Fine hematite particles of Martian interest:
absorption spectra and optical constants

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Abstract. Hematite is an iron oxide very important for the study of climatic evolution of Mars. It can occur in two forms: red and grey, mainly depending on the granulometry of the samples. Spectra of bright regions of Mars suggest the presence of red hematite particles. Moreover the Thermal Emission Spectrometer (TES), on board the Mars Global Surveyor mission, has discovered a deposit of crystalline grey hematite in Sinus Meridiani. TES spectra of that Martian region exhibit features at about 18, 23 and 33 µm that are consistent with hematite. Coarse grey hematite is considered strong evidence for longstanding water, while it is unknown whether the formation of fine-grained red hematite requires abundant water. Studies are needed in order to further characterize the spectral properties of the two kinds of hematite. For this reason we have analyzed a sample of submicron hematite particles in the 6.25-50 µm range in order to study the influence of particles size and shape on the infrared spectra. The optical constants of a particulate sample have been derived and compared with published data concerning bulk samples of hematite. Our results seem to indicate that particle shape is an important factor to take into account for optical constants derivation.

1. Introduction
Among the materials of Martian interest, hematite is certainly, for various reasons, one of the most important. Hematite is a ferric oxide (α-Fe₂O₃), naturally occurring in two forms: red and grey, mainly depending on the granulometry of the samples. On Earth the red kind is widespread: it is rust that forms readily whenever iron is exposed to air. Pure crystalline hematite particulate samples with grain size between 0.1 µm and 10 µm (hereinafter normal red hematite samples) exhibit reflectance spectra which are saturated (near zero) in the violet and ultraviolet and steeply increase throughout the visible: this behaviour explains the typical red colour of this kind of hematite. In addition, superimposed on this steep slope, three Fe³⁺ crystal-field bands are present at about 0.53, 0.63 and 0.86 µm. Because of the visual colour of Mars, red hematite and others ferric oxides have long been suggested as surface materials, especially for brighter, redder regions of the planet. Viking lander chemical analyses of the Martian soil confirmed a percentage of hematite of about 18-20 wt%. In 1989 Morris et al [1] have demonstrated that red hematite samples with grain size smaller than 0.1 µm (the so-called nanocrystalline or nanophase hematite) have reflectance spectra very similar to those observed on Mars with an intense, relatively featureless, slope in the visible. Morris et al [1] have also found that nanocrystalline hematite has a characteristic superparamagnetic behaviour (not shown by coarser-grained hematite) consistent with the
results of the Viking magnetic properties experiment.

All laboratory and observational works indicate that the majority of bright soil deposits on Mars appears to consist largely of nanocrystalline red hematite, even if this does not preclude the occurrence of normal red hematite in some regions of Mars. In addition, in some scattered spots of the Martian surface hematite particles with size even greater than those of normal red hematite (typically > 10 µm) are present. This kind of coarser-grained hematite has a spectral behaviour, both in the visible and in the infrared, which is very different from that of red hematite. For this reason, due to its colour, it is called grey hematite. Christensen et al [2, 3] found evidence for a large deposit of grey hematite in a low albedo area in the equatorial Sinus Meridiani region of Mars. It is important to note that on Mars crystalline grey hematite is only present in two areas, smaller than 100 km in diameter, Sinus Meridiani, 2.5° S, 4° W, and Aram Chaos, 2° N, 21° W, along with numerous spots, about 10 km in diameter, scattered through the interior of Valles Marineris. Estimated hematite areal abundance in these regions is about 10 - 15%. Detectable crystalline grey hematite regions larger than 10 km are lacking elsewhere on Mars from 60° N to 60° S [3]. The presence of grey hematite in Sinus Meridiani has been confirmed, based on its thermal infrared spectral signatures, by the Mini-TES spectrometer onboard the rover Opportunity, recently landed in that region [4].

A strong 0.864 µm band is also present in rovers Pamcam imagery of the soil, suggesting that red hematite is produced by the natural abrasion of larger grey hematite grains [4].

In any case red hematite is an important component of Martian surface materials and, due to the strong winds blowing on the surface, which are able to move a large number of sand-sized particles into the atmosphere, it is likely that it is also present in the atmospheric dust. For this reason the knowledge of the optical constants of hematite can be very useful in modeling the surficial and the airborne dust on Mars.

2. Experimental approach and theoretical calculations

The knowledge of the optical constants of hematite may help to elucidate the problem of its presence on the surface of Mars. The hematite sample analyzed in this work (HMMG1) was kindly provided by R. Morris at NASA JSC and it was already studied in 2002 by Lane et al [5]. It is a natural sample coming from Brazil and its chemical and mineralogical purity was determined using various methods [5].

In order to obtain very fine grains of hematite, we ground our sample in an agate mill and we also performed sedimentation. The analysis of images, taken in our laboratory by means of a Philips XL20 Scanning Electron Microscope, indicates an average size of hematite particles of about 0.1 µm, where the average size is the mean radius of a circle with the same area as the projected particle image. All transmission measurements were performed by means of a Perkin Elmer Spectrum 2000 in the spectral range 6.25-50 µm with a resolution of 1 cm⁻¹. We used the standard pellet technique with about 0.240 mg of hematite in 250 mg of CsI powder.

