Part 3. Formation, Composition, and Processing of Dust
ISO in Montpellier
Crystalline silicates in AGB and post-AGB stars

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Abstract. We discuss ISO spectroscopy of oxygen-rich dust shells surrounding evolved stars. The dust that condenses in the outflows of stars on the Asymptotic Giant Branch consists mainly of amorphous silicates and simple oxides. For high mass loss rates, crystalline silicates begin to appear at modest abundance. These crystalline silicates are cold and Fe-poor. ISO spectroscopy for the first time allows quantitative mineralogy of oxygen-rich circumstellar dust. Crystalline silicates are found at high abundance in sources with peculiar (disk) geometry, such as long-lived circum-binary disks. Some C-rich post-AGB stars, notably the Red Rectangle and several nebulae surrounding [WC] central stars of Planetary Nebulae, also show crystalline silicates. We speculate on the origin and evolution of the crystalline dust component in evolved stars.

1. Introduction

The evolution of stars on the Asymptotic Giant Branch (AGB) is strongly influenced by mass loss via a slowly expanding, dusty stellar wind. Mass loss rates can be as high as $10^{-4} \, M_{\odot}/\text{yr}$; at these rates, the stellar wind dominates the speed of evolution of the star (dictated by the rate at which the envelope is lost). Therefore, it is important to understand the physics of AGB mass loss, and its dependence on mass, chemical composition, rotation, and time. Our current understanding of the mass loss mechanism is still rather primitive, although recently impressive progress has been made (see e.g. the contributions by Fleischer et al., and by Höfner, in this volume). Most workers agree that dust formation in a pulsating, extended atmosphere drives AGB winds. While the dust which condenses in the outflow contains only about 1 per cent of the mass, it dominates the shape of the energy distribution due to its efficient absorption of stellar radiation: as mass loss increases, the dust in the outflow obscures the central star and most of the energy is radiated at (far-) IR wavelengths.

A critical question to address is the kind of dust which condenses, and the location where the dust first condenses from the gas phase. The detailed condensation sequence of dust in AGB stars is difficult to calculate from first principles, and observations are badly needed to constrain models. The com-

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position of dust around AGB stars can be studied spectroscopically at infrared wavelengths, while its spatial distribution requires sub-arcsec IR imaging observations. In this paper, we discuss recent spectroscopic observations of oxygen-rich dust around AGB and post-AGB stars using the spectrometers on board of the Infrared Space Observatory (ISO; Kessler et al. 1996), that reveal an incredible richness in previously unknown solid state bands. These observations give new insight into the condensation of dust in the winds of AGB stars, and into their chemical evolution. We will concentrate on results obtained with the Short Wavelength Spectrometer (SWS; de Graauw et al. 1996). For a description of results obtained with the Long Wavelength Spectrometer (LWS; Clegg et al. 1996), we refer to the papers by Barlow (1998, and in this volume).

2. Oxygen-rich dust in AGB and post-AGB stars

A significant fraction of the Guaranteed Time (GT) observing programme of the SWS consortium was aimed at the study of the composition of the photospheres and winds of late type stars, both low and high mass. Here we focus on the results for oxygen-rich AGB stars, post-AGB stars and Planetary Nebulae (PNe). The SWS spectra cover the wavelength range between 2.4 and 45 \( \mu \text{m} \), with a spectral resolution between several hundred and 2,500 (depending on the observing mode chosen). This spectral resolution is ideal to study the solid state emission and
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Figure 2. Top panel: joint SWS and LWS spectrum of AFGL 4106 (Molster et al. 1999). The dotted line represents the eye estimate of the continuum. Lower panel: continuum subtracted spectrum of AFGL 4106. Note the strong amorphous silicate bands near 10 and 18 μm, and the numerous narrow, weak emission bands at longer wavelengths due to crystalline silicates.

absorption, while the broad, uninterrupted spectral coverage allows a reliable determination of the continuum.

