Research Unit FOR 2285
“Debris Disks in Planetary Systems”

Semiconductor- & Metallic-Behavior of Iron(II) Sulfides: A Multi-Wavelengths Study

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Abstract

- Iron(II) sulfides: **Sulfur reservoirs in interplanetary dus**t (e.g. in comets, meteorites, IDPs)
- Prior spectral studies: Covers either the UV-VIS to NIR, or the FIR spectral range
- Our study: Reflectivity data from **VUV to FIR** for the determination of optical constants
- Five iron(II) sulfides with different Fe/S ratio: From **4C-pyrrhotite to troilite**
- **Binary spectroscopic behavior** between stoichiometric(-like) & iron depleted iron(II) sulfides
- **Optical constants** depend on Fe/S ratio & **IR reflectivity decreases** with **higher iron amount**

Previous Optical Studies

[1] W. G. Egan, T. Hilgeman, The interstellar medium: UV complex index of refraction of several candidate materials, Astronomical Journal 80, 1975, pp. 587-594.

[2] W. G. Egan, T. Hilgeman, The Rings of Saturn: A Frost-Coated Semiconductor?, Icarus 30(2) 1977, pp. 413-421.

[3] B. Begemann, J. Dorschner, T. Henning, H. Mutschke, E. Thamm, A Laboratory Approach to the Interstellar Sulfide Dust Problem, E. 1994, ApJ, 423, L71-L74.

[4] H. Mutschke, B. Begemann, J. Dorschner, H. Henning, Infrared Physics & Technology 35(2{3) 1994, pp. 361-374.

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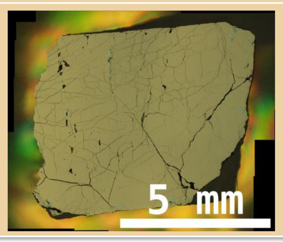
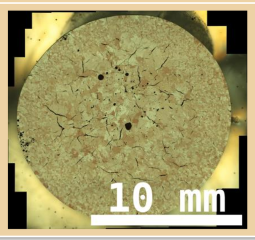
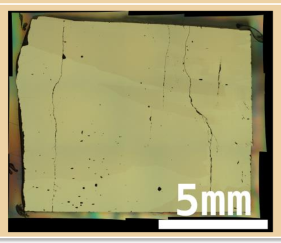
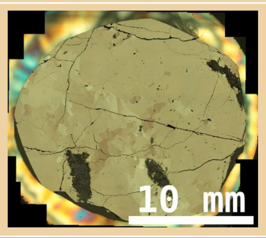
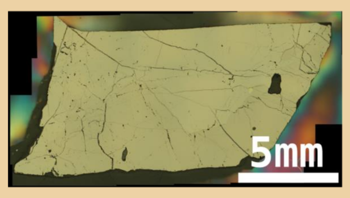
[6] T. Henning, H. Mutschke, Low-temperature infrared properties of cosmic dust analogues., A&A, 1997, pp. 327-743.

Samples

	Troilite	Synthetic [3,4,6]	DAL [7]	NYS [8]	TYS [8]	DEV [9]
Iron(II) Sulfide Type	Troilite	Troilite with iron	4C-Pyrrhotite	NC-Pyrrhotite: 4.78 – 4.96	NC-Pyrrhotite: 5.12 – 5.52	6C-Pyrrhotite
Iron/Sulfur Ratio	1	1	0.877(1)	0.896(2)	0.903(7)	0.929(2)
Crystal System	Hexagonal	Hexagonal	Monoclinic	Hexagonal		Monoclinic
Origin	MPIK Heidelberg	Begemann, MPS Jena	Harries, IGW Jena			de Velliers
Images						

Experimental Setup

- Four spectrometers from **VUV to mm** wavelength range **at 300 K**
- Two **frequency domain** spectrometers:
  - VUV: 115 nm – 230 nm (under vacuum)
  - UV-VIS-NIR: 190 nm – 2.5 µm (under ambient air)
- Two **time domain** spectrometers:
  - FTIR: 2.0 µm – 500 µm (under vacuum)
  - THz: 250 µm – 2 mm (under dry air)
- **Low temperature** measurements **down to 10 K for MIR & FIR**

