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Structure and transport properties of FeS at planetary core conditions

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ABSTRACT

The thermal conductivity of iron and its alloys are critically important to understand conductive heat flow and dynamo action within planetary cores, however the effect of sulfur alloying is poorly understood. We have measured and computed the thermal conductivity of FeS at high pressures and temperatures using experimental techniques and first-principles calculations. Experimental conditions range from 19-116 GPa and up to 3000 K. Computations ranged from 20-150 GPa and up to 4000 K. Over this range of conditions, theory shows that FeS is in a low to intermediate spin state with finite moments at least up to 40 GPa. We obtain thermal conductivity κ from 15 W m⁻¹ K⁻¹ at 1000 K to 69 W m⁻¹ K⁻¹ at 4000 K from first-principles calculations, and values of 14(5)-20(10) W/m/K from experimental measurements at temperatures above 1500 K and high pressures. In both cases the effect of structure and pressure is small. We find that FeS is metallic, but a poor metal at the conditions investigated. As a result, sulfur-rich core compositions are compatible with available observational constraints on the cessation time of the Martian dynamo.

1. Introduction

Observed magnetic remanence of ancient Martian crust requires that Mars had a magnetic field early in its geologic history (Mittelholz et al., 2020; Acuña et al., 1999). Available evidence indicates that this magnetic field was driven by thermal convection of the Martian core, and so the cessation of the magnetic field is directly related to the thermal conductivity of the core-forming material. However, a range of values have been reported for the thermal conductivity of iron and its alloys (Konôpková et al., 2016; Ohta et al., 2016; de Koker et al., 2012; Yong et al., 2019), and the composition dependence of thermal conductivity is largely unknown for a wide range of relevant alloys at planetary core conditions. This is particularly challenging for alloys relevant to Mars, as the most recent compositional models differ significantly from previous estimates and span a range of alloying elements and abundances that are outside what is typically expected for the Earth or other telluric planets (e.g. McDonough, 2023).

Estimates for the composition of the Martian core ranges from 5-25 wt% S, and 1-8 wt% O alloyed with Fe (Stähler et al., 2021; Gendre

et al., 2022; Khan et al., 2022; Brennan et al., 2020; Steenstra and van Westrenen, 2018; Khan and Connolly, 2008; Khan et al., 2018; Sanloup et al., 1999; Wang and Becker, 2017; Yoshizaki and McDonough, 2020). Synthesis of new seismic and geodetic data has led to an upward revision of the volatile-element fraction of the Martian core, reporting that for a binary Fe-S core the S content would reach approximately 25-35 wt% (Stähler et al., 2021). Such a core is cosmochemically unrealistic (Khan et al., 2022; Steenstra and van Westrenen, 2018), and so additional elements such as O and/or C and/or H are invoked to reduce the S content of the core. Previously it was expected that S and O would not partition together into an iron alloy at the low pressure of core formation expected for Mars (Brennan et al., 2020), but the strong interaction between S and O has been shown to result in the coupled dissolution of both into the core (Gendre et al., 2022; Tsuno et al., 2011). Available constraints on the temperature of the deep mantle provide a lower bound on the temperature of the core, between 1700 K and 1900 K (Huang et al., 2022) at a pressure range of 19 GPa to 40 GPa (Stähler et al., 2021).

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The volatile-rich composition of the Martian core and absence of a present-day magnetic field suggests that the core remains fully liquid, or that the crystallizing inner core is too small to detect (e.g. Hemingway and Driscoll, 2021; Steenstra and van Westrenen, 2018). During accretion and differentiation, the Martian interior was heated by the release of gravitational potential energy, impact processes, and the decay of radiogenic isotopes (Lichtenberg et al., 2023). The excess heat produced in these processes would give rise to the transfer of heat energy between core, mantle and crust. Available data indicates that Mars has not experienced significant geologic resurfacing for at least 3 Gyr, suggesting that a significant portion of the Martian lithosphere has remained immobile for that time (Nimmo and Tanaka, 2005). Within the deep mantle, convection may occur depending on the available heat budget as well as mantle viscosity (Plesa et al., 2022). The balance between the heat energy delivered from the core to mantle, and the ability of the mantle to dissipate heat delivered from the core plays a fundamental role in the dynamic and thermal evolution of Mars' deep interior over time. A thermally driven dynamo, believed to be the cause of Mars' early magnetic field, generally occurs when the heat flux out of the liquid core exceeds the dissipative ability of the mantle. This imbalance results in convection of the core, with characteristics which depend on the physical properties of the core (e.g. electrical and thermal conductivity, thermal expansivity, viscosity, (Jones, 2011)). Consequently, the thermal as well as electrical conductivity of the Martian core, and how these values vary with composition are important to provide an accurate description of core dynamics and magnetic field generation over geologic time.