The SWS spectra of oxygen-rich AGB stars are dominated by solid state emission from amorphous silicates, showing emission at about 10 μm and 18 μm (Fig. 1). These bands were already well known from earlier observations, and are ascribed to the stretching and bending mode of Si-O and O-Si-O respectively. We note a rich variety in the appearance of the 10 μm and 18 μm emission, which sometimes is very broad. This probably reflects a rich variety in chemical composition of the amorphous silicates (see also Tielens 1990). Also prominent is, in cases with modest 10 μm emission, a bump at 13 μm, often ascribed to corundum (Al₂O₃) (e.g. Kozasa & Sogawa 1998). The appearance of this solid state feature seems to be correlated with gas-phase CO₂ emission at 15 μm and other wavelengths (see Ryde et al. 1998; Justtanont et al. 1998). Both features disappear for high mass loss rates, i.e. when the 10 μm silicate feature becomes very strong or shows a self-reversal. Kozasa & Sogawa (1998) propose that the Al₂O₃ grains form a silicate mantle which for high mass loss rates suppresses the 13 μm feature.

At longer wavelengths, the spectra of AGB stars with low mass loss rates are smooth and do not reveal prominent emission (sometimes a weak bump near 30 μm is observed). For stars with high mass loss rates, and for post-AGB stars and PNe with cool detached dust shells, the SWS (and LWS) spectra reveal a very rich structure of new, narrow solid state emission bands (Waters et al.
which can be identified with crystalline silicates, both olivines (Mg$_{2-2x}$Fe$_{2x}$SiO$_4$) and pyroxenes (Mg$_{1-x}$Fe$_x$SiO$_3$). The Mg-rich end member of the olivines and pyroxenes (x = 0) are forsterite and enstatite respectively. So far, only very few stars have been investigated in detail. In Fig. 2, we show the continuum subtracted joint SWS and LWS spectrum of AFGL 4106, which is likely a very luminous post-red-supergiant (Molster et al. 1998, 1999). Table 1 contains a list of the detected features and identifications based on laboratory data published by Jäger et al. (1998), Koike et al. (1993), and Koike & Shibai (1998). The narrow emission features are weak, only a few per cent over continuum, and the amorphous dust component dominates: in AFGL 4106, only a few per cent of the dust is crystalline. Note also prominent bumps near 43 μm and 60 μm, that are attributed to crystalline H$_2$O ice (the 43 μm band is blended with crystalline pyroxene).

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Table 1. The characteristics of the dust features in the spectrum of AFGL 4106.
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3. Composition and abundance of crystalline silicates

The wavelength of the emission bands of crystalline silicates is sensitive to the Mg/Fe ratio (Koike et al. 1993; Jäger et al. 1998). Comparison of the ISO data with laboratory spectra indicates that the crystalline silicates are Fe-poor and Mg-rich, with Fe/Mg ratios less than 0.1. Especially the 69 \( \mu \text{m} \) band, which falls in the LWS wavelength range, is sensitive to the Fe/Mg ratio, and shifts from 69 \( \mu \text{m} \) (for Fe/Mg = 0) to 73 \( \mu \text{m} \) for Fe/Mg = 0.05. The observed wavelength of this band is always close to 69 \( \mu \text{m} \) (Barlow 1998), which suggests that the crystalline olivine is in fact pure forsterite (no Fe). A similar conclusion can be drawn for the pyroxenes. The low Fe/Mg ratio is in contrast with the composition of the amorphous silicates, that are believed to be much more Fe-rich.

The relative abundance of olivines to pyroxenes can be determined by measuring the strength of the 33 \( \mu \text{m} \) pyroxene band relative to that of the 33.8 \( \mu \text{m} \) olivine band. We show several examples in Fig. 3. For AFGL 4106 Molster et al. (1999) find a ratio of pyroxenes to olivines between 1 and 3. The stars in the SWS GT programme cover a range in luminosities; the data suggest that more luminous sources (red supergiants) have a higher pyroxene to olivine ratio than lower luminosity AGB stars (Molster et al., in preparation).

