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Condensation of MgS in outflows from carbon stars

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ABSTRACT

Aims. The basic mechanism responsible for the widespread condensation of MgS in the outflows from carbon-rich stars on the tip of the AGB is discussed with the aim of developing a condensation model that can be applied in model calculations of dust formation in stellar winds.

Methods. The different possibilities for how MgS may be formed in the chemical environment of outflows from carbon stars are explored by some thermochemical calculations and by a detailed analysis of the growth kinetics of grains in stellar winds. The optical properties of core-mantle grains with an MgS mantle are calculated to demonstrate that such grains reproduce the structure of the observed 30 μm feature. These considerations are complemented by model calculations of circumstellar dust shells around carbon stars.

Results. It is argued that MgS is formed via precipitation on silicon carbide grains. This formation mechanism explains some of the basic observed features of MgS condensation in dust shells around carbon stars. A weak secondary peak at about 33 … 36 μm is shown to exist in certain cases if MgS forms a coating on SiC. This new feature seems to have occasionally been observed.

Key words. circumstellar matter – stars: mass-loss – stars: winds, outflows – stars: AGB and post-AGB

1. Introduction

Magnesium sulphide is a wide-spread dust component in dust-forming carbon stars. Since Mg and S are abundant elements, this dust species forms a major component in the dust mixture injected by dying AGB stars to the interstellar medium. Any attempt to model the dust production by AGB stars and their contribution to the interstellar dust population requires a knowledge of the production mechanisms, at least, those of the abundant dust species. Since for MgS a condensation model for this species is presently lacking, we try to develop in this paper such a model. We will explain, why we believe that MgS condenses in stellar outflows as a mantle on SiC grains.

Magnesium sulphide was detected as a dust component in circumstellar dust shells enshrouding some carbon stars and in the environment of two planetary nebulae by Forrest et al. (1981) by observing a broad and prominent emission band in the far-infrared spectrum which apparently is centred around 30 μm. At the instant of its detection the nature of the carrier of this emission band was not immediately clear, except that the feature can only be a solid state absorption band. Goebel & Moseley (1985) proposed MgS as the carrier of this feature. MgS has an infrared absorption feature just in the wavelength region of the newly detected feature and chemical equilibrium condensation calculations of Lattimer et al. (1978) for carbon rich element mixtures, originally performed for identifying possible supernova condensates, had shown that MgS should be an abundant solid phase at temperatures of the order of 600 K or lower. A companion paper to the paper of Goebel & Moseley (1985) by Nuth et al. (1985) showed newly determined optical properties of a number of solid phases, MgS, CaS, FeS, SiS$_2$, FeS$_2$, and Fe$_3$C, that could be responsible for the 30 μm band and which were compared to observations in the paper of Goebel & Moseley. Though the

match between the observed feature and the absorption band of MgS was not perfect, the identification of MgS as carrier of the 30 μm band has been widely accepted since that time, though other interpretations are occasionally discussed (e.g. Papoular 2000; Grishko et al. 2001; Volk et al. 2002).

In order to allow a calculation of the MgS emission feature in model calculations of radiative transfer in circumstellar dust shells, and thus to enable a quantitative comparison between observations and theory, Begemann et al. (1994) determined optical constants of Mg$_x$Fe$_{1-x}$S ($0.9 \geq x \geq 0$). They obtained good agreement between the observed emission band profile and the calculated spectrum in the 30 μm region for a radiative transfer model of the circumstellar dust shell of IRC+10216, which left little doubt with respect to the interpretation of the 30 μm emission band as being due to MgS.

A number of observational and theoretical studies of the 30 μm emission from dust enshrouded AGB and post-AGB stars, and from the environment of planetary nebulae have appeared since that time (e.g. Omont 1993; Omont et al. 1995; Yamamura et al. 1998; Jiang et al. 1999; Szczerba et al. 1999; Hrivnak et al. 2000; Hony et al. 2002; Volk et al. 2002; Hony & Bouwmann 2004; Lagadek et al. 2006; Zijlstra et al. 2006; Leisenring et al. 2008). Good examples of the emission band can be found in Hony et al. (2002), Volk et al. (2002) for galactic objects and Lagadek et al. (2006) and Zijlstra et al. (2006) for the Magellanic clouds. They all show unequivocally that MgS formation is a common phenomenon for carbon stars on the tip of the AGB.

The formation mechanism of this MgS is not clear. It was already speculated in the first papers by Nuth et al. (1985) and Goebel et al. (1985) that MgS forms via a surface reaction on carbon grains and this scenario was favoured over MgS condensation as a separate dust species. A laboratory investigation on MgS condensation was conducted by Kimura et al. (2005), but
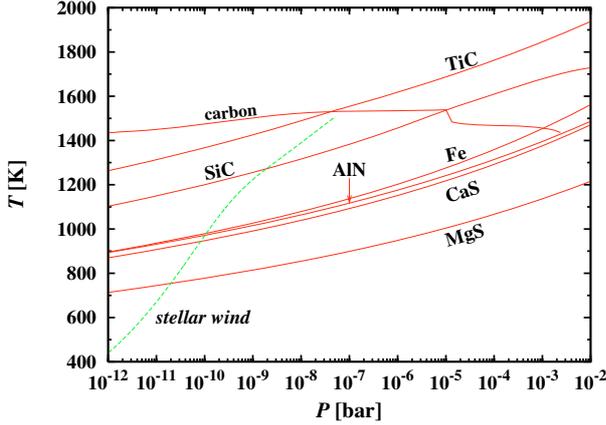
Fig. 1. Stability limits of solid phases formed from the most abundant elements in chemical equilibrium for a carbon rich element mixture ($\epsilon_C = 1.2\,\epsilon_O$). The dashed line shows the P-T-trajectory of a stationary dust driven stellar wind with a mass-loss rate of $\dot{M} = 10^{-5}\ M_\odot\ \mathrm{yr}^{-1}$.
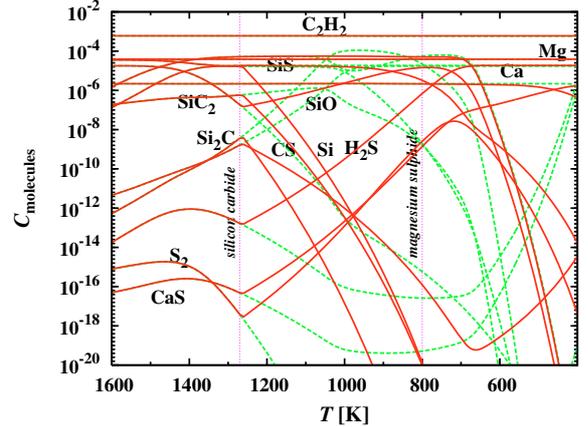