For radiative transfer computations needed to model Martian spectra, optical constants are always useful, since they serve as the basis for the calculation of the necessary absorption and scattering efficiencies for different size and shape distributions of the dust particles. However it is worthwhile to stress that the extinction spectra of submicron particles can be better reproduced using optical constants directly obtained in the laboratory for particulate materials of the appropriate size. In fact, when bulk optical constants are used to model the spectra of particulate samples, the agreement between laboratory results and model predictions can be very poor. For this reason particular caution must be exercised in extrapolating laboratory results concerning bulk samples to physical conditions where particles smaller than the wavelength are expected to occur [6].

The optical constants of a particulate sample can be directly calculated following the approach already described in previous papers [7, 8, 9]. The procedure, which uses both Mie theory and
Figure 1. The optical constants of hematite particles compared with those published for bulk samples by Onari et al [10] and by Querry [11].

Lorentz dispersion theory, allows to derive the dielectric constant starting from transmission measurements and it has been successfully applied by our group in order to calculate the complex refractive index of calcite and gypsum particles.

Hematite is an uniaxial crystal which crystallizes into the trigonal system. The dielectric constants of bulk hematite must therefore be measured for two principal polarizations of the incident light, namely one with the electric vector along the crystalline c axis and the other with the electric vector in any direction in the plane perpendicular to the c axis. The light beam polarized perpendicularly to the crystal symmetry axis is called the ordinary ray, the one with parallel polarization is called the extraordinary. The results of calculation in the case of hematite are shown in figure 1. The same figure also reports the comparison between our particulate optical constants with those by Onari et al [10] and by Querry [11] for bulk hematite.

The comparison clearly indicates that the particulate optical constants are very different from the bulk ones and this behaviour is not strange since, according to [12] and [6], possible discrepancies can occur, for some materials, between the optical constants valid for bulk samples and those valid for submicron particles. These discrepancies are generally due to intrinsic properties linked to the surface modes which occur in small particles \(2\pi a/\lambda < 0.1\), where \(a\) is the grain radius and \(\lambda\) is the wavelength) and are often disregarded in the literature. However it is important to note that our hematite particulate optical constants do not exhibit the spectral band at about 29 \(\mu m\) which is instead present in the experimental extinction spectrum as well as in the calculated spectrum obtained by means of the derived optical constants (without band) and Mie theory (see figure 2).

In this respect it is worthwhile to stress that our approach works in the Rayleigh approximation for spherical particles, which is a limiting case within the Mie theory. This approximation is valid when the grains are small compared to the wavelength \((x = 2\pi a/\lambda << 1)\), and in the limit of zero phase shift in the particle \(|m|x << 1\), where \(m = n + i k\) is the complex refractive index).
The condition $x << 1$ is certainly satisfied all over the spectral range, in particular at the longest wavelengths, since the average size of hematite grains is $a = 0.1 \mu m$. The condition $|m|x << 1$ instead requires the \textit{a priori} knowledge of the refractive index of hematite to be fulfilled and it could be not satisfied at the position of the main infrared features of hematite because of the high value of the refractive index. In fact, an analysis of the optical constants calculated by Onari et al [10] and by Querry [11] shows that $|m|x << 1$ in the spectral range 0.25-50 $\mu$m, with the exception of the position of hematite spectral features, where $|m|x$ rapidly increases. In particular if one considers the \textit{ordinary} ray optical constants given by Onari et al [10], $|m|x = 0.372$ at $\lambda = 34.97 \mu m$, with $a = 0.1 \mu m$. Such consideration can probably explain the strange behaviour of our \textit{particulate} optical constants and the absence of the spectral feature at 29 $\mu m$. For this reason our theoretical approach could be not valid to derive the optical constants of hematite, even if our \textit{particulate} optical constants are able to reproduce the spectral band at 29 $\mu m$. This probably means that our procedure in this case can produce a kind of \textit{effective} optical constants, valid only for our particular measurements.

**Figure 2.** Synthetic spectrum of hematite calculated by means of the \textit{particulate} optical constants for spherical particles with an average size of 0.1 $\mu m$ compared with the experimental one. It is clearly evident the features at about 29 $\mu m$, which is not present in the \textit{particulate} optical constants.