The richness of the emission bands of individual dust components offers the unique opportunity to determine the temperature of these components, by comparing observed peak strengths to laboratory data. Care should be taken to
properly define the continuum, which is in many cases not trivial due to strong blending of narrow bands. Comparison of the colour temperature of the olivine emission bands in AFGL 4106 with that of the underlying continuum shows that the olivine bands are significantly cooler (\(\sim 80\) K) than the continuum and the amorphous emission bands (\(\sim 120\) K). A similar trend is found for other sources. We conclude that crystalline silicates tend to be cool. The temperature difference suggests that we are dealing with separate grain components that are not in thermal contact with each other. This different temperature of amorphous and crystalline silicates may be the result of their different Fe/Mg ratio: Fe causes a significantly higher absorptivity at near-IR wavelengths, and hence higher thermal equilibrium temperatures than Fe-poor grains of the same size and shape.

From our spectral survey of late type stars, we find that crystalline silicates tend to appear only when the mass loss rate is high (either currently, or recently), i.e. when the colour temperature of the dust is below 200-300 K (there are some exceptions however). A beautiful example is the case of OH 32.8-0.3, which has a very high mass loss rate and shows strong absorption from amorphous silicates, but also in the crystalline silicate bands. In Fig. 3 we compare the continuum subtracted spectra of OH 32.8-0.3 and AFGL 4106, and find a good match between the emission bands in AFGL 4106 and those in absorption in OH 32.8-0.3. This demonstrates that crystalline silicates form in the outflows of late type stars.

The strength and appearance of crystalline silicate bands show a large degree of diversity from source to source, but certain trends can be distinguished. The strength of the bands (expressed in band over continuum ratio) varies from a few per cent (for sources as AFGL 4106) to more than 50 per cent (for objects as MWC 922, Barlow 1998; Voors, private communication). There is a clear trend that 'disk sources' (AC Her, van Winckel et al. 1998; 89 Her, Waters et al. 1993) show strong emission bands, while dust shells with less extreme geometry (HD 161796; AFGL 4106) have modest band strengths (less than 15 per cent over continuum). The interpretation of this trend is not clear; we will return to this point in Sect. 5.

4. Crystalline silicates in carbon-rich objects

The presence of crystalline silicates in circumstellar dust shells and their rich emission band spectrum at long wavelengths opens the possibility to determine the chemical composition of cool dust around evolved stars, both O-rich and C-rich. This has led to a number of remarkable detections of cool crystalline silicates surrounding carbon-rich AGB and post-AGB stars. Before the ISO data became available, warm O-rich dust was known to exist in a number of C-rich AGB stars (Willems & de Jong 1986; Little-Marenin 1986). Also, some O-rich PNe were known to show C-rich PAH bands (e.g. NGC 6302, Roche & Aitken 1986; see also Beintema 1998). Here, we discuss the case of the Red Rectangle and of the [WC] central stars of PNe.
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4.1. The Red Rectangle

The Red Rectangle (RR) is the 'standard' for the famous family of infrared emission (UIR) bands at 3.3, 6.2, 7.7, 8.6 and 11.3 \( \mu \)m (Russel et al. 1978), commonly attributed to Polycyclic Aromatic Hydrocarbons (PAHs; Léger & Puget 1984). It also shows prominent extended red emission (ERE) at optical wavelengths (Cohen et al. 1975), that are attributed to fluorescence from C-rich molecules (e.g. Witt & Schild 1988). However, recently, Witt et al. (1998) and Ledoux et al. (1998) showed that the ERE may be caused by very small silicate grains. Previous to ISO observations, the infrared spectral characteristics, and some of the optical properties of the nebula pointed to a rich C-based chemistry, and the RR was long considered as prototype for C-rich post-AGB stars. The X-shaped nebula (Cohen et al. 1975) hosts a central binary with a luminous post-AGB star with \( T_{\text{eff}} \sim 7500 \) K and an unseen companion in a 318 day period orbit with eccentricity 0.38 (Waelkens et al. 1996). High-resolution optical and near-IR imaging revealed the presence of an optically thick circum-binary disk with reflection lobes above and below the disk (Roddier et al. 1995).