Investigation of the Fe-S system has been carried out here on FeS, which represents the end member composition for a sulfur-rich Martian core. Additionally, FeS may play a role at the core-mantle boundary of Mercury (e.g. Namur et al., 2016), and sulfur may be present in small quantities in the core of the Earth (Morard et al., 2013).

FeS adopts at least seven different structures over its studied pressure and temperature range. The primary phases of relevance to planetary interiors are FeS IV, V and VI which have reported stability fields extending from ambient pressure to 180 GPa at high temperatures (Fei et al., 1995; Urakawa et al., 2004; Ono et al., 2008; Sata et al., 2008; Shorikov et al., 2018). FeS V is the NiAs structure, with space group $P6_3/mmc_2$, IV is distorted NiAs with space group $P6_3mc$. These phases are stable up to melting for pressures up to at least 35 GPa (Fei et al., 1995; Urakawa et al., 2004; Ono et al., 2008), however the respective stability fields of these structures are poorly constrained, and reported melting curves for FeS differ by over 1000 K at these conditions (Williams and Jeanloz, 1990; Boehler, 1992; Anderson and Ahrens, 1996). Above 35 GPa, FeS VI, another distorted NiAs phase, becomes most stable at ambient temperature and high pressure (Ono and Kikegawa, 2006; Ono et al., 2008). There are no constraints on the relative stability of phases VI, V and VI at conditions close to melting above 20 GPa.

Until now, the thermal conductivity of FeS at high pressures and temperatures has been studied primarily by electrical resistivity methods in a multi-anvil press. A large range of values has been reported for the electrical resistivity of FeS at from ambient pressure to 8 GPa, as well as one direct study of thermal conductivity to 40 GPa (Argyriades et al., 1959; Pound et al., 1955; Pommier, 2018; Manthilake et al., 2019; Littleton et al., 2021; Hsieh et al., 2024). These contrasting results differ by four orders of magnitude in resistivity, and by an order of magnitude in thermal conductivity. Experiments so far have mostly been restricted to conditions below 10 GPa. At 5-10 GPa there are large changes in the axial ratios of FeS IV (Fei et al., 1995; Urakawa et al., 2004), which are expected to relate to a spin transition observed in a different phase of FeS at lower temperatures but similar pressures (Rueff et al., 1999; Kobayashi et al., 2001). Consequently, there are large uncertainties when extrapolating reported thermal conductivity values to the conditions of the core of Mars (19 GPa to 40 GPa). First-principles calculations have been previously carried out on Fe-S alloys with compositions Fe₃S and Fe₇S, however with limited data at 2000 K or below

with which to test against direct laboratory experiments (Wagle et al., 2018). Determining electrical and thermal conductivity at high pressures and temperatures in solids and liquids are cutting edge problems for both theory and experiment. As first-principles calculations allow computation with the same approximations on crystals and liquids, and for electrical and thermal conductivity. They thus provide strong constraints on the Lorenz number of a material at high pressures and temperatures, and the relative transport properties of liquids and crystals. Both experiment and theory are needed to fully address the electrical and thermal conductivity of planetary materials at the extreme conditions of planetary cores.

To address these uncertainties, a combination of experimental methods and first-principles simulations are employed in the present study in order to determine the structure and transport properties of FeS at direct conditions of interest for planetary cores, and to clarify the effect of sulfur on the transport properties of iron alloys at extreme conditions.