Multi-Wavelengths Reflectivity

- **Binary spectroscopic behavior**:
  - **Semiconductor-like** for stoichiometric troilite
  - **Metal-like** for iron deficient pyrrhotites
- Mid-IR reflectivity deceases with increasing Fe/S ratio (@ 10 µm)

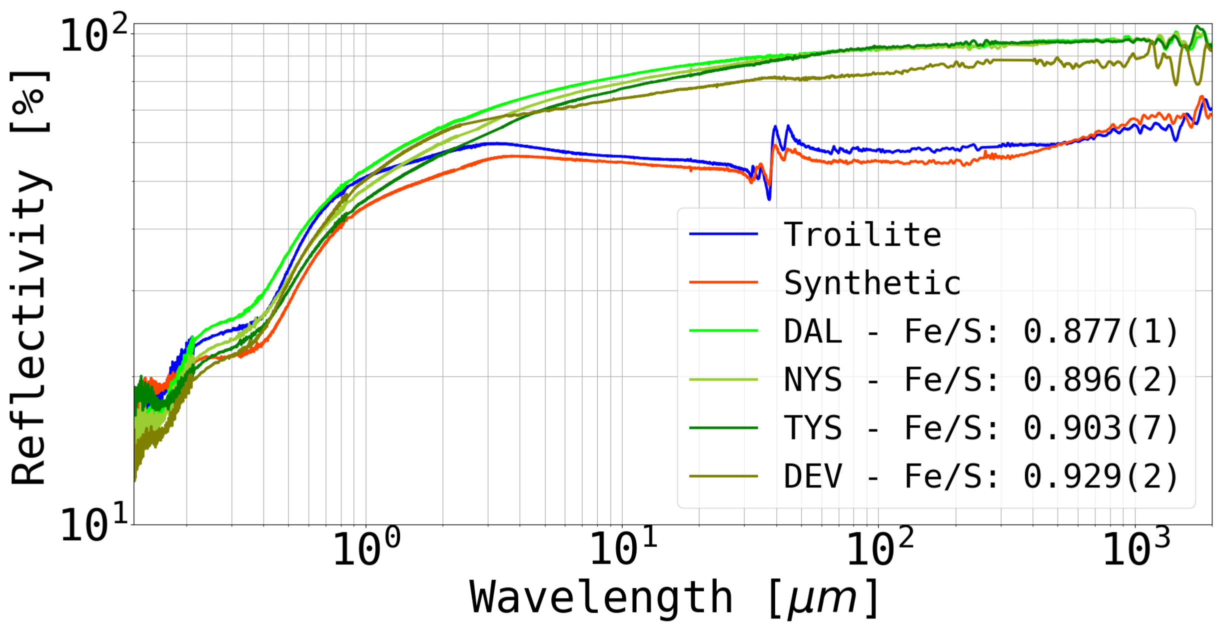


Figure 1: *Room temperature reflectivity for samples troilite and pyrrhotites from VUV to mm wavelength regime.*

Optical Constants

- **Fitting routine** based on **Levenberg-Marquardt** method
- Optimize n, k parameters based on comparison between measured and computed reflectivity
- **Drude-Lorentz-oscillator-model** for troilite & pyrrhotites
- New data in agreement with measured literature values