The ISO-SWS spectrum of the RR is shown in Fig. 4 and displays the familiar PAH bands. In addition, at longer wavelengths emission from crystalline olivines and pyroxenes can clearly be distinguished (Waters et al. 1998a). Also,
absorption from gas-phase CO$_2$ is observed at 4.3 and 15 μm. The ISO observations indicate that about 4 $10^{-5}$ M$_\odot$ of oxygen-rich dust is present, and from the absorption of the CO$_2$ and the distribution of PAH emission in the nebula, Waters et al. (1998a) conclude that the crystalline silicates must be in the circum-binary disk. The abundance of the oxygen-rich dust is difficult to estimate due to the simultaneous presence of emission from C-rich dust. Waters et al. (1998a) derive an abundance of 13 per cent, but this is likely a lower limit.

The origin of the oxygen-rich dust in the RR is probably related to the chemical evolution of the central star on the AGB. During the oxygen-rich phase of the AGB, mass somehow accumulated in the circum-binary disk and remained there while the central star evolved into a C-rich AGB star. Note that the orbital separation of the RR binary does not accommodate a luminous AGB star, and that some interaction must have taken place, however without destroying the binary. The old disk in the RR has properties that are reminiscent of the disks surrounding young pre-main-sequence stars: a highly gas-depleted disk with large grains (Jura et al. 1997) and a high abundance of crystalline silicates; it is tempting to conclude that the processes that modify the disk composition in young stars (which eventually lead to planet formation) also work in the RR disk (Waters et al. 1998a). Recently, the notion of planet formation has gained support from an observation by Jura & Turner (1998) of a cool dust clump in the outer regions of the RR disk with a mass comparable to that of Jupiter.

Circum-binary disks in evolved post-AGB stars are also observed in e.g. AC Her and 89 Her; in these cases also a high abundance of crystalline silicates is found, but no evidence for C-rich dust.

4.2. [WC] central stars of planetary nebulae

[WC] central stars of PNe (CSPNe) are a sub-class of C-rich PNe with a central star that shows a He-rich and C-rich atmosphere and no strong evidence for H. The central stars also exhibit a dense, fast outflow very similar to the population I counterparts. The infrared spectra of [WC] nebulae show strong emission from the familiar UIR bands, indicating that the dust in the nebula is also C-rich. The origin of the [WC] CSPNe is still not well understood, but is probably related to the occurrence of a thermal pulse at the end of the AGB or in the very early phase of the post-AGB evolution (Iben 1984; Zijlstra et al. 1991; see also Werner et al., in this volume).

The ISO-SWS spectra of two [WC] nebulae were analysed by Waters et al. (1998b), and show convincing evidence for the presence of crystalline silicates at wavelengths longward of 20 μm. Cohen et al. (1998; see also in this volume) and Barlow (1998) show that the C-rich [WC] nebula CPD-56°8032 exhibits strong emission from crystalline olivines and pyroxenes, as well as from crystalline H$_2$O ice. SWS spectra of several [WC] nebulae published by Szczerba et al. (1998) also reveal emission from crystalline silicates, although the authors do not comment on this in their paper. It appears that a large fraction of PNe with [WC] central stars show cool crystalline silicates. The question arises whether this is a property of PNe in general (i.e. independent from the chemical composition of the central star) or restricted to [WC] stars.

If the presence of cool oxygen-rich dust is correlated with the central star spectral type, the explanation must be found in the formation of [WC] CSPNe.
Waters et al. (1998b) have suggested that the late thermal pulse which removes the remaining H-rich layers from the atmosphere is also the thermal pulse which changes the chemistry from O-rich to C-rich. This transition must then have taken place very recently, typically less than 1000 years ago, an perhaps even less than a few 100 years (see also Cohen et al. 1998). The [WC] CSPNe are only a minor fraction of all known CSPNe (about 50 are known, Gorny & Stasinska 1995). If we assume that the transition is related to a thermal pulse, and that at the end of the AGB thermal pulses occur at intervals of about $10^4$ years (see e.g. Blöcker, in this volume), then 10 per cent of the thermal pulses may occur close enough to the termination of the AGB to be consistent with the presence of cool, oxygen-rich material in a C-rich inner nebula. However, this final thermal pulse also must be the one changing the chemistry, and this may be statistically implausible. Perhaps the efficiency of mixing is much higher in 'fatal thermal pulses' than in earlier thermal pulses. It is clear that a better overview of the occurrence of C-rich nebulae with O-rich cool dust is highly desirable.