Fig. 2. Concentrations in the gas phase of S, Si, and Mg atoms and their abundant molecular compounds with H, C, O, and S for a cooling sequence with $P = 10^{-10}$ bar if formation of solid SiC in chemical equilibrium is allowed for (full lines) and if the formation of SiC is suppressed (dashed lines)

this gives no direct insight into the formation process. No further discussion of this problem seems to have appeared in the astrophysical literature so far. In this paper we will show that MgS can only be formed in the outflows of stars by precipitating on pre-existing grains and that MgS in all likelyhood forms as mantle on the silicon carbide grains formed closer to the star at higher temperatures.

The plan of the paper is as follows: first, we discuss some aspects of the chemistry associated with sulphur bearing condensed phases in Sect. 2. The kinetics of dust particle growth in a stellar outflow is discussed in Sect. 3. The results of some model calculations for MgS condensation in stellar winds are presented in Sect. 4 and the optical properties of grains formed by MgS grown on a silicon carbide or carbon core are briefly discussed in Sect. 5. Our final conclusions are presented in Sect. 6.

2. Stability of sulphur compounds

We start with a brief discussion of the equilibrium chemistry of sulphur compounds in a carbon rich element mixture. Figure 1 shows the results of a calculation of the chemical equilibrium composition of an element mixture with cosmic element abundances (e.g. Grevesse & Sauval[1] 1998) with carbon abundance set to 1.2 times the oxygen abundance. The lines in this P-T-diagram correspond to the upper stability limits of the indicated solid phases. For comparison we also show the wind trajectory of a stationary dust-driven wind model for the outflow from a carbon star. In unconditional chemical equilibrium also some oxygen bearing condensed phases would exist at temperatures below 800 K (cf. Lattimer et al. 1978). The oxygen for their formation has to come from a reduction of CO. It is unlikely that such reactions are kinetically possible and we assumed here that the oxygen is completely blocked in CO which does not react with other species in the system, i.e., we consider a conditional chemical equilibrium where O is arrested in CO[2].

From the abundant elements with abundances relative to H exceeding 10^{-6}, only CaS and MgS are formed as solid sulphur

bearing phases in chemical equilibrium. Troilite (FeS), that is abundant in oxygen rich environments, is not formed in the carbon rich environment because MgS is more stable than FeS, and in a carbon rich environment the Mg is not consumed by the even more stable magnesium silicates as in the oxygen rich case. The first sulphur bearing solid compound that appears in a cooling sequence at pressure 10^{-10} bar is CaS at about 950 K, followed by MgS at about 750 K. The temperatures where CaS and MgS become stable in a stellar outflow depend somewhat on the mass-loss rate and are of the just mentioned order of magnitude for a mass-loss rate of $\dot{M} = 10^{-5}\ M_\odot\ \mathrm{yr}^{-1}$ or somewhat less for smaller values of $\dot{M}$.

Calcium sulphide may be formed in a carbon rich environment prior to MgS condensation, but because of the low calcium abundance (which is only 1/17 of the Mg abundance) it would be difficult to detect this dust component in infrared spectra from circumstellar dust shells in the presence of MgS dust. The formation of CaS cannot consume all of the S since the sulphur abundance is about eight times the Ca abundance, i.e., MgS is formed in addition to CaS at lower temperatures. Since the Mg abundance is about twice that of the S abundance, at most half of the available Mg can be consumed by the formation of MgS. The remaining fraction of Mg stays in the gas phase and may or may not precipitate later on other condensed phases.

The abundance of S bearing molecules in the gas phase is shown in Fig. 2 for a cooling sequence with total pressure 10^{-10} bar that is representative for the pressure in the dust formation zone of a stellar wind (cf. Fig. 1). The figure shows the composition of the gas phase in a restricted chemical equilibrium where carbon is not completely condensed into solid carbon, a situation encountered in an outflow, where carbon formation cannot keep pace with cooling and only part of the carbon is converted from gaseous species into the condensed phase. Results for the sulphur chemistry are shown for the two cases that (i) the Si condenses into silicon carbide (SiC) at temperatures below about 1250 K; and (ii) for the case that formation of SiC is suppressed. A comparison of the results for both cases shows:

– If no SiC is formed, the sulphur is almost completely bound in SiS below 1500 K and no other S bearing species are abundant in the gas phase.
– Only if the Si is consumed by the formation of solid SiC, is the sulphur liberated to form increasing amounts of other

S-bearing molecules – in particular H_2S – in pace with conversion of Si from SiS into silicon carbide.

This means that the sulphur chemistry of the gas phase and the formation of S-baring solid phases are strongly coupled to the process of silicon carbide condensation.

As long as not much solid silicon carbide has formed the sulphur is blocked in the rather stable SiS molecules and the formation of MgS from abundant gas phase species requires the following reaction

$$SiS \ + \ Mg \ \xrightarrow{k_1} \ MgS(s) \ + \ Si. \tag{1}$$

The change in free enthalpy by this reaction is $\Delta G_1 = -30$ kJ/mol at 800 K (thermochemical data are from Chase 1998). After the consumption of SiS by silicon carbide formation and formation of abundant H_2S the following reaction becomes possible

$$H_2S \ + \ Mg \ \xrightarrow{k_2} \ MgS(s) \ + \ H_2. \tag{2}$$
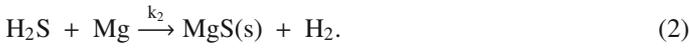
The change in free enthalpy in this case is $\Delta G_2 = -350$ kJ/mol. The corresponding laws of mass action for these two chemical reactions are

$$a_{MgS(s)} p_{Si} = p_{SiS} \, p_{Mg} \, e^{-\Delta G_1/RT} \tag{3}$$

$$a_{MgS(s)} p_{H_2} = p_{H_2S} \, p_{Mg} \, e^{-\Delta G_2/RT} \tag{4}$$

where $a_{MgS(s)}$ is the activity of solid MgS. In chemical equilibrium the activity of the solid compound equals unity. These equations determine the equlibrium pressure in Sect. 3.2.