However we are interested in reproducing a generally valid extinction spectrum of hematite particles: therefore we tried to reach this goal by using the bulk optical constants of this mineral. Since it is reasonable to assume the particles embedded in a transparent matrix to be randomly oriented, a proper mean of the extinction of hematite particles can be calculated as

$$
\frac{Q_{\text{ext}}(\lambda)}{a} = \frac{2}{3} \frac{Q_{\text{ext}, o}(\lambda)}{a} + \frac{1}{3} \frac{Q_{\text{ext}, e}(\lambda)}{a}
$$

(1)

where $Q_{\text{ext}, o}(\lambda)/a$ and $Q_{\text{ext}, e}(\lambda)/a$ are the extinction efficiency for the \textit{ordinary} and \textit{extraordinary} ray respectively [6, 13]. In this work synthetic extinction spectra of hematite particles have been calculated by means of the optical constants of bulk hematite derived by Onari et al [10] and by Querry [11]. Figure 3, where the results of these calculations are shown, clearly indicates that both position and spectral contrast of the main features of the experimental extinction spectrum of particulate hematite cannot be well reproduced by means of the bulk optical constants and

**Figure 3.** Experimental extinction spectrum of hematite grains compared with those calculated by means of the optical constants of bulk hematite derived by Onari et al [10] and by Querry [11]. Calculations were performed by means of Mie theory for particles with an average radius of 0.1 $\mu m$. 


Figure 4. Experimental extinction spectrum of hematite particles compared with those calculated for a flat CDE and a peaked CDE starting from the optical constants of bulk hematite.

Mie theory. Note that the large differences in the spectral contrast among the different curves in figure 3 needed the use of a logarithmic scale on the ordinate axis.

It is well-known that accurate calculations of the extinction properties can be done in the framework of Mie theory, which is the theory of light scattering by a sphere. However most of the particles which occur in nature differ from perfect sphere. In the case of hematite, SEM images of our sample show that the classical Mie theory cannot be used if one wants to accurately calculate the extinction properties of such particles. For this reason in the last few years many methods have been developed in order to better reproduce the real shapes of grains in a laboratory sample. As a first approximation, a distribution of randomly oriented ellipsoids, with various continuous distributions of relative lengths of the three semiaxes, comprising a variety of shapes, from long needles to spheres to thin disks, offers a chance to approximate the possible real shapes in a collection of particles [6]. Two types of continuous distribution of ellipsoids (CDE) in the Rayleigh limit were used in this study:

- **a flat distribution** of the shape parameters that does not favour any particular shape; spheres and needles and disks are equally probable [14, 15];
- **a peaked distribution**, that favours the almost spherical grains and minimizes the contribution of the disks and needles [16].

In this respect $C_{ext}(\lambda)/V$ spectra for CDEs of hematite have been calculated for particles embedded in a CsI matrix and the results compared with the experimental measurements in figure 4.

3. Results and discussion
An important result of our study is the fact that shape effects could play an important role for the interpretation of astronomical spectra [17].
In the case of hematite, as a consequence of the production of small irregularly-shaped particles by mechanical grinding, a model based on a collection of randomly oriented ellipsoids can reproduce the experimental extinction spectrum better than the Mie theory spherical approximation. In particular, as it is evident in figure 4, flat CDE calculations fit reasonably well the bands at 18 and 21 $\mu$m, while peaked CDE results agree relatively well with the experimental spectrum in the region of the 21 and 29 $\mu$m bands.

It is worthwhile to note that $C_{\text{ext}}(\lambda)/V$ spectra for CDEs have been calculated in the Rayleigh limit and this can explain some differences between the experimental spectrum and the synthetic ones. In fact, as previously stated, for our hematite grains the Rayleigh condition could be not completely fulfilled in correspondence of the spectral band at 29 $\mu$m (where in our case $|m|x = 0.372$) and this could invalidate the results of the fit in that spectral region. In any case, in the other part of the spectral range, the Rayleigh limit is surely valid, in particular for the optical constants given by Query [11] and this consideration allows to state that CDE reproduce the spectral behaviour of hematite better than Mie theory for spherical particles. However these are only preliminary results and we are now looking for other shape distributions of particles which could reproduce the experimental spectra of hematite grains better than Mie theory or CDE approximations.

Moreover we are also trying to calculate the optical constants of bulk hematite with a completely different approach, starting from emission measurements performed on the same sample (HMMG1) already studied by Lane et al [5] (see section 2). In this way we will try to reproduce our experimental extinction spectrum of particulate hematite with the bulk optical constants of the same sample.

In any case it seems that the bulk optical constants of hematite, linked with an adequate shape distribution of grains, can be used in order to reproduce the spectra of submicron particles. Such conclusions cannot be extrapolated directly to other particles and/or materials, since every case has to be treated independently. In fact several laboratory spectra of particulate samples cannot be interpreted by using the bulk optical properties with the appropriate grain shape distribution. For example, only the optical constants directly derived for particulate samples can reproduce the experimental spectra of calcite submicron particles [17].

In conclusion, as far as particulate hematite sample is concerned, we tried to obtain directly its optical constants. Unfortunately we did not reach the goal and this was impossible to be predicted a priori, due to the fact that the condition $|m|x << 1$ can be tested a posteriori only tentatively, looking at other sets of $n$ and $k$. Waiting for other techniques more suitable to derive the particulate optical constants, at the moment we checked if bulk optical properties could be used in order to overcome the problem. We showed that using bulk optical properties together with various shape distributions different from spheres can be a promising direction and we are now working to improve our approach.

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