Is SiS$_2$ the carrier of the unidentified 21 micron emission feature?

G.F. Kraus[1]**, J.A. Nuth III**[2]**, and R.N. Nelson**[3]

[1] Physical Science Department, Charles County Community College, LaPlata, MD 20646, USA
[2] Astrochemistry Branch, Code 691, NASA/GSFC, Greenbelt, MD 20771, USA
[3] Chemistry Department, Georgia Southern University, Statesboro, GA 30460, USA

Abstract. Spectra are presented of SiS$_2$ samples in a variety of crystal forms taken at both room temperature and at 600 K over the wavelength range from 5-25 microns. All spectra show strong features at 22.5 and 9.5 microns as well as less intense bands at 7.5, 8.5, and 12.5 microns. All room temperature spectra also show a feature at 10.7 microns that disappears on heating. One form of SiS$_2$ shows strong correlated absorption features at 20 and 17 microns that are rapidly quenched by exposure to humid air with no significant change to the 7-13 and 22 micron features also present in the sample. These SiS$_2$ spectra are consistent with previous spectra obtained by Nuth et al. (1985), are marginally consistent with the identification of SiS$_2$ as the source of the observed 21 micron peak in several carbon-rich stellar sources, and suggest additional observations of these stellar sources that might confirm or refute the presence of SiS$_2$. Specifically, if no feature at 17 microns is detected in objects that display the strong 21 micron emission feature then SiS$_2$ should be ruled out as a candidate for this band.

Key words: line: identifications – stars: circumstellar matter – ISM: dust – infrared: lines and bands – methods: laboratory

1. Introduction

A variety of IRAS sources have been reported recently having an, as yet unidentified, emission feature near 21 microns (Kwok et al. 1989; Chan et al. 1995). Many of these sources are intermediate-mass, carbon-rich stars in a post-AGB evolutionary stage on their way to becoming planetary nebulae (Hrivnak, Kwok, and Volk 1989). Suggested carriers of the 21 micron feature include SiS$_2$ (Goebel 1993), polycyclic aromatic hydrocarbons (PAHs) (Buss et al. 1990; Hrivnak et al. 1989) and iron oxides (Cox, 1990). Although the spectra of a wide range of PAHs and several forms of iron oxide are available in the literature from the UV to the IR (e.g. Salisbury et al. 1988; Donn et al. 1989; Clar, 1964 for PAHs or Steyer, 1974; Digiorgi et al.

Send offprint requests to: J.A. Nuth III

1987; Henning et al. 1995 for iron oxides), the spectrum of SiS$_2$ is only available in the range from 12.5-120 microns (Nuth et al. 1985; Begemann et al. 1996). Within the range of the aforementioned studies SiS$_2$ exhibits one major peak at a wavelength near 21 microns, as well as a moderately strong feature near 17 microns.

The purpose of the present study is to extend the range of the previous measurements of SiS$_2$ into the mid-infrared and to investigate possible variations in the spectra of samples due to different morphology or crystal structure and temperature. We will present spectra covering the range from 5-25 microns of SiS$_2$ samples obtained from three different suppliers having three distinct appearances and two distinct crystallographic natures measured at both room temperature and 600 K. In addition to the previously known features near 21 and 17 microns, we have now characterized several additional features in the interval 7-13 microns which may serve to test the hypothesis that SiS$_2$ solids are present in the spectra of some carbon-rich infrared sources.

In what follows we will first describe the natures of the materials used in this study and the methods used to obtain the reported spectra. We will then present the spectra and discuss the variations observed in those spectra in the context of diagnostic indicators suitable for comparison with observation. These discussions naturally lead to suggestions for additional observations.

2. Materials and their characteristics

The solid SiS$_2$ used in the original study (Nuth et al. 1985), obtained from Pfaltz and Bauer Chemicals [P&B] was a gray solid with a "rocky" texture consisting of hard, brittle, irregularly-shaped granules a few millimeters across. This sample was also used in the present study. In addition, samples of SiS$_2$ were purchased from ICN Biomedical [ICN]. The ICN samples exhibited a wide range of physical appearance both for different lot numbers and even for two different bottles of the same lot number. Some resembled the "gray rocky" P&B sample, some "white crusty" samples consisted of plates about a millimeter across and two millimeters thick with a white crust on one side