Alternatively, the presence of oxygen-rich dust may be unrelated to the [WC] nature of the central stars (although so far the correlation seems to hold). In that case, the origin of the material may be related to the destruction of a pre-existing cloud of dust, similar in nature to the Kuiper belt or to the Oort Cloud in our Solar System (Cohen et al. 1998; see also Cohen et al., in this volume).

5. Discussion

The new solid state bands discovered in the ISO spectra of oxygen-rich AGB stars and related objects demonstrate the power of high quality infrared spectroscopy. We can now determine the mineral composition of specific dust components in the outflows and circumstellar disks of stars: mineralogy of oxygen-rich dust shells has now become possible. Several questions come to mind when confronted with the ubiquitous presence of crystalline silicates, and we address some of these below.

The first point to consider is the occurrence and chemical composition of crystalline silicates. The lack of crystalline silicates in dust shells of low mass loss AGB stars and RSG stars suggests that the density in the dust forming layers must be high in order for the crystalline silicates to be detected. Tielens et al. (1998) speculate that the crystalline Mg-rich silicates are the grains that form first in dusty outflows of any density, since their condensation temperature is high. At lower temperature (below or close to 1000 K), amorphous, Fe-rich silicates are formed by adsorption of Fe in the lattice of the Mg-rich grains. This reaction can only take place at temperatures below the glass temperature of silicates, and hence the grain becomes amorphous. For low mass loss rates, all Mg-rich crystalline silicates are transformed to amorphous grains by adsorption of Fe. In a high density environment, Fe may be incorporated in other dust species (for instance metallic Fe, Gail, private communication) at high temperature before the reaction with the silicates can occur, depleting the gas-phase Fe and leaving some crystalline grains without Fe. This could explain why crystalline silicates only appear in stars with very high mass loss rates.
A second point to address is the (very) high abundance of crystalline silicates in sources with stationary, circum-binary disks. As mentioned earlier, sources as the RR, 89 Her and AC Her, all binaries with wide orbits, show a high abundance of crystalline silicates when compared to sources with simpler geometries, i.e. detached, slowly expanding AGB remnants. A notable case is NGC 6302, an outflow source which shows prominent crystalline silicates (see Waters et al. 1996; Beintema 1998; Barlow 1998) and whose geometry is strongly bi-polar. The question arises whether the high abundance is the result of the longevity of the grain population, or due to an intrinsically high abundance of the crystalline grains formed in the AGB outflow.

In stationary disks, the grain population may become more crystalline with time, perhaps due to exposure to high energy UV photons, or by the interaction between a slow and a fast wind. We note here that it is not sufficient to change the lattice structure of the Fe-rich amorphous grains, but it also requires Fe removal from the lattice. This process may not occur at the low temperatures observed in circum-binary disks. Alternatively, the amorphous grains may be selectively removed because of the difference in radiation pressure between Fe-poor, cool (transparent) crystalline grains and Fe-rich, warm (opaque) grains. This mechanism can only be effective in an environment where gas and dust are not dynamically coupled. This issue is not yet settled.

In non-spherical outflow sources (such as NGC 6302), it is possible that the abundance of crystalline grains is different in the polar (low density) and equatorial (high density) regions. The subsequent dynamical evolution of the nebula, with the fast wind clearing out the polar regions more quickly than the equatorial regions, may increase the relative abundance of crystalline silicates.


References

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Koike C., Shibai H., 1998, ISAS report no. 671
Nicolas Epchtein surveying surveys