2. Methods

2.1. Experimental methods

As starting materials we used troilite FeS from the Cape York meteorite of NW Greenland. This material was obtained from the University of Copenhagen Geological Museum. Electron microprobe analysis indicates that the sample stoichiometry is 1:1.008(4) Fe:S, with trace Ni (<0.002 at%). No other impurities are detected in the samples, indicating that the starting material is highly pure and nearly stoichiometric FeS. At ambient pressure, synthetic, stoichiometric FeS is challenging to produce as it melts incongruently to Fe_7S_8 and FeS_{1-r} (Williams and Jeanloz, 1990). Experiments have been carried out using screw-driven diamond anvil cells (DACs) using either a symmetric or BX90 design. Diamond culet diameters range between 300 μm and 100 μm depending on target pressure, with pressures measured using the equation of state of KCl, ruby fluorescence or raman spectroscopic measurements of the stressed T_{2e} diamond phonon (Dewaele et al., 2012; Shen et al., 2020; Akahama and Kawamura, 2006). Sample chambers are formed from the indentation of 250 µm thick Re gaskets to a target thickness of 50 µm to 15 µm depending on diamond culet diameter. In all experiments, KCl is used as the pressure transmitting medium in order to thermally and chemically insulate the samples from the diamond anvils. Plates of FeS have been made by compressing a chip of the starting material between two diamond anvils until good surface quality and an appropriate thickness is produced, typically between 2 µm to 5 µm thick. After loading FeS and KCl into the DAC, it is placed in a vacuum oven. The vacuum pump could pump down to pressures of approximately 120 mbar, and so prior to raising temperature in the vacuum oven, the oven is flushed with high purity Ar six or seven times to reduce oxygen and moisture levels to a few ppm or below. After this process, the DAC is left at 120 °C for at least 12 hours, after which the cell is promptly removed from the oven and the cell chamber is sealed. Thicknesses of the KCl and FeS plates are measured in situ using white-light interference methods and ex situ employing microscopy of recovered samples using a focused ion beam. In situ sample geometry is calculated from measurements of the diamond/KCl/diamond optical path-length and the sample/KCl/diamond path lengths of the two opposing faces of the FeS sample. Optical path lengths are converted to physical distances using the experimentally determined refractive index of KCl (Johannsen et al., 1997), recently extended to Mbar pressure using the methods reported in Lobanov and Geballe (2022); Schifferle et al. (2022).

Thermal conductivity measurements have been carried out at the Earth & Planets Laboratory (EPL) and GeoSoilEnviroCARS (GSECARS). At EPL, these measurements have been carried out using streaked optical pyrometry using a Sydor streak camera, where continuous and pulsed laser heating is employed as described previously (McWilliams et al., 2015; Konôpková et al., 2016; Geballe et al., 2020; Hsieh et al., 2020). The light from a continuous-wave (CW) IR laser is split into two optical

paths with coaxial alignment on the two opposing faces of the FeS sample. A pulsed IR laser ($\lambda = 1064$ nm, IPG Photonics) is focused onto one side of the sample. The pulsed laser is modulated by a Pockels cell, allowing for precise control of the shape and timing of the laser pulse. In this study, experiments are performed with the Pockels cell set to output a 1.5 µs pulse. The temperature perturbation induced by the pulsed laser heating event is studied by taking separate measurements from each side of the sample surface using a 10 µs streak camera window. Repeated measurements are carried out to ensure reproducibility of the temperature histories of the sample. FIB imaging of the recovered samples is used to ensure that the samples remained intact during heating. The total duration of CW IR heating has been kept to below 30 s per sample position in order to minimize the effect of laser thinning and the possibility of chemical contamination. This has been done by limiting the number of heating attempts per heated spot and limiting the number of pressure points per DAC loading. Figs. S1a and S1b show the results of chemical analysis of a recovered sample where there is no significant difference in composition laterally across solid, heated sample, or generated due to solid/liquid partition during melting. Images of thermal emissions versus time from the streak camera are binned into 70 ns or 140 ns slices and fit to a Planck function using the greybody assumption, with the system response calibrated against measurements of a tungsten lamp. Finite-element models are employed to determine thermal conductivity using measured temperature histories. In these models, model inputs are ρ , C_P (varied together as ρC_P) of each component of the sample chamber (diamond, FeS, KCl), thermal conductivity of each material, sample chamber dimensions, laser dimensions and laser energies. The pulsed laser has a defined shape in the time coordinate which must be modelled accurately to produce good fits to the experimental data, and this shape is taken from time-dependent intensity measurements recorded on an oscilloscope. Thanks to the use of a Pockels cell, modification of the measured intensity profile is not necessary to reproduce experimental temperature histories. Uncertainties in the density and heat capacity of KCl do not significantly influence the correspondence between models and experiments as shown in Fig. S2. Uncertainties in the density and heat capacity of diamond do not have a significant effect on modelled FeS thermal conductivity (Geballe et al., 2020). The Re gasket is omitted from these models as temperature history measurements are not carried out near the gasket. This is justified in Fig. S3 where it is shown that the region of high temperature generated by laser heating decays to less than 500 K within 20 microns of the centre of the 7.5 micron laser spot. Distant, unheated material does not influence heat diffusion through the centre of the heated region. Thermal conductivity of diamond is fixed to its 1 bar value, and KCl thermal conductivity is used as a free parameter. Laser energies are used as free parameters in the models - the power of the US and DS CW lasers are used to match baseline temperatures, and the power of the DS pulsed laser is used to match the amplitude of the DS temperature disturbance. The diameter of the pulsed laser is set to be equal to that of the DS CW laser, and both CW lasers are modelled with diameters of 7.5 µm. Where available, KCl and FeS densities have been measured with synchrotron X-ray diffraction at the pressure of the temperature history measurement. Otherwise, densities are determined using literature equations of state (Dewaele et al., 2012; Sata et al., 2010). The specific heat of FeS is fixed to 700 J/Kg/K in our finiteelement models, as our FPMD calculations indicate that a Dulong-petit value (3R) for heat capacity describes well the behaviour of solid FeS. When converted into specific heat using literature thermal equations of state for FeS IV and V (Urakawa et al., 2004), this results in specific heat values of about 640-720 J/Kg/K at the temperatures studied here. Variations in this range are not significant (-10%, +2%) compared to other experimental uncertainties (typically 30-50%), justifying the use of a fixed value for modelling.