and a dark gray surface on the other side while a third sample consisted of thin needle-like "white fluffy" crystals. This last material resembles the "long, white, flexible, asbestos-like needles" described as chain-like orthorhombic crystals by Rochow (1973). The "gray rocky" samples from both P&B and ICN appeared to be less uniform in composition and probably contain small quantities of both free elemental silicon and free elemental sulfur in a glassy matrix. Elemental sulfur was detected in the ICN "white crusty" sample by x-ray diffraction and close microscopic examination revealed variations in color from dark gray to pure white and pure yellow. This sample appears to be an amorphous mixture of SiS$_2$ with sulfur and silicon impurities but with a greater degree of compositional variation within the sample than in the "gray rocky" samples. Nonetheless both the "gray rocky" and "white crusty" samples may well be more representative of the type of material formed by secondary reactions between solids and gas in a circumstellar outflow than the crystalline "white fluffy" SiS$_2$ sample. Despite the differences in color and texture noted above, the infrared spectra of these disparate samples were remarkably similar as noted below.

A third sample of SiS$_2$ was obtained from Strem Chemicals in order to check the possibility that features observed near 10 microns in our other samples might be due to SiO$_x$ impurities on the surfaces of the SiS$_2$ grains (Begemann et al. 1996). Strem Chemicals synthesized crystalline SiS$_2$ in "cotton-like lumps" of greater than 99.5% purity and delivered the sample double sealed under dry nitrogen. Upon opening this sample in a dry nitrogen-filled glove bag samples were removed for XRD and FTIR analyses that will be discussed in detail below.

3. Sample preparation and spectral measurements

In the previous study (Nuth et al. 1985) the P&B "gray rocky" samples were ground with an agate mortar and pestle, diluted with granular polyethylene, heated to about $110 - 120\,^{\circ}$C (380-390 K) to form a pellet, and the transmission spectrum measured at room temperature from 80-700 cm^{-1} (125-14 microns). In the present study, two different sample preparation methods were used which gave very similar spectra. In both of these methods, the SiS$_2$ sample was ground in an agate mortar and pestle, diluted with KBr to a concentration of 10-15% SiS$_2$, and the diffuse reflectance spectrum was measured from 4000 to 400 cm^{-1} (2.5-25 microns). The difference between the two types of measurements was in the use of an Harrick environmental chamber for taking measurements at 600 K in vacuo as opposed to measuring the spectrum at room temperature in air. In the experiments using the environmental chamber, it was evacuated using a mechanical vacuum pump to the milliTorr level before and during heating and during spectral measurement. Typically the spectrum was measured both at room temperature (300 K) and then again after the temperature stabilized at 600 K. In a second series of measurements diffuse reflectance spectra were measured in air at room temperature and then again after the same sample had been heated in air at 110 °C (380 K) for periods of up to one hour and then cooled back to room temperature. Aside from a transient feature seen briefly in the environmental

chamber spectra upon reaching 600 K, the spectra obtained by both these techniques were consistent with each other. In the overlap region from 400-700 cm^{-1} (25-14 microns) both sets of spectra were completely consistent with the earlier spectrum of Nuth et al. (1985). We attribute the transient feature at 600 K to traces of H$_2$S released by pumping from the SiS$_2$ sample and reabsorbed onto the larger surface of the KBr dilutent. H$_2$S could easily form by reaction of the SiS$_2$ with an atmospheric water contaminant picked up during sample preparation. This reaction would result in a small amount of silica contaminant in the sample.

Because Begemann et al. (1996) had stressed the very high reaction rate of SiS$_2$ with humid air and because they had also demonstrated that both crystalline and glassy SiS$_2$ yield similar (though not identical) spectra, we tried a new set of experiments designed to address the issue of reactive contamination. Strem Chemicals synthesized "cotton-like lumps" guaranteed to be more than 99.5% pure SiS$_2$: they shipped this material to us double bagged in dry nitrogen. A sample was removed in a nitrogen filled glove bag, ground with KBr and measured in diffuse reflectance. A second, larger sample was removed for XRD measurement in air. The remaining material was stored in a desiccator in the original bottle after flushing with dry N_2. The XRD pattern is completely consistent with $> 99\%$ crystalline SiS$_2$ as shown by comparison with data for orthorhombic SiS$_2$ from the Joint Center for Powder Diffraction Studies (JCPDS 1988) (Fig. 1). The FTIR spectrum of this sample contains significant absorbance from 8-13 microns as shown in Fig. 2a.

