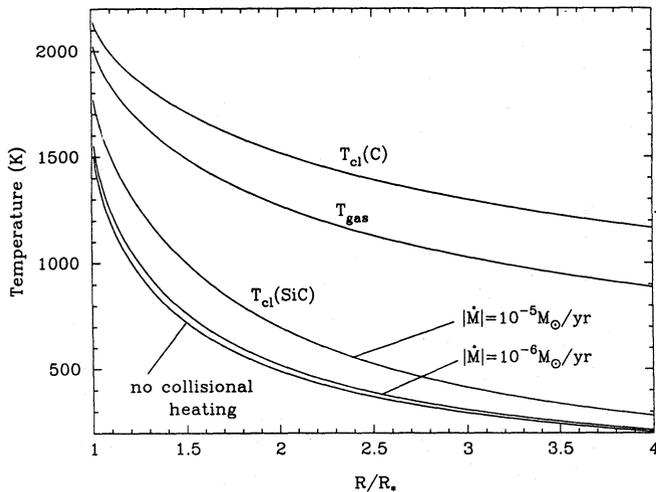
Fig. 6. Radial dependence of the temperatures of small carbon and SiC clusters together with the gas temperature for the mass loss rates $|\dot{M}| = 10^{-6}$ and $10^{-5} M_{\odot}$/yr

gaseous species. We consider H, H_2 and He as the dominant gaseous species for the collisional heating and cooling. The temperature T_{cl} depends on the size of the small clusters $a = a_0 n^{1/3}$, where n is the number of monomer molecules, due to the inclusion of the collisional heating and cooling. As the size increases, the radiative heating and cooling becomes dominant. Considering the nucleation process, we should take the size of a critical cluster as the size a in Eq. (23). For simplicity, in the following calculations we put $n = 5$, which is the typical size of a critical cluster in the situation we are considering now.

Figure 6 shows the radial dependence of the temperatures of small carbon and SiC clusters and the gas temperature for the mass loss rate $|\dot{M}| = 10^{-6}$ and $10^{-5} M_{\odot}$/yr. Because carbon is an opaque material, the heating and cooling of carbon clusters are dominated by radiation and everywhere their temperature is much higher than the gas temperature. On the other hand, SiC is transparent and the radiative equilibrium temperature of SiC clusters is very low in comparison with the gas temperature. Therefore, the heating by collisions with gas is important, which results in the dependence of T_{cl} on the mass loss rate; as the mass loss rate increases, the temperature of small SiC cluster becomes higher at the same distance from the star. SiC clusters show the inverse greenhouse effect as pointed out by McCabe (1982). The dependence on the mass loss rate plays a crucial role in considering the formation process of dust grains in circumstellar envelopes of carbon stars.

The non–LTE effect described above being taken into account, the gas temperatures T_e at distances where the modified supersaturation ratio $S' = 1$ and T_c at the condensation distances of carbon and SiC grains are shown in Fig. 7a as a function of the mass loss rate. Hereafter, T_e and T_c are referred to as the equilibrium and the condensation temperature, respectively, as in the LTE case. Figure 7b shows the number densities of SiC grains at the condensation distances and the radii of SiC grains expected for the case that all key species are consumed due to

the grain growth. In contrast to the LTE case presented in Fig. 5, the nucleation of SiC grains occurs at very high temperatures and always precedes that of carbon grains in the range of mass loss rates considered in the present calculations. Anyway, in this case we can expect the formation of the core–mantle type grains consisting of a SiC core and a carbon mantle, being different from the LTE case. It should be noted, that contrary to common sense, the equilibrium temperature as well as the condensation temperature of SiC decreases as the mass loss rate increases. This is because of the increase of the cluster temperature of SiC clusters with increasing mass loss rate as shown in Fig. 6.

The interesting fact is that the curve of the condensation temperature of SiC grains intersects the curve of the equilibrium temperature of carbon grains around a mass loss rate $|\dot{M}| = 1.5 \times 10^{-5} M_{\odot}$/yr. The condensation temperature of silicon carbide $T_c(SiC)$ is higher than the equilibrium temperature of carbon $T_e(C)$ in the case of $|\dot{M}| \lesssim 1.5 \times 10^{-5} M_{\odot}$/yr, otherwise $T_e(C) > T_c(SiC) > T_c(C)$. It should be also emphasized that the temperature of SiC clusters at the condensation distance is very low in comparison with the gas temperature as shown by the dashed curve in Fig. 7a. Therefore, the vapor related to the condensation of carbon grains is supersaturated on the surface of SiC grains, and we can expect the condensation of carbon on the SiC grains at the time of the formation of SiC nuclei. In the case of $|\dot{M}| \gtrsim 1.5 \times 10^{-5} M_{\odot}$/yr, $T_e(C)$ is higher than $T_c(SiC)$, so that the carbon condensed on SiC grains is stable against evaporation. Thus, after the avalanche of the formation of SiC nuclei, the condensation of SiC and C simultaneously occurs and results in composite grains. The volume ratio of carbon and SiC are determined only by the abundances of the key species and the composite grains contain SiC as an impurity whose volume fraction is limited to less than 0.05. The absorption cross sections of such grains in the Rayleigh limit are the same as those of the core–mantle type grains in Figs. 3 as mentioned in Sect. 2. The emission feature due to SiC is for such grains almost depressed. Note that the radii of SiC grains in Fig. 7b have no meaning in this region, because the composite grains are so opaque that the acceleration of the gas flow due to the radiation pressure forces controls the growth rate of the composite grains and prevents the growth in the outer region beyond the sonic point.