3. Formation of MgS in a stellar wind

In stellar outflows temperature and density variations occur on shorter timescales than particle growth. In this case condensation proceeds far from chemical equilibrium and particle growth has to be treated by reaction kinetics. We consider here the conditions under which MgS condensation may occur in a rapidly expanding stellar outflow.

3.1. The wind model

3.1.1. Stationary wind model

The formation of MgS in stellar outflows from AGB stars seems to be associated with late phases of AGB evolution of low and intermediate mass stars, where the mass-loss rate is very high and the stars have already lost most of their hydrogen rich envelope.

At the tip of the AGB, radiation pressure on dust becomes the dominating driving source of the wind. The underlying stars all seem to be variables, either Miras or LPVs. The structure of the outflow is complicated in this case, since there are always several shocks running outwards, which are superposed on the average outflow of stellar material. This is demonstrated by several model calculations of dust forming stellar outflows of pulsating stars (e.g. Bowen 1988; Fleischer et al. 1991, 1992; Feuchtinger et al. 1993; Höfner & Dorfi 1997; Höfner et al. 1998; Winters et al. 1997, 2000; Jeong et al. 2003).

Calculating dust formation rates for multi-component dust mixtures of stars with quite different elemental compositions and widely varying stellar parameters presently seems impossible for reasons of computational time requirements if the shock structure of the wind is to be taken into account. For the purpose of calculating the composition of the dust mixture and the amount

of dust formed in the outflows of AGB-stars we use a simpler model, which assumes a stationary outflow. If one compares the velocity and density profiles of such stationary winds with published models of dust forming pulsators (e.g. Winters et al. 2000; Jeong et al. 2003), one observes in most cases a strong resemblance of the average velocity and density profiles with that of the stationary models, except that in the pulsation models outward propagating shocks are superposed on the average flow structure. So we can hope to obtain at least an estimate of the average quantities of dust formed in the outflow if dust formation is calculated for such an average outflow structure. One important consequence of this neglect of the detailed structure of the flow is that we cannot determine self-consistently the mass-loss rate $\dot{M}$. We have to treat this as a free parameter, which has to be fixed in some other way.

3.1.2. Stellar parameters

The central star is assumed to be on the tip of the AGB. Its luminosity then is typically $L_* = 1.5 \times 10^4 \, L_\odot$.

For stars forming MgS in their outflow a rather high metallicity is required since at low metallicities the abundances of Mg and S would be too low for this to be possible. Only a small fraction of the carbon stars in the Small Magellanic Cloud, for instance, seem to form MgS dust (Sloan et al. 2006), while for carbon stars in the Large Magellanic Cloud the formation of MgS seems to be more common (Zijlstra et al. 2006), and in the Milky Way it is quite common for highly evolved carbon stars (e.g. Hony 2002). We note already that according to observations MgS formation seems to be associated with SiC formation: Stars showing the MgS feature also show the SiC feature, but not all stars showing a SiC feature also show the MgS feature in their spectra (e.g. Zijlstra 2006). In order that low and intermediate mass stars of Pop I (or not much lower) metallicity become carbon stars, their initial masses must be from the mass range between about 1.5 $M_\odot$ and about 4 $M_\odot$.

After massive mass-loss on the AGB the stellar mass is likely to be substantially reduced and we assume in the model calculation a fixed stellar mass of 1 $M_\odot$. The stellar radiation is approximated by a black body spectrum. The effective temperature (in the inter-pulse phase) is determined from the relation

$$\log T_{eff} = .234 \log M - .2 \log L - .116 \log \frac{Z}{0.02} + 4.146 \tag{5}$$

given by Vassiliadis & Wood (1993) for stars on the AGB. The mass M and luminosity L are in solar units. With the assumed stellar parameters and solar metallicity one finds $T_{eff} = 2250$ K.

The mass-loss rate is estimated from the relation

$$\dot{M} = 2.1 \times 10^{-8} \, \frac{L}{v_\infty} \tag{6}$$

given by Vassiliadis & Wood (1993) for stars in the superwind phase. The luminosity is in units of $L_\odot$, the outflow velocity v_∞ in km s^{-1}, and the mass-loss rate in units of $M_\odot$ yr^{-1}. With the estimated stellar parameters and a typical outflow velocity in the superwind phase of $10 \ldots 15$ km s^{-1} one obtains a mass-loss rate of about $\dot{M} = 2 \ldots 3 \times 10^{-5}$ $M_\odot$ yr^{-1} for stars at the end of their AGB evolution. A value of $\dot{M} = 3 \times 10^{-5}$ $M_\odot$ yr^{-1} is used in the model calculations.

A typical run of density and temperature in a stationary stellar wind model of a carbon star calculated for a dust driven stationary wind model (cf. Gail & Sedlmayr 1986, 1987 for the details of how such models are constructed) is shown in Fig. 1.

The C/O abundance ratio of the outflowing material in any case exceeds unity since MgS is not formed in an oxygen rich environment.