The sample used for XRD was left exposed to air for 1.25 hours in the hood after we obtained the XRD pattern; it gave the spectrum shown in Fig. 2b. Subtraction of the spectrum in Fig. 2b from that in Fig. 2a yields a spectrum shown in Fig. 2c that is similar to that reported by Begemann et al. (1996) for SiS$_2$. We remeasured the diffuse reflectance spectrum of a sample of SiS$_2$ removed from the sample bottle after a months storage in dry N_2 and obtained a result virtually identical to Fig. 2a. Finally we placed a sample of SiS$_2$ in the FTIR and measured its diffuse reflectance spectrum each hour for more than two days without observing any significant change due to exposure to the air in our FTIR. Note that this air is dried to a dew point of -100 °C by a Balston Air Drying Unit. These studies demonstrated to our satisfaction that SiS$_2$ is reasonably stable in dry air and that the sharp features observed at 20, 17 and 12 microns are extremely sensitive to humidity.

Fig. 3a-3d are the spectra of various SiS$_2$ samples measured in dry air at 300 K. Fig. 3e-3h are spectra of SiS$_2$ samples measured in vacuo at 600 K. All of the spectra in Fig. 3 share some common features with one another as well as some significant differences from the spectra of Begemann et al. (1996) and the spectrum in Fig. 2a. The most significant difference between the spectra in Fig. 3 and that in Fig. 2a is the lack of sharp features at 12 and 17 microns as well as a shift and broadening of the peak absorption from ~ 20 to $\sim 21 - 22$ microns in the SiS$_2$ samples shown in Fig. 3. However, the similarities in the spectra are extremely significant. All of the spectra in Fig. 3 show features near 7.5 (shoulder), 8.5, 9.5, 12.5 and 21- 22 microns.
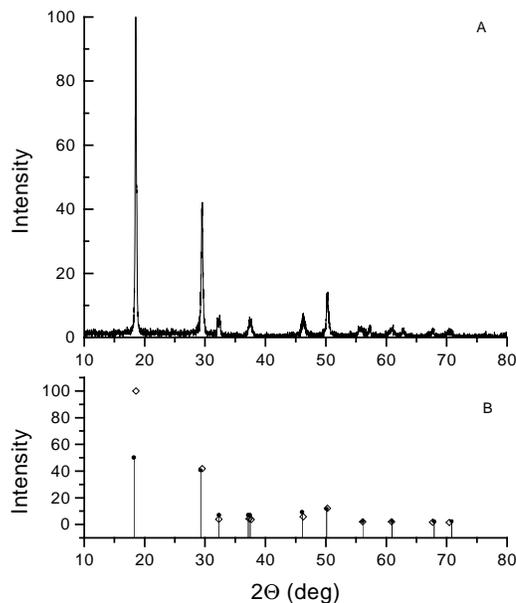
Fig. 1. A. SiS₂ X-ray Diffraction Pattern measured at room temperature in air using Cu Kα radiation, B. Comparison of observed (diamond) and expected (line) (JCPDS 1988) positions and intensities of reflections for orthorhombic SiS₂ crystals. The intensities and positions for the observed data match those for the reference except for the peak at 18.5 for which the observed intensity is roughly twice that expected from the standard.

Fig. 2. a. Diffuse Reflectance Spectrum of SiS₂ sample from Strem Chemical whose x-ray diffraction pattern is shown in Fig. 1; b. Diffuse Reflectance Spectrum of SiS₂ after 1.25 hours exposure to laboratory air; c. Difference spectrum (2a-2b) showing the changes caused by exposure to laboratory air. Both the unexposed and the air exposed spectra have had a linear baseline subtracted to make the changes clearer. Note that even 50 hours exposure to ultradry air ($-100\,^{\circ}$C dewpoint) causes no change in the spectrum so the changes observed are presumably due to exposure to moisture and not to oxygen.

All spectra taken at room temperature also show a feature at 10.7 microns that disappears on heating to 600 K. The spectrum in Fig. 2a shows a shoulder near 8.5 microns as well as distinct features near 9.3, 10.8, 12.2 and 22.5 microns, although the intensities of the peaks differ somewhat from the pattern displayed by the spectra in Fig. 3.

We also observed two additional features that appear to be due to impurities. A peak near 15 microns which disappears on heating is due to a KNO₃ impurity present in KBr. A feature at 23.9 microns (not shown) appeared (briefly) only in those samples whose spectra were run in the environmental chamber. This feature disappeared on long heating. It was not present in any samples which were run in air whether heated or not. It is suspected that this feature may be due to a volatile impurity, possibly H₂S, which is initially trapped in the SiS₂ matrix but which on evacuation and heating of the environmental chamber is released and readsorbs on the much larger surface area of the KBr dilutant before being pumped away.