On the other hand, if the mass loss rate is less than 1.5×10^{-5}/yr, the condensation of carbon on SiC grains is unstable against evaporation because of $T_c(SiC) > T_e(C)$. Although the condensation of carbon on SiC grains is possible since the vapors are saturated, the condensation of carbon make the dust grains opaque and the resulting increase of dust temperature inhibits carbon from condensing. Therefore, the SiC grains grow first and then they are gradually coated by carbon; the temperature of the dust grains is adjusted by the amount of carbon in the mantles so as to be $S' = 1$ for the condensation of carbon as the gas temperature cools down. The radii of SiC cores are less than 0.05μm and are very small in comparison with the presolar SiC grains discovered in meteorites; $r_{\infty} = 0.005\mu$m for $|\dot{M}| = 10^{-6} M_{\odot}$/yr and 0.05$\mu$m for $|\dot{M}| = 1.5 \times 10^{-5} M_{\odot}$/yr. Note that the radii of the core–mantle grains are at most two
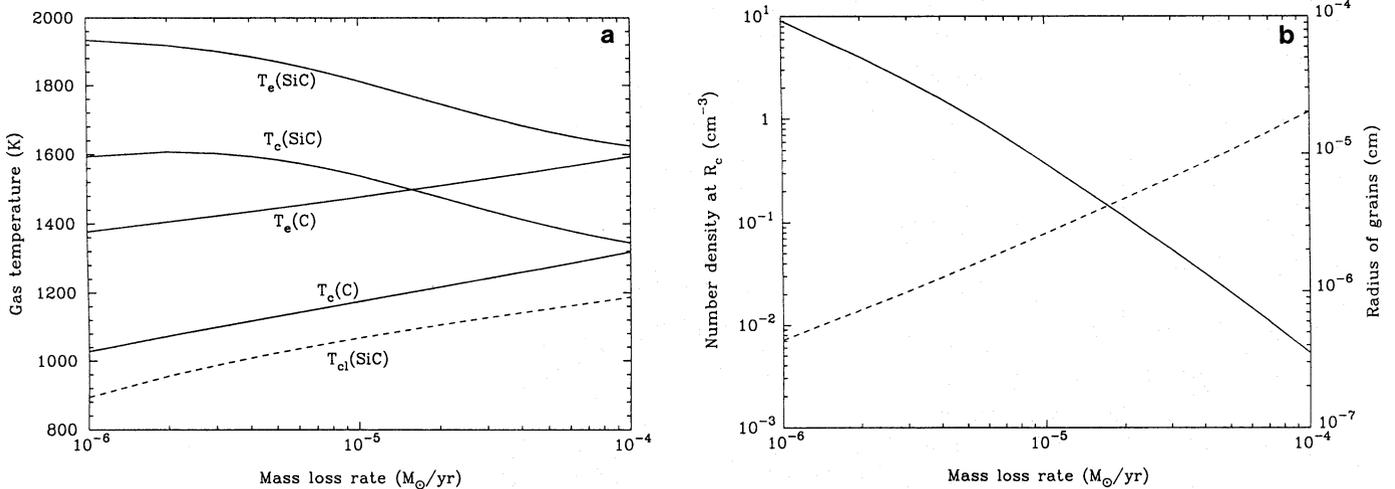
Fig. 7. a Equilibrium temperature and condensation temperature of carbon and SiC grains versus the mass loss rate, where the non–LTE effect is taken into account by considering the radiative and collisional heating and cooling of small clusters. The dashed curve shows the temperature of SiC clusters at the locations of the condensation. **b** Number density of SiC grains condensed at the condensation distances versus mass loss rate (solid curves). The dashed curve denotes the radii expected in the case that all key species are consumed due to grain growth

times of those of the SiC cores even if all available carbon condenses on the SiC cores.