Synchrotron X-ray diffraction experiments have been performed at GeoSoilEnviroCARS at the Advanced Photon Source, Sector 13 ID-D. In this study, monochromatic X-rays with a wavelength of $\lambda = 0.3344$ nm are used with a Pilatus 1M CdTe X-ray detector (Goncharov et al., 2010).

Table 1

Starting structure, magnetization, pressure, and temperature for each FPMD simulation run.

Structure	Magnetic?	Pressure (GPa)	Temperature (K)
IV/V	Yes	20	1000/2000
		40	1000/2000/3000
VI	Yes	100	1000
IV/V	No	20	1000/2000
		40	1000/2000/3000/4000
VI	No	100	1000/2000/3000
Pmmn	No	150	2000/3000

X-ray diffraction measurements are combined with double-sided laser heating (IPG photonics, $\lambda = 1064$ nm) to generate static high temperature states and to study the structural evolution of FeS upon variation of temperature. Additionally, experiments have been carried out employing a combination of pulsed and continuous laser heating in order to measure thermal conductivity at high temperatures and pressures. In this experimental configuration, time-dependent thermal emissions are recorded using a time-gated iCCD (PIMAX 3, Princeton Instruments) which collects thermal emissions within 200 ns windows. Using a 2 µs laser pulse to heat the sample dynamically from one side, and a CW laser to generate a high baseline temperature on the other side, the temperature histories from each face of the sample are measured by varying the time delay between the iCCD collection window and the arrival time of the laser pulse. The iCCD is synchronized with the X-ray detector such that X-ray diffraction patterns are taken at each time-step. The collection of thermal emissions and X-ray diffraction images at each timestep corresponds to about 10⁵ pulsed heating events. Thermal conductivity is determined from temperature histories using the same finite-element methods employed for EPL measurements, as described above.

2.2. Computational methods

In order to compute transport properties at high temperatures, we first perform first-principles molecular dynamics (FPMD) within density-functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (Perdew et al., 1996) using QUAN-TUM ESPRESSO (Giannozzi et al., 2009). Supercells contain 72/96/108 atoms for FeS phases V/VI/VII. We use Ultrasoft pseudopotentials obtained from the Garrity-Bennett-Rabe-Vanderbilt (GBRV) high-throughput pseudopotential library (Garrity et al., 2014). The plane-wave cutoff energy is 40 Ry. The temperature of ions was regulated for each temperature using velocity re-scaling (Bussi et al., 2007) in the N-P-T ensemble, while the electronic temperatures were kept constant with the Fermi-Dirac smearing function. The Brillouin zone was sampled at the Γ -point with a time step of 1 fs, and the simulations were carried out for about 10 ps. Macroscopic quantities such as temperature, pressure, and the c/a ratio are determined by averaging over at least 3000 equilibrium steps. The simulation runs for all three phases are listed in Table 1. FeS is predicted to adopt the Pmmn structure above 120 GPa (Ono et al., 2008), however it has not been observed experimentally. Both magnetic spin-polarized and non-spin polarized runs are performed.