3.2. Dust particle growth

The model calculation of condensation in the outflow from a carbon star considers the following dust components: Carbon dust, silicon carbide dust, and iron dust. The formation of these dust species is calculated as outlined in Ferrarotti & Gail (2006). Here we add the growth of magnesium sulphide to our model. The dust formation is calculated by solving the equations for dust growth (e.g. Gail 2003)

$$\frac{\mathrm{d} a}{\mathrm{d} t} = V_0 \, \alpha \, n_{gr} \, \sqrt{\frac{k T_g}{2 \pi m_{gr}}} \left\{ \Phi(w) - \frac{p_{eq}(T_d)}{n_{gr} k T_d} \sqrt{\frac{T_d}{T_g}} \right\} \quad (7)$$

for all species of interest. Here a is the radius of a dust grain, V_0 the volume of one formula unit[3] of the chemical compound in the solid, α is the growth coefficient, n_{gr} is the particle density of the growth species in the gas phase, m_{gr} its mass, p_{eq} is the partial pressure of the growth species in a state of chemical equilibrium between the condensed phase and the gas phase, and T_g and T_d are the gas temperature and the internal lattice temperature of the dust, respectively. The quantity

$$\Phi = \sqrt{1 + \frac{\pi \mu m_H}{8 k T_g} w^2} \quad (8)$$

depends in principle on the drift velocity w of the grains relative to the gas. Here drift is neglected and we put $\Phi = 1$ since for high mass-loss rates drift velocities are small compared to the sonic velocity. The volume V_0 of one chemical formula unit occupied in the solid is

$$V_0 = \frac{A_d m_H}{\varrho_d}, \quad (9)$$

where A_d is the atomic weight of the chemical formula unit and ϱ_d the bulk density of the condensate.

The growth equation has to be complemented by an equation for the consumption of the growth species from the gas phase. The details are described in the paper by Ferrarotti & Gail (2006) and are not repeated here.

As the rate determining step for the formation of MgS via reaction (2) we assume the addition of a H_2S molecule from the gas phase since this is the least abundant of the molecules involved in the reaction. p_{eq} in Eq. (7) is calculated from Eq. (4) with activity $a_{MgS} = 1$. The thermodynamic data for calculating ΔG are taken from the JANAF-tables (Chase 1998).

The growth coefficient α, the probability that a collision is followed by a growth step, seems not to be known. For the similar solid MgO with the same structure and similar bonding properties Hashimoto (1990) measured a growth coefficient of about 0.2 and we will use the same value for MgS. Results for growth coefficients of Zn obtained under microgravity conditions seem to be much smaller (e.g. Michael et al. 2003), but it is unclear whether this can be applied to the present case.

3.3. Conditions for grain growth

Some insight into the origin of the difficulty to explain how MgS forms in the outflow can be gained from considering a simplified

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[3] The formula unit corresponds to the chemical formula of the condensed phase, if it is written with integer stoichiometric coefficients.

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growth model. We neglect in the growth equation (i) the vaporization and (ii) the consumption of the growth species by grain growth. Additionally we use in the expression for the thermal velocity a representative value for the temperature in the growth zone of the dust. The first factor is generally not too bad for dust growth problems since the vapour pressure p_{eq} usually decreases rapidly with decreasing temperature below the stability limit of a solid. The second factor restricts the applicability of our considerations to the early growth phase before the gas phase becomes exhausted of condensable material. This initial growth phase is that which we now consider.

The particle density n_{gr} is the least abundant gas phase species involved in the rate determining reaction for the growth. Its abundance is usually some fraction g of the least abundant element from which this gas phase species is composed. In our case, where reaction (2) is assumed to be the key reaction for MgS growth, the least abundant growth species is H_2S and sulphur is the least abundant of the elements forming this molecule. We write $n_{gr} = g \epsilon_{el} N_H$, where N_H is the number density of H nuclei which can be calculated from the mass density ρ of the wind

$$N_H = \frac{\rho}{(1 + 4\epsilon_{He}) m_H} . \quad (10)$$

The mass density is given in a stationary outflow with mass-loss rate $\dot{M}$ and outflow velocity v by

$$\rho = \frac{\dot{M}}{4 \pi r^2 v} . \quad (11)$$

Since the condensation of MgS becomes possible only at a temperature much lower than the condensation temperature of carbon dust, the radiation pressure on carbon dust has driven the outflow velocity already nearly to the terminal outflow velocity of the stellar wind if MgS condensation commences. For the problem of MgS condensation we can consider the wind velocity v therefore to be constant. By changing the independent variable t to r by means of $v \mathrm{d} t = \mathrm{d} r$ we can write the equation for the initial growth of dust as

$$\frac{\mathrm{d} a}{\mathrm{d} r} = V_0 \, \alpha \, v_{gr} \, \frac{\dot{M}}{1.4 \, m_H \, 4 \pi r^2 v^2} . \quad (12)$$

Here v_{gr} is the thermal velocity of the growth species (assumed to be constant). Integrating from the inner radius R_d of the onset of growth of the dust species to infinity we obtain

$$a_\infty = a_0 + V_0 \, \alpha \, v_{gr} \, g \epsilon_{el} \, \frac{\dot{M}}{1.4 \, m_H \, 4 \pi R_d \, v^2}, \quad (13)$$

where a_0 is the radius of the seed nuclei for dust growth and a_∞ the radius at infinity. This equation requires that the grain radius a_∞ remains smaller than the maximum radius a_{max} attained if all condensable material is condensed. This maximum possible radius is given by

$$\frac{4\pi}{3} a_{max}^3 \epsilon_d = \frac{V_0 \epsilon_{key}}{\nu_{key}} . \quad (14)$$

Here ϵ_d is the number of dust grains per hydrogen nucleus, ϵ_{key} the key element for the formation of the dust species considered, and ν_{key} the number of atoms of the key element in the chemical formula of the solid.

We can now write

$$a_\infty = a_0 + a_{max} \, \frac{\dot{M}}{\dot{M}_{cr}} \quad (15)$$

Table 1. Basic data used for calculation of MgS grain growth.