4. Discussion

4.1. Assignment of SiS₂ Absorption Features

Previous studies of the spectrum of SiS₂ show both similarities to and significant differences from the measurements reported in this work. We do not believe that these differences are due to carelessness on the part of past researchers (or on our part) but rather are due to differences in the interpretation of the measured spectra as well as slight differences in the SiS₂ itself; differences
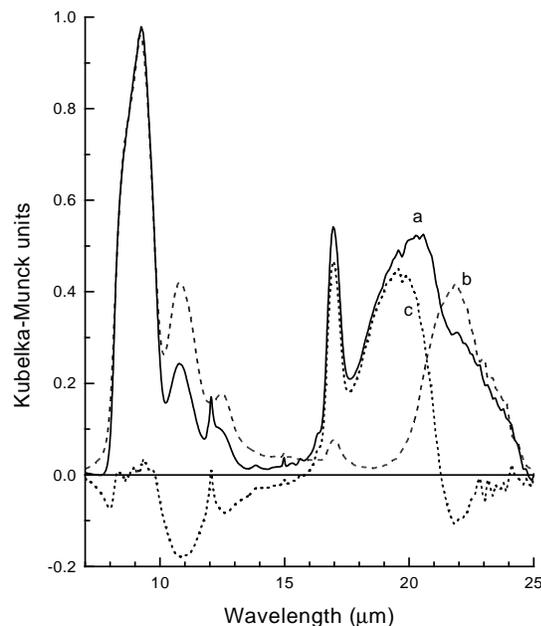
in crystal structure, the relative importance of surface vs. bulk modes, or the relative proportions of amorphous, glassy or crystalline material in the samples measured. A major disagreement between our measurements and those of Begemann et al. (1996) lies in the interpretation and handling of features observed by both groups near 10 microns. Begemann et al. (1996) treat these features as a silica contaminant (as we did initially) rather than as due to SiS stretching vibrations.

4.2. The 8-13 micron features

A feature at 10 microns due to a silica stretching mode is usually accompanied by a bending feature of nearly comparable strength. In our initial attempts to obtain "pure" SiS₂ spectra we assumed that the features observed at 10 microns were due to SiO stretching modes in an amorphous silica contaminant and we spent several months fruitlessly trying to subtract spectra of mixtures of SiO_x ($1 < x < 2$) of varying degrees of oxidation and crystallinity from our measured spectra in order to obtain the "true" spectrum of SiS₂. While no combination of silica spectra completely eliminated all of the features observed between 8-13 microns, several did lead to a significant degree of suppression of these features. Unfortunately, since silica spectra consist of both SiO stretching modes near 10 microns as well as OSiO bending modes near 22 microns, all such attempts at eliminating the 10 micron silica "contaminant" resulted in significant neg-
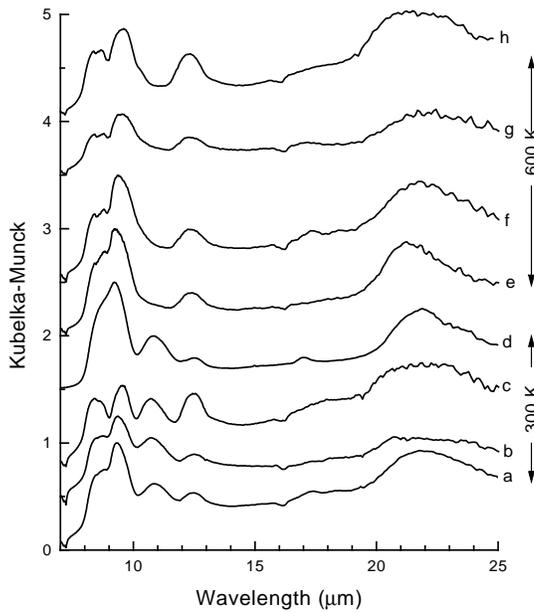
Fig. 3. Diffuse reflectance spectra measured in dry air (300 K) or in vacuo (600 K) of: a. P&B Gray Rocky sample at 300 K, b. ICN White Crusty sample at 300 K, c. ICN White Fluffy sample at 300 K, d. Strem air exposed sample at 300 K, e. P&B Gray Rocky sample at 600 K, f. ICN Gray Rocky sample at 600 K, g. ICN White Crusty sample at 600 K, h. ICN White Fluffy sample at 600 K.

ative absorbance values for the "corrected" SiS$_2$ sample near 22 microns. We were unable to simultaneously minimize the 10 micron features and salvage any sensible data in the 20 micron region. We were therefore led to the conclusion that the features we observed between 8 and 13 microns were due not to SiO$_x$ but to SiS$_2$.