We then compute transport properties for snapshots from the MD runs, using a modified Spin-polarized Relativistic KKR (SPRKKR) package (Ebert et al., 2011). Each of the snapshots is taken with a separation of at least 500 frames, which is greater than the velocity correlation time under the given conditions. For each configuration, we perform a self-consistent DFT computation and a self-consistent Dynamical Mean Field Theory (DMFT) within the FLEX approximation (Minár et al., 2005). Transport calculations are then performed using converged potentials (Ködderitzsch et al., 2015). The electrical conductivity (σ) and thermal conductivity (κ) are obtained from: (Xu et al., 2018b)

$$\sigma = \mathcal{L}_{11} \tag{1}$$

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$$\kappa = \frac{1}{eT} \left(\mathcal{L}_{22} - \frac{\mathcal{L}_{12}^2}{\mathcal{L}_{11}} \right). \tag{2}$$

 \mathcal{L}_{ij} is given by:

$$\mathcal{L}_{ij} = (-1)^{(i+j)} \int d\varepsilon \sigma_{\mu\nu} (\varepsilon - \mu)^{(i+j-2)} \left(-\frac{\delta f_T(\varepsilon)}{\delta \varepsilon} \right)$$
(3)
$$\sigma_{\mu\nu} \propto Tr \langle \hat{j}_{\mu} ImG^+ \hat{j}_{\nu} ImG^+ \rangle$$
(4)

where \hat{j}_{μ} is the current density operator, and ImG^+ is the imaginary part of retarded Green function. $f_T(\varepsilon)$ is the temperature dependent Fermi-Dirac distribution function.

The uncertainty in computed resistivity is estimated to be about 20 $\mu\Omega$ cm. Notably, our DMFT calculations showed electrical resistivity results that closely matched those from DFT, with a difference of less than 3%, so we have opted to exclusively report the full set of DFT results in our manuscript. Further details are given in Xu et al. (2018a); Zhang et al. (2020).

3. Results

3.1. Structure of FeS at high temperatures and pressures

The phase diagram of FeS has been studied using a variety of experimental methods and finite temperature first-principles DFT computations. Firstly, X-ray diffraction (XRD) has been used in conjunction with laser heated diamond anvil cells at a range of pressures and temperatures between 22 GPa to 116 GPa and up to 2600 K. Data below 1500 K have been omitted due to the persistence of large nonhydrostatic stresses prior to annealing. The low thermal conductivity of FeS results in steep temperature gradients within the sample and therefore requires high surface temperatures to anneal the bulk of the sample. Prior to annealing, large deviatoric stresses were identified based on anomalously low c/a ratios and poor le Bail fits to the diffraction data. Above 35 GPa, FeS VI was observed in quenched diffraction patterns after annealing at >1500 K (Ono and Kikegawa, 2006; Ono et al., 2008). After annealing, this phase was observed to directly transform into phase IV at temperatures which were too low to measure until 50 GPa. Fig. 1 shows the phases observed with X-ray diffraction at variable pressures and 2000 K. Varying pressure at this high temperature, phases V, IV and VI were observed sequentially with increasing pressure. Transformations between solid phases are interpreted as follows: the most pronounced difference between FeS IV and V diffraction patterns is the difference in d-spacing between the (102) reflections of FeS IV and V, which have been used to track the onset of the transformation between phases IV and V (Supplemental Fig. S4a). The transformation between phases VI and IV have been interpreted based on the splitting of the former (111) reflection of FeS VI into the (201) and (102) reflections of FeS IV (Supplemental Fig. S4b). Melting is determined based on the first appearance of diffuse scattering, shown in Fig. S5.