Quantity	Value	Unit
A	56.37	
ϱ_d	2.68	g cm^{-3}
V_0	3.51×10^{-23}	cm^3
α	0.2	
ϵ_{Mg}	3.85×10^{-5}	
ϵ_{Si}	3.58×10^{-5}	
ϵ_{S}	1.85×10^{-5}	
ϵ_d	10^{-13}	
a_{max}	0.12	μm
v_{th}	1.52×10^4	cm s^{-1}

with

$$\dot{M}_{cr} = \frac{a_{max}\, 1.4\, m_H\, 4\pi R_d\, v^2}{V_0\, \alpha\, v_{gr}\, g\epsilon_{el}} \,. \qquad (16)$$

The quantity $\dot{M}_{cr}$ defines a critical mass-loss rate for particle growth. If the mass-loss rate $\dot{M}$ of the stellar outflow is lower than $\dot{M}_{cr}$, the final particle radius of dust grains of the considered kind in the outflow is *smaller than the maximum radius* attained in case of complete condensation. Condensation by growth starting with some kind of small seed particles is always incomplete in this case and most of the condensable material remains in the gas phase. If, however, the mass-loss rate $\dot{M}$ of the stellar outflow is of the order of $\dot{M}_{cr}$ or exceeds $\dot{M}_{cr}$, the final particle radius in the outflow approaches a_{max}; complete condensation is possible in this case by growth starting with some kind of small seed particles (at least this is not kinetically forbidden).

Applying this to MgS condensation we obtain

$$\dot{M}_{cr,MgS} = 5.4 \times 10^{-4}\, M_\odot\, \text{yr}^{-1}. \qquad (17)$$

Here we assumed a typical outflow velocity of $v = 10\,\text{km s}^{-1}$ and a radius of $R_d = 2 \times 10^{14}$ cm corresponding to about 5 stellar radii. As the key element for MgS condensation we assume sulphur since it has lower abundance than Mg. The growth species is H_2S. As a typical temperature for calculating v_{gr} we choose 600 K. All other quantities are given in Table 1. The critical mass-loss rate is about a factor of ten higher than the highest mass-loss rates observed for highly evolved AGB stars (e.g. van Loon et al. 1999). As a result the radius can approach at most 1/10 of that for complete condensation and only about 1/1000 of the condensable material can be condensed into MgS grains if the dust grains start their growth for instance from seed particles with sizes of the order of 1 nm that are typical for seed particles resulting from nucleation from the gas phase.

For such a low fraction of condensation of S and Mg into MgS this dust component would not be detectable in the infrared emission from circumstellar dust shells of AGB stars. Since MgS is frequently observed in highly evolved AGB stars, it cannot be formed by condensation from the gas phase via nucleation and subsequent growth. We therefore need to look for some other formation mechanism.

3.4. Heterogeneous growth

The most promising alternative is heterogeneous growth on some other kind of dust particles that already have moderate radii at the onset of MgS growth in order that the frequency of collisions of such a particle with growth species from the gas phase is high from the beginning. We derive the condition for this type of growth to occur by considering the initial growth phase, where the growth of a coating of MgS on some type of carrier grain has not yet significantly increased the total grain radius.

We use essentially the same type of simplifications as before and consider the following equation for the increase of the volume V of the coating on the surface of carrier grains of radius a_c

$$\frac{dV}{dt} = V_0 \alpha v_{gr} n_{gr}\, 4\pi a_c^2. \qquad (18)$$

Introducing again r as the independent variable we obtain upon integrating this equation from the radius R_d of the onset of formation of the coating to infinity

$$V_\infty = V_0 \alpha v_{gr}\, 4\pi a_c^2\, g\epsilon_{el}\, \frac{\dot{M}}{1.4\, m_H\, 4\pi R_d\, v^2}\,. \qquad (19)$$

This is the final volume of the coating at large distances. The maximum possible volume V_{max} of the coating on a carrier dust grain is, again, given by Eq. (14). We can now write

$$V_\infty = V_{max}\, \frac{\dot{M}}{\dot{M}_{het}}, \qquad (20)$$

where

$$\dot{M}_{het} = \frac{\epsilon_{key}}{\nu_{key}\epsilon_d}\, \frac{1.4\, m_H R_d v^2}{\alpha v_{gr}\, a_c^2\, g\epsilon_{el}} \qquad (21)$$

is a characteristic mass-loss rate of the stellar outflow for formation of coatings on the surface of pre-existing grains. If the mass-loss rate $\dot{M}$ of the stellar outflow is less than the characteristic mass-loss rate $\dot{M}_{het}$ only part of the condensable material will condense in the form of a coating on the surface on some carrier grains. If the mass-loss rate $\dot{M}$ of the stellar outflow exceeds the characteristic mass-loss rate $\dot{M}_{het}$ the volume of the coating approaches the maximum possible volume and complete condensation is possible, at least in principle.

Inserting numerical values for MgS condensation and assuming that the carrier grains for the formation of the coating have a radius of $a_c = 0.1\,\mu$m one obtains

$$\dot{M}_{het} = 2.8 \times 10^{-4} \left(\frac{0.1\,\mu m}{a_c} \right)^2\, M_\odot\, \text{yr}^{-1}. \qquad (22)$$

This characteristic mass-loss rate, again, is about a factor of ten higher than the highest mass-loss rates observed for AGB stars, but since it now refers to the volume we have the result that at the end of the AGB evolution up to about 10% of the condensable material for MgS formation can really be condensed as a coating on suitable carrier grains, if such exist. If the core grains have a larger radius than the assumed 0.1 μm, or if the mass-loss rate should be exceptionally high then the fraction of condensed material may be even larger. Such amounts of condensed MgS should be clearly visible in the infrared spectrum.

Hence, we come to the conclusion that the observed MgS in the outflows from carbon stars on the AGB does not form as a separate dust species but condenses as a coating on the surface on some different kind of carrier grains. The formation of significant amounts of MgS dust requires mass-loss rates of at least a few times $10^{-5}\, M_\odot\, \text{yr}^{-1}$, i.e., this is possible only during the superwind phase short before termination of AGB evolution if the mass-loss rates have grown to very high values. This is just what one seems to observe.

As a side-remark we note the following: Since the available amount of S does not suffice for the formation of thick coatings

of MgS such that the final volume is much bigger than the volume of the carrier grains, the volume of condensed material on the surface of the carrier grains increases quadratically with the radius of the carrier grains (cf. Eq. (19)). Therefore it may well be that most of the MgS is concentrated on a sub-population of larger-than-average grains, if one has a broad distribution of grain sizes for the possible carrier grains.