We believe that the 8-13 micron and 22 micron absorption features are due to SiS$_2$ for a variety of reasons. The most important of these is that the features appear in strength in all SiS$_2$ samples measured in our lab, including a fresh sample whose XRD pattern is consistent with pure, crystalline SiS$_2$. Furthermore, an absorption feature near 10 microns was consistently observed by Begemann et al. (1996) despite the extreme measures taken during that study to avoid contamination by atmospheric oxygen or water vapor. They could not eliminate these features from their laboratory spectrum: they chose to identify them as silica contaminants. However, since silica has features of comparable strength near both 9-10 and 22 microns, subtraction of sufficient silica contaminant spectra from that of SiS$_2$ to eliminate the 10 micron features will also remove a comparable amount of absorption at 22 microns. If the 10 micron feature were due to a silica contaminant, then its removal should still preserve the SiS$_2$ absorption near 20 microns. This was never possible with any of the spectra obtained in our laboratory: subtraction of sufficient silica "contaminant" absorption to eliminate features near 10 microns always resulted in an unphysical (negative) absorbance near 22 microns.

4.3. Possible source of the 8-13 micron features

We could find no value for the molecular force constant of the SiS bond in SiS$_2$ in the literature, so a calculation of the position of the SiS stretch from first principles is not possible. However, the energy of the CS stretch in CS$_2$ is approximately 1500 cm^{-1} while that of the SiO stretch in SiO$_2$ is near 1100 cm^{-1} (Conley 1966). If we calculate a value of the force constant for the (OSi) = O stretch, assume that this force constant remains the same for the (SSi) = S stretch and calculate the new energy for the vibration due to the substitution of the heavier sulfur for the lighter oxygen atoms, the (SSi) = S stretch will occur near 800 cm^{-1}. If we perform a similar calculation for the (SSi) = S stretch based on the known energy of the (SC) = S stretch at 1500 cm^{-1}, we obtain a value of 1400 cm^{-1}. Of course CS$_2$ is a molecular liquid while SiO$_2$ is an infinite solid: we make no claim that the 8-13 micron features in the spectrum of orthorhombic, needle-like SiS$_2$ crystals must be due to the (SSi) = S stretch. However, we do argue that, based on the above, the energy of the SiS stretching vibration in solid SiS$_2$ could lie in the range from 800- 1200 cm^{-1}, the range over which we observe significant absorption in each of the SiS$_2$ samples measured in our laboratory.

4.4. The effect of reaction with H$_2$O

If we examine the reaction of crystalline SiS$_2$ with humid air (shown in Fig. 2) we find additional support for the argument that the 8-13 and 22 micron features are due to vibrational modes in SiS$_2$. First, we know from the XRD pattern shown in Fig. 1 that the original sample is more than 99% crystalline SiS$_2$. Therefore if the 8-13 and 22 micron features are due to a "contaminant" present in this sample, the absorption strength of this contaminant must be nearly two orders of magnitude stronger than that of SiS$_2$ in order to appear at nearly comparable strength. Reaction of the crystalline SiS$_2$ sample with humid air results in the rapid loss of sharp features at 12, 17 and 20 microns, but in no significant increase in the strength of the other 8-13 or 22 micron absorptions as would be expected if the reaction of SiS$_2$ with humid air was the source of the "contaminant" in our samples. Our observations indicate that the vibrational modes responsible for the 12, 17, and 20 micron absorptions appear to be quenched by reaction with humid air and could therefore be due to surface modes in the orthorhombic crystals.

4.5. Composite spectra

Examination of the spectra in Figs. 2 and 3 reveal a range in intensities of various features, but three distinct groups of spectral features. Each of the spectra measured at room temperature after some exposure to humid air contains a feature at 10.7 microns that is missing from the spectra of samples heated in vacuo to 600 K. In addition, the spectrum of SiS$_2$ "surface modes" is distinctly different from any other spectra in Figs. 2 and 3. For ease of comparison with astronomical observations and with the spectra of possible "contaminants" we constructed the following composite spectra. First the spectrum of SiS$_2$ "surface