Previous studies suggested the possibility of a strong wavelengthdependent emissivity in FeS at high pressures and temperatures (Kavner et al., 2001). As this would influence the interpretation of both XRD and thermal conductivity data, optical reflectivity measurements of FeS have been carried out at 23(3) and 33(3) GPa up to 1920 K and the optical changes are used to infer phase transformations in the sample in the context of the XRD data. The results are shown in Supplemental Figs. S6 and S7, with methods outlined in Supplemental Text S1 and Fig. S8. In short, the wavelength dependence of FeS reflectivity is weak and deviations from greybody behaviour can be ignored. Discrete changes in the reflectivity spectra of FeS upon increase in temperature appear to coincide with structural transitions in FeS determined by X-ray diffraction.

Fig. 2 shows the XRD experiments alongside the results of firstprinciples computations and experimental literature. At ambient pressure, FeS V is the liquidus phase, while IV and then VI are expected to become the stable liquidus phases at higher pressures (Fei et al., 1995; Urakawa et al., 2004; Ono et al., 2008). However the boundary P-T



Fig. 1. X-ray diffraction patterns of FeS at high pressures and temperatures demonstrating the successive stability of FeS V, IV and VI with increasing pressure, and at temperatures of about 2000 K. Uncertainties in temperature are around 150 K. Thick black lines indicate peaks which correspond to the relevant FeS phase at each pressure, while thin black dotted lines denote diffraction peaks from KCl. Asterisks indicate residual FeS IV reflections. Miller indices, observed d-spacings and calculated d-spacings of the phases shown here can be found in Table S1.



Fig. 2. Pressure-Temperature phase diagram of FeS. The FeS IV-V phase boundary is consistent with previous literature (U04, Urakawa et al. (2004)). FeS III-IV and IV-VI boundaries occur at low temperatures and are observed to be highly sensitive to nonhydrostatic stresses and thus not plotted here. B93, W90 and A96 indicate melting curves reported in Boehler (1993), Williams and Jeanloz (1990) and Anderson and Ahrens (1996) respectively. Grey line indicates postulated IV/VI and VI/Liquid boundaries.

conditions are poorly constrained. The present study clearly establishes FeS V as the liquidus structure of FeS at the conditions of the Martian core. The FeS IV-V-liquid triple point is bracketed to between 46 GPa and 52 GPa, and 2220(150) K. The conditions of the FeS IV-V transition are consistent with an extrapolation of multi-anvil measurements at lower pressures and temperatures (Urakawa et al., 2004). The position of the VI-IV-liquid triple point at higher pressures and temperatures is less well constrained by the present dataset, and is estimated to occur above 70 GPa. Reports on the melting temperature of FeS differ by upwards of 600 K at the pressure range of the Martian core (Boehler, 1993; Williams and Jeanloz, 1990; Anderson and Ahrens, 1996). The present



Fig. 3. Histograms of calculated Fe magnetic moments as a function of temperature (plot a) and as a function of pressure at 2000 K (plot b). Finite Fe magnetic moments are observed in FeS at the conditions of the Martian core, with a change in exchange coupling from antiferromagnetic to ferromagnetic at the highest temperatures and pressures studied.

study supports the melting curve reported in Boehler (1993). The study reporting the highest melting curve for FeS using static DAC experiments reported a reaction between FeS and the ruby pressure transmitting medium (Williams and Jeanloz, 1990). Our material is natural troilite, however the small deviation in composition from stoichiometric FeS is not expected to have a significant influence on melting temperature and we do not find evidence for incongruent melting (Fig. S1). While previous dynamic compression studies support a low melting temperature for FeS (Anderson and Ahrens, 1996), that study employed sapphire windows which were later discovered to be unsuitable for pyrometry measurements at these conditions (Fat'yanov et al., 2005). Synthetic temperature fits presented in Supplemental Fig. S9 show that while deviations from greybody behaviour can be ignored below about 3000 K, at higher temperatures deviations can become as large as 160 K between 'thermodynamic' temperature and measured temperature. At these temperatures, the maximum of the Planck function approaches the wavelength range measured by the spectrometer, which results in enhanced sensitivity of the temperature fit to changes in the optical characteristics of the sample.