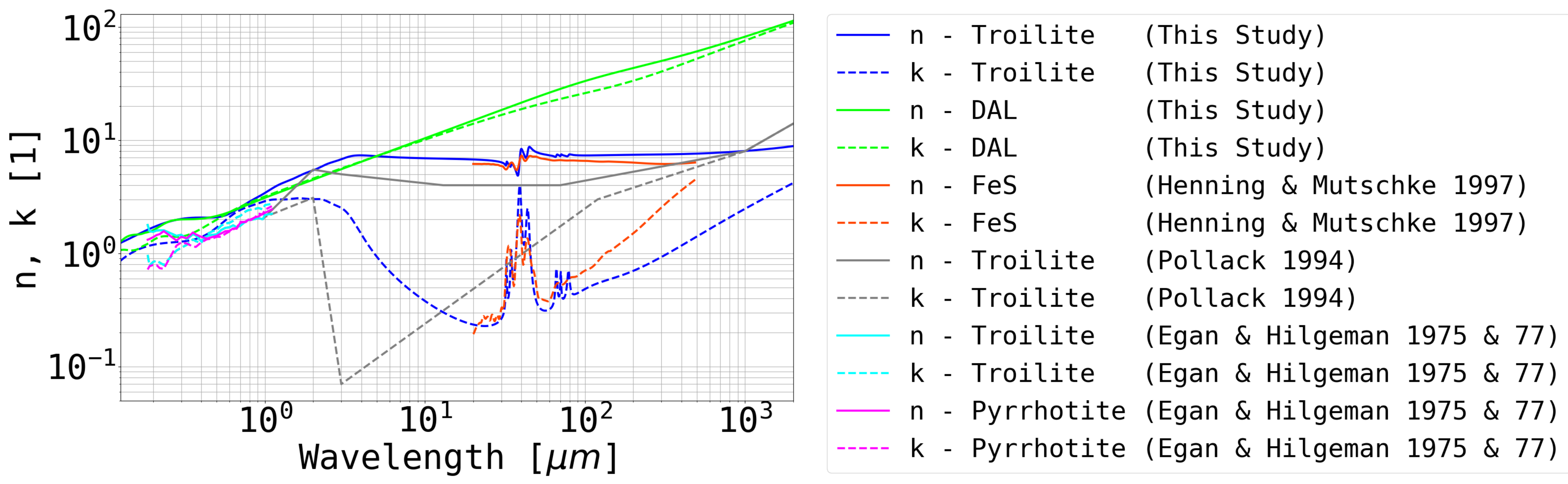


Figure 2: *Comparison of n & k values for samples troilite and 4C-pyrrhotite with literature [1, 2, 5, 6].*