modes" was obtained by subtracting Fig. 2b (the sample exposed to moist air and scaled such that the height of the 9.5 micron feature equaled that in 2a) from Fig. 2a (the unexposed sample) and displaying this difference as Fig. 4b. Second, a 300 K composite was constructed by scaling Figs. 3a-3d to a constant area of the 10.7 micron feature and averaging these spectra to yield Fig. 4c. Finally, a 600 K composite was constructed by first scaling the spectra in Figs. 3e-h as was done for the 300 K composite, then averaging the four spectra to obtain Fig. 4d. For comparison with these spectra we have included the spectrum of an amorphous, underoxidized silica smoke sample produced via the combustion of silane in our laboratory (Fig. 4e), the spectrum of monodisperse silica spheres kindly provided to us by Dr. Thomas Henning (Fig. 4f) and the spectrum of elemental sulfur (Fig. 4g) all measured using the Harrick Diffuse Reflectance Attachment in our laboratory. Note that the spectrum of a freshly-condensed, underoxidized silica smoke tends to maximize the relative contribution of the 10 micron SiO stretch compared to the OSiO bending mode near 20 microns (Nuth and Hecht, 1990). Finally an astronomical spectrum of 07134+1005 (SAO96709, HD56126, DM+10 1470), a proto planetary nebula candidate star of spectral Class F5, obtained from Dr. Sun Kwok (1996) is shown for comparison as Fig. 4a.

The most obvious aspect of Fig. 4 is the very great difference between SiS$_2$ "Surface Modes" (4b) and any of the other SiS$_2$ or silica spectra. Initial comparison of this spectrum (4b) with astronomical observations (4a) looks quite promising in fitting the sharp peak seen at 20 microns, but falls short of perfection for two reasons. First, the 20 micron "Surface Mode" peak is insufficient by itself to explain the astronomical observation, additional absorption at longer wavelengths and much less absorption near 19 microns is required. Second there is no evidence for a sharp and reasonably strong feature in the astronomical spectrum at 17 microns, although there is some evidence for the presence of a minor feature at a slightly shorter wavelength. Neither of the composite spectra (4c and 4d) can explain the sharp peak at 20 microns seen in the astronomical spectra, although these spectra can help to explain the long wavelength wing and do contain features near 11 and 12 microns as seen in the spectrum of 07134 + 1005.

Comparison of the SiS$_2$ "Surface Modes" to the spectrum of elemental sulfur (4g) easily demonstrates that elemental sulfur is not an important contaminant in this sample. Similarly elemental sulfur does not seem to contribute to the more amorphous SiS$_2$ composite sample spectra (4c or 4d). However, comparison of spectra 4a and 4g does indicate that elemental sulfur could be responsible for the minor spectral components observed in 07134 + 1005 in emission near 21 and 17 microns and in absorption at 12 microns. The spectra of both amorphous silica smoke and the monodisperse silica spheres are also interesting: there are significant similarities between these spectra and both composite SiS$_2$ spectra, supporting the interpretation of Begemann et al. (1996) that the features between 8-13 microns could be due to a silica contaminant. We have previously argued that the XRD pattern (Fig. 1) of the sample that yielded Fig. 2a conclusively demonstrates that crystalline SiS$_2$ can produce features in
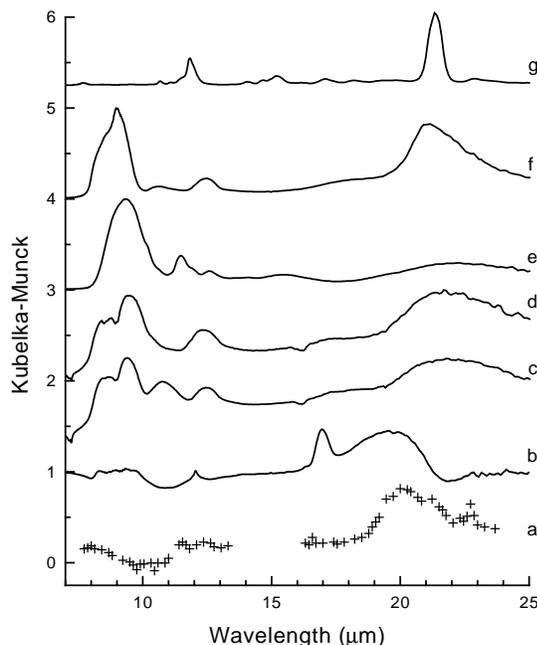

Fig. 4. a. Spectrum of the carbon-rich source 07134 + 1005, b. Difference spectrum showing SiS$_2$ surface modes, c. Composite Diffuse Reflectance Spectrum of 300 K SiS$_2$ samples, d. Composite Diffuse Reflectance Spectrum of 600 K SiS$_2$ samples, e. Diffuse Reflectance Spectrum of amorphous silica smoke, f. Diffuse Reflectance Spectrum of monodisperse silica spheres, g. Diffuse Reflectance Spectrum of elemental sulfur.