3.2. Spin state of FeS at Martian core conditions

The spin state of FeS, alongside sulfur-rich iron alloys, is significant due to its inferred implications for the elasticity and transport properties of these compounds under high-pressure and temperature conditions. Normalized histograms of magnetic moments from the present FPMD calculations are shown in Fig. 3, indicating that finite magnetic moments persist in FeS IV and V throughout the conditions of interest for Mars. Interestingly the exchange coupling varies between antiferromagnetic and ferromagnetic configurations with increasing pressure and temperature, but highlights the necessity in incorporating magnetic effects to interpret the physical characteristics of FeS at these conditions.

3.3. Electrical resistivity of FeS

Electrical resistivity values computed in the present study are shown in Fig. 4. At pressures of 20 GPa and above, we find that FeS is a much better metal than at low pressures, where experiments below 10 GPa find electrical resistivity 2 to 15 times higher. Both spin-polarized and non-spin-polarized calculations have been carried out over a wide range of conditions to assess how magnetism effects FeS transport properties. At the lowest pressures and temperatures studied (20 GPa, 1000 K), the difference between these calculations is about 25%, but at higher temperatures and pressures the difference becomes less than 10%, since moments decrease with pressure. At 40 GPa, FeS is liquid at temperatures above 2000 K in FPMD calculations based on the analysis of Fe and



Fig. 4. Electrical resistivity of FeS at high pressures and temperatures as calculated using DFT. Black boxes indicate the starting structures for the FPMD runs. *Pmmn* is a theoretically predicted high-pressure structure (Ono et al., 2008).

S mean-square displacements. Variation of resistivity with temperature is generally weak for both solid and liquid FeS at 20-40 GPa, which likely reflects strong impurity scattering as well as the competition between enhanced electron-phonon scattering, and weakened electron-magnon scattering upon increase in temperature. At higher pressures, the *Pmmn* structure exhibits a decrease in resistivity with temperature due to the suppression of magnetism at Mbar pressure.

3.4. Thermal conductivity of FeS

The thermal conductivity of FeS was measured over a range of pressures and temperatures using flash heating in a diamond anvil cell as shown in Fig. 5. In these experiments, a time-resolved measurement of heat propagation through a sample of defined thickness is carried out, where thickness is determined *in situ* using white light interference. Focused ion beam milling is employed to study the sample after recovery to ambient conditions to verify sample chemical integrity and the possibility for thickness variation across the sample. Flash heating provides a direct measurement of heat flow through the sample, and as such it probes heat conduction mediated by both electrons and phonons



Fig. 5. a) Temperature as a function of time as measured in an experiment from run 6 (coloured circles) and calculated using finite-element models (coloured lines). Pink indicates the downstream side of the sample, where the heating laser pulse first arrives. Blue indicates the upstream side of the sample. b) Intensity profile of laser pulse which generates the temperature perturbation. Oscillations in intensity at the beginning and end of the pulse are caused by electrical interference of multiple signals arriving to the oscilloscope. c) Focused Ion Beam cross section of the recovered sample from Run 6.

whereas electrical resistivity measurements and calculations probe electronic conduction. The comparison of experimental measurements of total thermal conductivity and FPMD calculations of electronic thermal conductivity provide a means to qualitatively probe the different components of thermal conductivity, which are important if one is to evaluate the influence of iron alloy composition on the characteristics of a core dynamo. Thermal conductivity values from the present experiments, alongside calculated values using FPMD are shown in Fig. 6. At 20 GPa and 40 GPa, only the results of spin-polarized FPMD calculations are shown. It is observed that experimental thermal conductivity values are comparable to 1000 K calculations, which may reflect the role of temperature gradients in the experiments, or stronger scattering effects, possibly due to the use of natural samples with trace impurities, in experiments. Thermal conductivity anisotropy is calculated to be smaller than uncertainties in the calculations for all structures studied with the exception of FeS VI, where anisotropy reaches 40% at the lowest temperatures studied (1000 K). Nevertheless, a comparison of these quantities indicates that the electronic thermal conductivity of FeS is dominant over phonon contributions at the conditions of the Martian core (19 GPa to 40 GPa, 1600 K to 2400 K). High pressure values for the thermal conductivity of FeS are five to ten times higher than that of FeS at ambient pressure (Argyriades et al., 1959), but significantly different from extrapolations of other values in the literature (Pommier, 2018; Manthilake et al., 2019; Littleton et al., 2021). This highlights the significant physical changes which occur in FeS around 5-10 GPa (Fei et al., 1995; Rueff et al., 1999; Urakawa et al., 2004). Time-domain thermoreflectance measurements of thermal conductivity from 300 K to 1000 K at ~28 GPa yield consistent values to what is measured here at 33 GPa when extrapolated to the temperatures of measurement (Hsieh et al., 2024). It is also important to note that the conversion from electrical resistivity to thermal conductivity requires an assumed value for the Lorenz number of the material. Our DFT calculations show that the Lorenz number of FeS differs by at least 20% from its most commonly assumed value (see Fig. 7).