3.5. Possible carrier grains

The dust species that may serve as carrier grains for MgS formation need to form dust grains with a size not much smaller than about $a_c = 0.1$ μm because otherwise the condensed fraction of MgS becomes too small if the radius of the cores is smaller than this. This restricts the possibilities as to which dust species may serve as substrates of MgS growth, to the most abundant dust species.

The outflowing gas enters the temperature regime below about 650 K favourable for MgS condensation with two major dust species that have grown farther inside in the shell to the required size: SiC grains and carbon grains. From investigations of presolar dust grains it is known that from the many polytypes of SiC only two are formed in circumstellar environments (Daulton et al. 2003): the cubic 3C poly-type (usually denoted as β-SiC) is found in 79.4% of all observed grains, and the hexagonal 2H poly-type (usually denoted as α-SiC) is found in 2.7% of all observed grains. In 17.1% of all grains the material is an intergrowth of these two poly-types, the remaining fraction of 0.8% being other polytypes or disordered.

The lattice structure of the SiC grains in stellar outflows, thus, in most cases is cubic. Magnesium sulphide also has a cubic lattice structure. The electronegativity difference (cf. Pauling 1960) of MgS is 1.3 and that of SiC is 0.7. Both compounds therefore show a significant ionic contribution to their bonding. There are obvious similarities of structure and bonding properties of SiC and MgS. On the other hand, no such similarity exists between MgS and solid carbon. This suggests that SiC is much better suited as a substrate for MgS precipitation than carbon. We therefore propose that MgS grows on SiC grains.

A possible core grain is any compound that has a lattice structure similar to the MgS lattice structure and a higher condensation temperature. Among the compounds possibly formed in the stellar outflows CaS also satisfies both conditions. It has a crystal structure, that is the closest to that of MgS and becomes stable at a more than 200 K higher temperature than MgS (Fig. 1). The abundance of Ca in a stellar wind, however, is 16 times lower than the Mg abundance, which is not very favourable for its potential role as the core grain for MgS growth. Nevertheless, we will also check this possibility.

4. Models with core-mantle grains

We performed model calculations of dust formation in stellar outflows according to the wind model described in Sect. 3 to check the assumption of the core-mantle growth scenario of MgS formation. Grain growth is calculated as described in Sect. 3.2.

First we check the model of MgS condensation on tiny seed nuclei. The existence of such seeds of 1 nm is taken for granted and the growth of MgS is calculated. This results in grain sizes of only about 0.02 μm and a very low fraction of Mg bound in dust, the condensation degree, of about 0.01. This is in line with our analytical findings in Sect. 3.3. The evolution of grain radius and condensation degree for this kind of model are shown
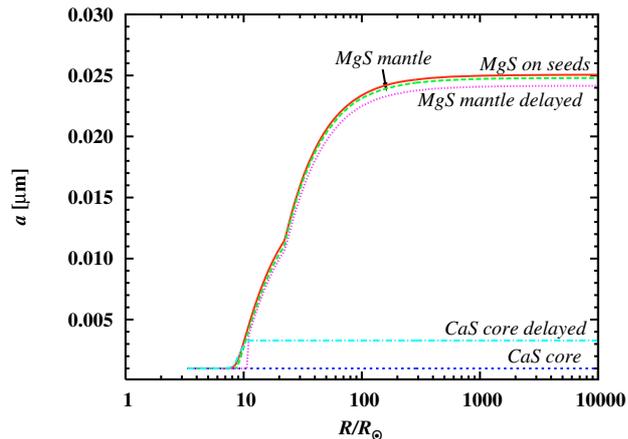

Fig. 3. Evolution of MgS and CaS grain radius as function of distance from the centre of the star, for MgS formation (i) on seed nuclei of 1 nm size; and (ii) as mantle on a CaS core. Also shown are the results of a model with delayed onset of MgS condensation on CaS core; details are given in the text.
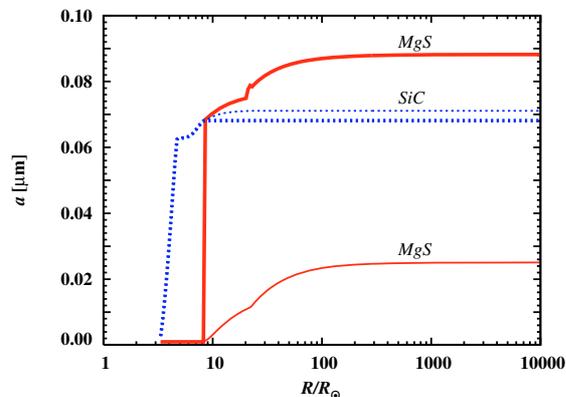

Fig. 4. Evolution of radii of SiC and MgS grains as predicted (i) by the model for MgS condensation on seed nuclei; and (ii) as a mantle on a SiC core (thin and thick lines, respectively).

in Figs. 3 and 5, respectively. The small amount of condensed MgS found in this case is obviously not enough to explain the observed 30 μm emission in the spectra of carbon stars, underlining, again, the need for a core-mantle growth mechanism for MgS formation.

Next we check an alternative growth scenario for MgS formation, in which first CaS condenses on seed nuclei by the analogue of reaction (2), and then MgS grows as a mantle on this core. The model calculations show that the size of CaS grains is much smaller than the required radius of 0.1 μm. We also tested the case that MgS condensation is delayed by imposing the additional condition for the growth rate $J_{gr,MgS} \geq 3 J_{gr,CaS}$ to gain additional time for CaS core growth in order to get bigger grains. This artificial delay results, indeed, in bigger CaS cores, but this does not help to increase the final size of the MgS mantle. The results of these calculations of the evolution of the MgS grain radius with distance from the centre of a star for normal and delayed condensation on CaS are also shown in Fig. 3. The figure shows that the condensation of MgS on a CaS core results in almost the same grain radius as the growth of MgS on seeds grains. Neither of these formation mechanisms can provide the amount of MgS dust that is observed to condense in stellar outflows.