When the mass loss rate is less than $|\dot{M}| = 1.5 \times 10^{-5} M_{\odot}$/yr, the core–mantle type grains consisting of a SiC core and a carbon mantle can be formed. As discussed in Sect. 2, the emission feature due to SiC for such grains clearly appears, the peak position and strength depending on the volume fraction of the carbon mantle. In reality, our simple model for the circumstellar envelopes cannot answer how much carbon condenses as the gas cools down, because with increasing volume fraction of the carbon mantles the radiation pressure forces acting on the grains results in the acceleration of the gas flow and controls the growth rate of the carbon mantle, and vice versa. Referring to the number density of SiC grains given in Fig. 7b, we can say that the volume fraction of the carbon mantles of 0.1 is enough to drive the mass loss in the case of the stellar parameters $L_* = 10^4 L_{\odot}$, $T_* = 2500$K and $M_* = 1M_{\odot}$; the ratio of the radiation pressure forces to the gravity f is then $f = 0.8$ for $|\dot{M}| = 10^{-6} M_{\odot}$/yr and $f = 1.4$ for $|\dot{M}| = 1.5 \times 10^{-5} M_{\odot}$/yr if the volume fraction of the carbon mantles is 0.1.

4. Concluding remarks

We have shown that the core–mantle grains consisting of a SiC core and a carbon mantle can reproduce an emission feature similar to the 11.3μm features observed toward infrared carbon stars, using the optical constants of the bulk α–SiC tabulated by Choyke & Palik (1985). The formation of such core–mantle grains has been investigated by using a theory of nucleation and grain growth taking into account the non–LTE effect with a simple model for circumstellar envelopes of carbon stars. Although there are uncertainties in the optical properties of small clusters in relevance to the nucleation process, the calculations have shown that SiC grains condense first and act as the condensation

sites for carbon and the core–mantle grains can be realized in the case of $|\dot{M}| \lesssim 1.5 \times 10^{-5} M_{\odot}$/yr.

So far, only the formation of carbon grains has been considered to investigate the mass–loss phenomena around carbon stars. However, the results of our calculations suggest that the understanding of the formation process of SiC grains is essential to realize what kind of dust grains are responsible to drive the mass loss of carbon stars as well as to reveal the size, the chemical composition, and the structure of dust grains formed in circumstellar envelopes of carbon stars. As shown in Sect. 3, the chemical composition and the structure of the dust grains depend on the mass loss rate. They reflect the physical and chemical conditions prevailing in the circumstellar envelopes, which control the formation process of SiC grains and the resulting condensation process of carbon.

It should be noted again, that the behaviour of the emission features due to SiC lattice vibration modes heavily depends on the chemical composition and the structure of dust grains. We must be careful in deriving the emission feature due to the SiC lattice vibration modes from the observations by subtracting an underlying continuum, because both the emission feature and the continuum arise from the same dust grains. The strength of the emission feature does not necessarily reflect the abundance of SiC condensed in the envelopes, in contrast to the results of radiative transfer calculations by Lorenz–Martins & Lefèvre (1993, 1994), where they treated amorphous carbon and SiC separately. Furthermore, this aspect is very important in relation to the abundance of SiC grains in interstellar space and in meteorites. In contrast to silicates, the SiC feature has been observed only as an emission band in circumstellar envelopes of carbon stars. Also there is no confirmative observation for the absorption feature due to SiC grains in interstellar space. Whittet et al. (1990) estimated that the abundance of Si locked in SiC grains in interstellar space is less than 5% of all Si, assuming

bare SiC grains. In meteorites, the abundance of Si in SiC grains whose sizes range from 0.1 to 1μm is very small and is 0.004% of all Si (Tang et al. 1989). Referring to these results, Whittet et al. (1990) have suggested the destruction of SiC grains due to oxidation in interstellar space. However, our result has shown that the strength of the emission feature is depressed with increasing volume fraction of the carbon material. This could explain, why the 11.3μm band is not observed in absorption in optically thick envelopes around carbon stars. Also the radius of the SiC grains formed in the circumstellar envelopes of carbon stars will be less than 0.05μm. The small core–mantle grains as well as the composite grains would solve the problem of the absence of the interstellar absorption feature. The origin of the large presolar SiC grains in the meteorites remains unexplained.

The knowledge of the nature of dust grains formed in circumstellar envelopes of late–type stars is crucial for the investigation of the origin and nature of interstellar dust grains, to get information about dust grains in space from primitive solar system bodies as well as to elucidate the physical and chemical processing the dust grains suffered during the course of the evolution from molecular clouds to primordial solar nebulae. A more detailed treatment of the nucleation process taking into account the non–LTE effect coupled with realistic gas dynamics is inevitable to understand the formation process as well as to realize the nature of dust grains in circumstellar envelopes of carbon stars. The comprehensive knowledge of the interaction of small molecular clusters with photons is essential to make the investigation of the nucleation process more realistic. Also, being independent of the formation process of dust grains, radiative transfer calculations using the core–mantle type grains proposed in this paper will be useful to deduce the size, the chemical composition and the structure of dust grains formed in circumstellar envelopes of carbon stars in comparison with the observations.

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