Low Temperature Measurements

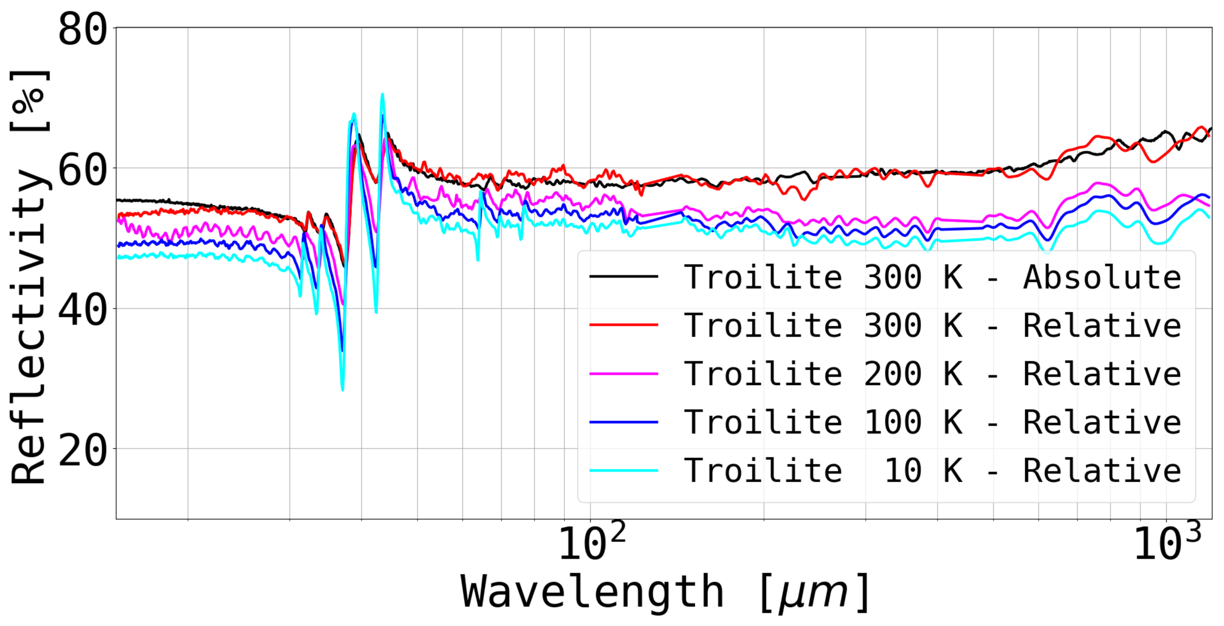


Figure 3: *MIR and FIR reflectivity of troilite at low temperatures.*

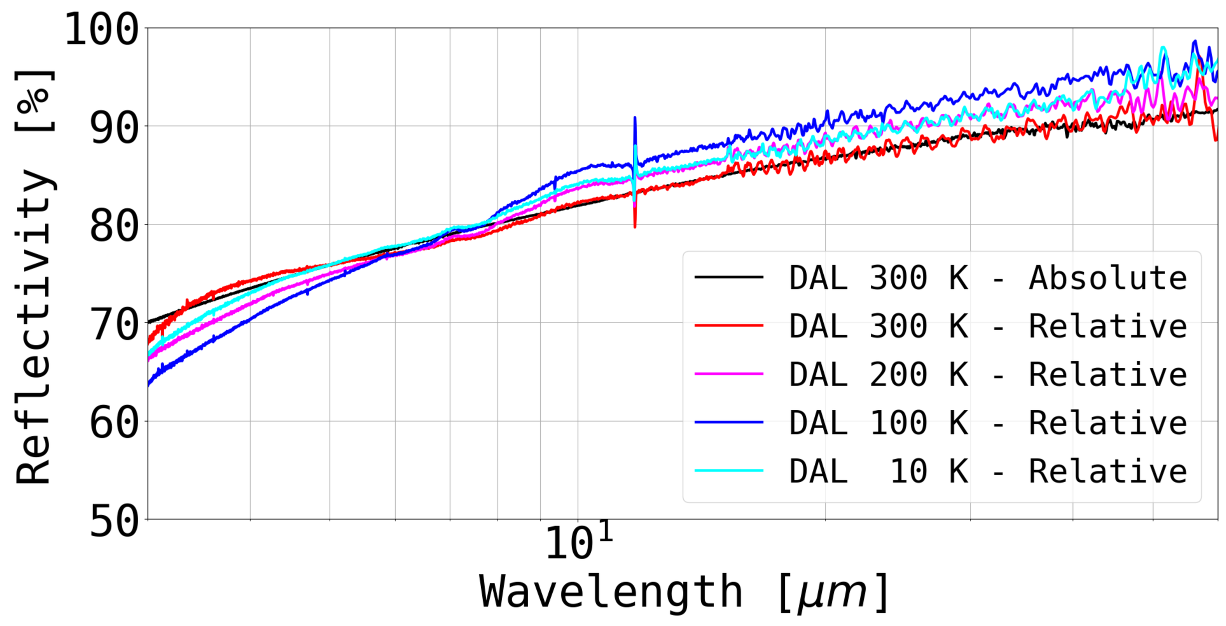


Figure 4: *MIR reflectivity of 4C-pyrrhotite at low temperatures.*

- **Troilite – Semiconductor:**
  - **Seven phonon bands:** 32.4 µm, 34.9 µm, 39.7 µm, 44.5 µm, 67.1 µm, 71.1 µm, 79.7 µm (at room temperature)
  - Blue-shift & sharpening of phonon bands
- **4C-Pyrrhotite – Metal**:
  - **Free charge carrier** characteristics
  - Change of sign for reflectivity change in IR
  - Possible origin: **Besnus transition at 32 K** [10]

Acknowledgements

This work was conducted in the Research Unit FOR 2285 “Debris Disks in Planetary Systems” of the Deutsche Forschungsgemeinschaft (grant MU1164/9-2).

References

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[8] D. Harries, K. Pollok, F. Langenhorst, Translation interface modulation in NC-pyrrhotites: Direct imaging by TEM and a model toward understanding partially disordered structural states. American Mineralogist 96, 2011, pp. 716–731.

[9] J. P. R. de Velliers, D. C. Liles, The crystal-structure and vacancy distribution in 6C pyrrhotite, American Mineralogist 65, 2010, pp. 148-152.

[10] D. Koulialias, B. Lesniak, M. Schwotzer, P. G. Weidler, J. F. Löffler, A. U. Gehring, The besnus transition in single-domain 4C pyrrhotite. Geochemistry, Geophysics, Geosystems 20, 2019, pp. 5216– 5224.