the 8-13 micron region. We have also argued that the spectrum of solid SiS$_2$ (consisting of edge-sharing, SiS$_4$ tetrahedral units) should resemble the spectrum of solid silica (made up of corner-sharing SiO$_4$ units) as is the case in Fig. 4. Amorphous silica smokes show strong absorption at 9.2 microns with a shoulder near 8.5 microns, small features near 11.4 and 12.5 microns, and a second absorption at 22 microns. The monodisperse silica spheres show a similar set of more distinctive features and a much stronger feature near 22 microns. The silica and SiS$_2$ sample spectra do differ in the relative widths, and exact positions of the features. Another difference is the presence of the 10.7 micron feature in cold SiS$_2$ that is not seen in any silica sample. This comparison illustrates the difficulty of subtracting a significant silica "contaminant" spectrum from that of SiS$_2$. Subtraction of sufficient silica intensity to eliminate the 8.5, 9.5 and 12.5 micron features in SiS$_2$ spectra more than eliminates the 21-23 micron absorption in SiS$_2$ and still leaves residual features in the 8-13 micron region. Nevertheless, it is obvious from Fig. 4 that spectra of bulk SiS$_2$ are similar to those of SiO$_2$, except in the case of the SiS$_2$ surface modes. The spectrum of this particular component of SiS$_2$ is quite distinctive.

4.6. Spectra of astronomical sources

If the spectra obtained by Chan et al. (1995) are due to SiS$_2$, then one reasonable morphology for the astronomical sources is that of a large shell or disk of cold dust (100-200 K) sur-
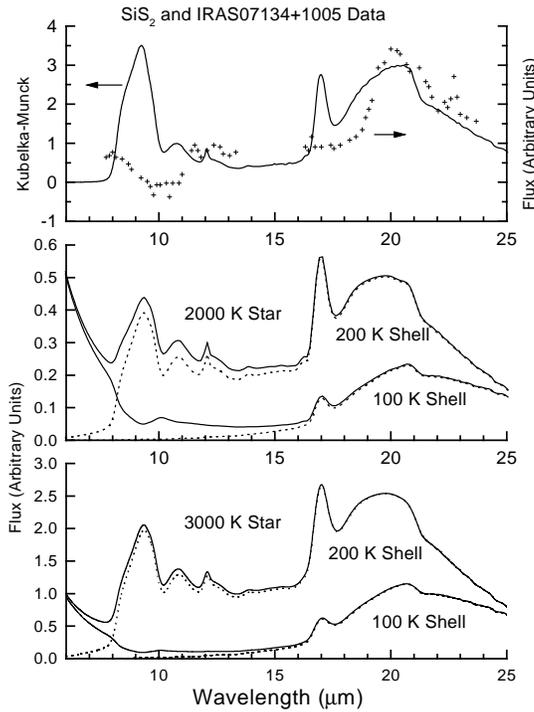
Fig. 5. The calculated spectra of 100 K and 200 K SiS$_2$ shells surrounding 2000 K and 3000 K stars compared to the spectrum of IRAS 07134 + 1005 over the range from 6-25 microns. The SiS$_2$ spectrum used in the calculations is that of the unexposed Strem SiS$_2$ shown for clarity at the top of the figure.

rounding the central star. The cold dust would absorb radiation near 10 microns emitted by the central star but would produce an emission maximum near 15-30 microns from the extended, cold dust shell. We have examined a simplified model of such a system as a test of this model and to suggest future observations. In our model a cool star (2000-3000 K) is surrounded by a "gray body" dust shell with a temperature of 100-200 K. The shell radius is adjusted to achieve radiative equilibrium in the dust shell. We calculated mass-absorption coefficients for SiS$_2$ as a function of energy from 80 - 2000 cm^{-1} derived from the mass-absorption coefficients in (Nuth et al. 1985) and the spectrum of the fresh, Strem Chemical sample shown in Fig. 2a. The stellar emission as seen from outside the shell is then corrected for the absorption of a SiS$_2$ shell and the shell emission is corrected for the enhanced emissivity associated with the absorption features of SiS$_2$. The net emission of the combination can then be determined. Fig. 5 shows the results of several such calculations.

Of particular interest is the fact that the 15 to 30 micron region always shows up in "emission" since the shell emission dominates this region. However, the SiS$_2$ features between 8.5 and 12.5 microns can show up in either absorption or emission depending on the balance between the light absorbed and that emitted by the shell. This balance is particularly sensitive to the shell temperature with these features barely appearing in absorption for a 100 K shell and in emission for a 200 K shell. Thus,

the 21 micron feature is far more diagnostic of SiS$_2$ than is the 9.5 micron feature despite the latter feature's strong absorption coefficient. However it would seem prudent to obtain visible to near-infrared spectra of astronomical sources exhibiting the 21 micron emission feature so that adequate radiation-transfer models could be constructed in order to test the hypothesis that a shell of cold SiS$_2$ dust surrounds a hotter stellar source.