SiC grain growth, however, commences at higher temperature and proceeds faster than CaS growth, so that at the
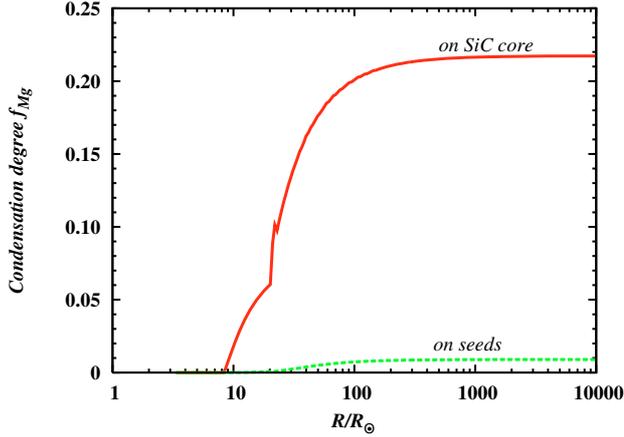
Fig. 5. Evolution of condensation degree of Mg with distance from the centre of the star for condensation of MgS (i) as mantle on top of a SiC core; and (ii) on seed particles (solid and dashed line, respectively).

Fig. 6. Wavelength variation of the absorption efficiency C_λ^{abs} of spherical grains with SiC core of radius r_c coated with MgS mantles of thickness r_m for a total grain radius $r_c + r_m$ of 0.1 μm and for MgS-mantle thickness to total radius ratios from 0 to 1 in steps of 0.1 (from bottom to top).

onset of MgS formation the SiC core radius reaches $\propto 0.07$ μm as shown in Fig. 4. The results of MgS condensation on tiny seed nuclei are shown in Fig. 4 for comparison. The SiC core is big enough to allow the formation of a considerable thickness of the MgS coating, of order 0.02 μm, which results in a final grain size of 0.9 μm. This value is very close to the grain sizes required to explain the shape of the extinction feature in the spectra of carbon stars. We assume in the calculation that SiC grains do not grow anymore as soon as the formation of the MgS mantle begins. Figure 4 shows that the growth of SiC grains with and without termination due to MgS mantle formation does not change the grain size very much. Thus, a model with MgS mantle formation on SiC does not change noticeably the fraction of Si condensed in SiC dust, but results in a much higher value of the degree of condensation of Mg in MgS as compared to the case of growth on seeds. This is illustrated in Fig. 5.

A similar test calculation for MgS formation as a coating on carbon grains also gave sufficient thicknesses of MgS layers. Basically, condensation of MgS on carbon cores cannot be excluded, but from a physical point of view, MgS mantle formation is more likely on a SiC core, since the bond lengths and bonding properties of SiC are similar to that of MgS. Laboratory experiments would be necessary to arrive at a final conclusion about the carriers of MgS mantles.

5. Optical properties of grains with a SiC core and MgS mantle

In order to study the difference in the optical properties of grains with coatings of MgS either on a SiC core or on a carbon core we calculate the absorption efficiency C_λ^{abs} (i.e. the ratio of absorption to geometrical cross-section) in the small particle limit (cf. Bohren & Huffman 1983)

$$C_\lambda^{abs} = 4x \operatorname{Im} \frac{\alpha}{4\pi(r_c + r_m)^3} \tag{23}$$

with

$$\alpha = 4\pi(r_c + r_m)^3$$
$$\times \frac{(r_c + r_m)^3(\epsilon_2 - 1)(\epsilon_1 + 2\epsilon_2) + r_c^3(2\epsilon_2 + 1)(\epsilon_1 - \epsilon_2)}{(r_c + r_m)^3(\epsilon_2 + 2)(\epsilon_1 + 2\epsilon_2) + r_c^3(2\epsilon_2 - 2)(\epsilon_1 - \epsilon_2)}. \tag{24}$$

Here r_c is the core radius, r_m the thickness of the mantle and ϵ_1 and ϵ_2 are the complex dielectric functions of the core and mantle material, respectively. x is the size parameter $2\pi(r_c + r_m)/\lambda$.
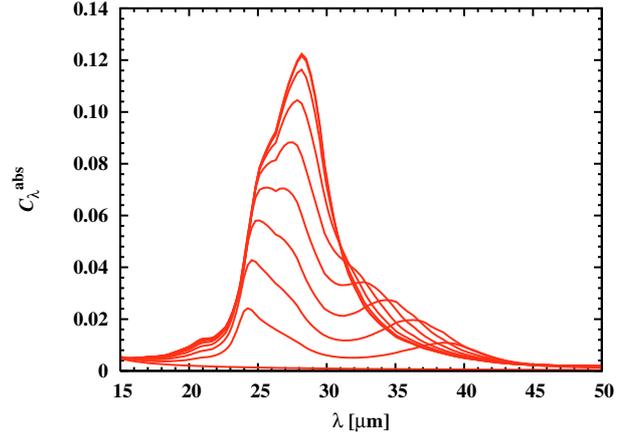
The small particle approximation $x \ll 1$ is valid in our case since we are interested in wavelengths from the region from 10 to 40 μm that are much larger than the size of the circumstellar dust particles.

Optical constants for MgS are taken from Begemann et al. (1994) for $Mg_xFe_{1-x}S$ with $x = 0.9$. For carbon we use data for the BE carbon dust of the evaluation of the data of Colangeli et al. (1993) by Zubko et al. (1996). For SiC we used the data for SiC from Laor & Draine (1993). Extinction efficiencies have been calculated for SiC grains coated with MgS mantles and, for comparison, also for carbon grains with MgS mantles.

Figure 6 shows results for grains of total radius $r_c + r_m$ of 0.1 μm and mantle thicknesses between 0 and 0.1 μm, i.e., for grains ranging in composition from pure SiC to pure MgS grains. The results show the rather broad MgS absorption band centred at about 26 μm, which in itself shows some structure. Additionally a secondary peak appears to be centred around $\approx 33 \ldots 38$ μm for moderate mantle thicknesses. Its position depends on the size ratio of core and mantle. This feature is not present in the extinction efficiencies of pure MgS or SiC grains and results from the particular run of the complex dielectric functions of the core and the coating in this wavelength region[4].