A more serious problem with SiS$_2$ as the source of the 21 micron feature is the poor fit of the 21 micron feature of SiS$_2$ to the astronomical spectrum. The "surface mode" SiS$_2$ fits the onset of the 21 micron feature reasonably well, but is not wide enough to account for all of the absorption. Even worse is the fact that the 20 micron surface mode feature is always accompanied by a sharp feature at 17 microns that is nearly as intense as the 20 micron peak in all available laboratory spectra (e.g., Fig. 2a and Begemann et al. 1996) but that is not observed in any of the astronomical sources. The "bulk" SiS$_2$ laboratory spectra do not exhibit a 17 micron absorption feature, but the onset of their 21 micron absorption maxima is at longer wavelength than observed in astronomical sources. Combining the 20 micron "surface mode" SiS$_2$ feature with the bulk composite SiS$_2$ spectrum (e.g. as for the fresh Strem Chemical sample in 2a) while arbitrarily excluding the "surface mode" feature at 17 microns produces a good match to the observations but is not justifiable based on the available laboratory data.

The 7-25 micron spectrum of 07134+1005 is shown on Fig. 5 for comparison with our model of an SiS$_2$ shell as is the spectrum of the fresh Strem Chemical SiS$_2$ sample from Fig. 2a. As noted above, SiS$_2$ does not provide a very good fit to the 21 micron feature. It should be noted that 07134 + 1005 may be considerably hotter than the 3000 K black body used in our model calculation, shifting the minimum in stellar flux to shorter wavelength and putting the 9.5 micron feature prominently in emission, thus increasing the discrepancy between observation and an SiS$_2$ model. An alternative material which may produce spectra consistent with the astronomical observations is nanodiamonds (Hill et al. 1996). Kwok and Bernath (1996) argued that the 21 micron feature could be due to PAHs based on the presence of strong C$_2$ and C$_3$ absorption bands in 21 micron sources (Hrivnak 1995) and the presence of the well known UIBs near 3.3, 3.4, 7.7 and 11.3 microns in many of the carbon-rich sources of the 21 micron emission band. These same arguments would be consistent with the production of nanodiamonds in such sources, especially since the infrared spectrum of such diamonds sometimes contains an absorption band at 475 cm^{-1} (Hill et al. 1996) and because Nuth (1987) has argued that diamond is thermodynamically stable at very small particle size. More detailed spectra of unaltered microdiamonds are needed in order to confirm or refute this working hypothesis.

5. Summary

We have presented the spectra of a variety of SiS$_2$ samples for comparison with spectra of astronomical sources displaying an emission feature near 21 microns and have demonstrated that the spectrum of SiS$_2$ is only marginally consistent with the astro-

nomical observations. We have shown that solid SiS$_2$ has strong absorption bands in the 7-13 micron region but that such bands may be masked in astronomical spectra due to uncertainties in the underlying emission spectra of the sources. Specifically, small differences in the temperature of the shell shifts features in the 8- 13 micron region from emission to absorption and may result in complete elimination of the feature for the "proper" combination of shell temperature and stellar surface temperature. Nevertheless, the peak absorbance for the "bulk-mode" SiS$_2$ occurs at longer wavelength than is observed in the astronomical sources and so is not a good match to the observations. Similarly, although the peak absorption of "surface-mode" SiS$_2$ does match the observed peak in the astronomical sources, the SiS$_2$ feature is too narrow to account for all of the observed emission and is always accompanied by a relatively strong companion absorption at 17 microns that has never been observed in astronomical sources. Again this would appear to rule out SiS$_2$ as the source of the 21 micron feature in carbon-rich stellar shells.

We have noted that the spectrum of solid sulfur is consistent with several minor features observed in the spectrum of 07134 + 1005. Specifically, sulfur might account for the minor features observed in emission near 21 and 17 microns, and in absorption at 12 microns in this source. Of course it would seem prudent to firmly verify the composition and spectrum of the major dust component around this star before trying to identify minor species.

We have recently seen the spectrum of nanodiamonds (Hill et al. 1996) and were amazed to learn that this material sometimes displays an absorption near 475 cm^{-1} that is not accompanied by any nearby features. Arguments put forward to advance the PAH hypothesis are equally applicable to the formation of nanodiamonds. In fact, there should be no reason to suspect that nanodiamonds can not co-exist with PAHs in some carbon-rich sources. Given the difficulty of fitting the observations using SiS$_2$, more detailed spectra of nanodiamonds are needed to adequately consider this alternative.

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