Figure 7 shows the variation of the extinction coefficient with varying core to mantle size ratios – both for MgS grains with SiC and with carbon cores – in a different representation and an extended wavelength region that also covers the 11 μm feature of SiC. The total grain radius $r_c + r_m$, again, is 0.1 μm and the fraction $r_m/(r_c + r_m)$ is varied between 0 and 1. In the upper part of the picture one recognises how the SiC feature disappears and the MgS feature appears as the composition of the grain varies from pure SiC to pure MgS. The extra feature peaking at about $33 \ldots 38$ μm, depending on the mantle thickness, is clearly seen in coatings of moderate, but not too small fraction of the total size. For thick coatings the extra feature disappears together with the 11 μm feature from the SiC core. The feature is not very distinct and will probably hardly be detectable in many cases.

The particular feature peaking at about $33 \ldots 38$ μm is missing in the extinction of carbon grains coated with MgS, as can

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[4] It has been checked if this results from a Fröhlich mode in coated particles at a frequency where the denominator in Eq. (24) vanishes, cf. the discussion of this effect in Bohren & Huffman (1983), but this seems not to be the case.
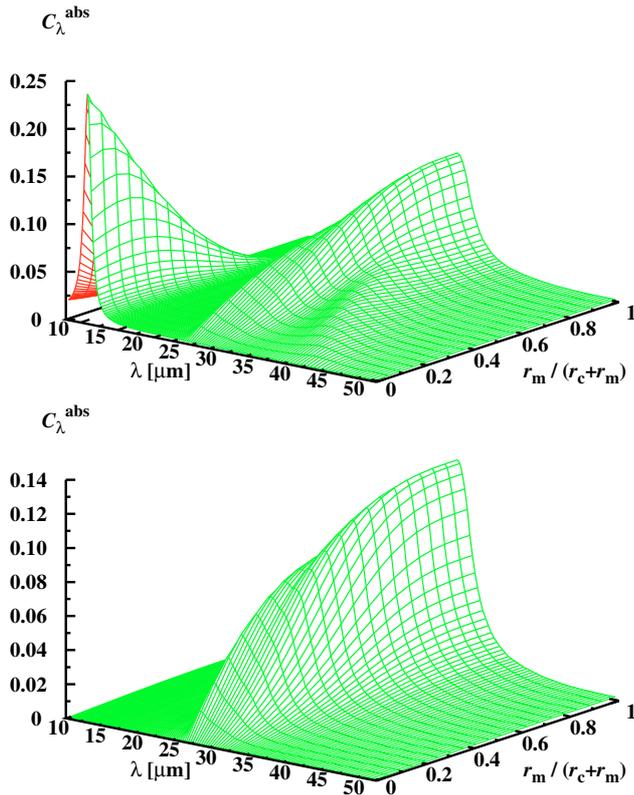
Fig. 7. Wavelength variation of the absorption efficiency C_λ^{abs} of spherical grains with SiC (*top*) or carbon (*bottom*) core and MgS mantle with total radius of 0.1 μm. The MgS mantles range in thickness from zero to unity in steps of 0.05 for the ratio of mantle thickness r_{m} to total radius $r_{\mathrm{c}} + r_{\mathrm{m}}$, where r_{m} is the core radius. The extinction properties vary from that of pure SiC or carbon grains to that of pure MgS grains. An extra extinction feature centred on 33 μm for MgS grains with SiC core shows up at moderate mantle thickness. This is missing in case of carbon cores.

winds is much too low to explain the observed strong emission band from MgS in the infrared spectra of many carbon stars.

A model of heterogeneous growth of MgS on SiC precursor grains is proposed here as the most promising mechanism of MgS formation. Analysis of the equilibrium chemistry of sulphur compounds in a carbon rich mixture shows that the formation of MgS is strongly coupled to the process of silicon carbide condensation. If no SiC is formed in a stellar outflow, the sulphur is almost completely bound in SiS molecules. Only after significant consumption of the abundant gas phase SiS by SiC formation, is H_2S formed in abundance and reactions of this with Mg makes possible MgS condensation.

Our model calculations of MgS formation in stellar outflows show that only MgS growth as mantles atop SiC cores that condensed before the on-set of MgS formation, results in sufficiently high degrees of condensation of Mg into MgS (of the order of ~0.2) which are required so that MgS may be clearly visible in the infrared spectrum. Condensation of MgS on tiny seed particles would result in a fraction of the Mg condensed in MgS dust much too small to be detectable (of the order of only 0.01).

Additionally, we performed calculations of the extinction properties of grains with SiC core and MgS coating of various thicknesses. The presence of a SiC core inside of MgS grains results within some range of core/mantle volume ratios in a secondary peak near $33 \ldots 35$ μm in the broad emission band associated with MgS, that seems to be observed in some spectra of AGB stars. This feature is absent if MgS forms as a mantle on carbon grains. We propose this feature as an indicator for the presence of a silicon carbide core of MgS grains, if the presence of MgS is indicated by its absorption band around 26 μm.

be seen from the lower part of Fig. 7, because of the completely different properties of the dielectric function. Therefore this extra feature can be considered as an indicator of a silicon carbide core of MgS grains, if the presence of MgS is indicated by its absorption band around 26 μm. Observationally it was found by Volk et al. (2002) that the so called "30 μm feature" of carbon stars shows in some cases some structure, and seems to consist of two overlapping features at 26 μm and 33 μm. Our results for the extinction of SiC-core-MgS-mantle grains indicate that one just sees that the MgS in outflows from carbon stars grows as mantles on silicon carbide cores. If it is not seen this probably does not mean that in this case MgS precipitates on carbon, but merely that the feature is not sufficiently well defined to be unambiguously detectable.

6. Concluding remarks

In this paper the mechanism of MgS formation in stellar outflows of AGB stars is studied. From some elementary considerations on the kinetics of MgS condensation we estimate a critical mass-loss rate of about 5×10^{-4} $M_\odot$ yr^{-1} for efficient MgS formation if this would condense as a separate dust species via nucleation and subsequent growth. This value of the mass-loss rate is much higher than any observed mass-loss rate of AGB stars. Within the observed range of mass-loss rates of AGB stars, however, the amount of MgS that can condense on seed particles in stellar

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