Above 5-10 GPa both experiments and theory demonstrate that pressure variation of the transport properties of FeS is weak up to at least 180 GPa. Discrepancies lie in the different temperature dependence of experiments and calculations; for experiments there is little resolvable difference across measurements at different temperatures. This may reflect the necessity of generating large changes in temperature across the



Fig. 6. Thermal conductivity measurements and electronic thermal conductivity calculations from the present study and previous experimental literature for FeS (Pommier, 2018; Manthilake et al., 2019; Littleton et al., 2021) at high temperatures and pressures.

sample (>300 K) in order to produce a resolvable temperature rise on the opposing face of the FeS sample due to its low thermal conductivity. This is demonstrated in Fig. S10, where the FeS phase diagram is presented alongside the range of temperatures probed by experiments. When combined with a low melting point for FeS, and high required temperature for streak camera measurements (>1400 K), the effective temperature range which can be probed at a given pressure is relatively narrow. Due to the use of microsecond pulsed heating, it has been observed that as long as baseline temperature remains below the melting point of FeS, the sample generally does not dissociate even if peak temperature is above the melting point. The combined results presented here regarding the thermal and electrical conductivity of FeS demonstrate that this compound is metallic, but remains a poor metal at the conditions of the Martian core. Moreover, FPMD results for both solid and liquid FeS demonstrate that the thermal conductivity of FeS is largely independent of structure, but strongly temperature dependent.



Fig. 7. Lorenz number computed from computed resistivity and computed thermal conductivity of FeS at high pressures and temperatures. Black dashed line indicates the low-temperature (Sommerfeld) value of the Lorenz number (L = $2.445 \cdot 10^{-8} W\Omega/K^2$). *Pmmn* is a theoretically predicted high-pressure structure (Ono et al., 2008).

4. Discussion

4.1. Lorenz number for FeS

The relationship between electrical conductivity (i.e. inverse of the electrical resistivity) and thermal conductivity is given by the Weidemann-Franz law, Equation (5).

$$k_{el} = L \cdot T \cdot \rho^{-1} \tag{5}$$

where k_{el} is the electronic component of the thermal conductivity, L is the Lorenz number, T is temperature and ρ is the electrical resistivity. The ideal, low temperature Lorenz number in a Fermi liquid is given by the Sommerfeld value, $2.445 \cdot 10^{-8} W\Omega/K^2$, which is often used in experiments and even some theory papers to estimate metallic thermal conductivity from electrical conductivity. We have calculated L from electrical resistivity and thermal conductivity values computed with DFT/DMFT, shown as circles in Fig. 7. We find that all structures besides FeS VI exhibit L values which are 10% to 20% lower than the Sommerfeld value, shown as a black dashed line in Fig. 7. As electrical resistivity experiments use the Sommerfeld value, reported k_{el} estimates are likely higher than what is expected when using calculated L values (Pommier, 2018; Manthilake et al., 2019; Littleton et al., 2021). At 40 GPa, L values are calculated for both solid and liquid structures, and are similar in both cases.

4.2. Thermal conductivity of the Martian core

In order to address the thermal conductivity of the Martian core, the effect of different light elements must be estimated. It has been shown in the present study that FeS has a thermal conductivity significantly lower than iron at the conditions of interest. Here it is hypothesized that the dominant effect of S, and likely also O at the conditions of the Martian core is to deplete the electron density of Fe at the Fermi level. There is the caveat that phonon conduction in FeO at ambient pressure and high temperature is potentially larger than for FeS (Slowik et al., 1990; Akiyama et al., 1992; Manthilake et al., 2019), however the difference is only 1 W/m/K to 4 W/m/K which would be a small effect relative to the bulk changes in electrical conductivity. The thermal conductivity of the



Fig. 8. Thermal conductivity of the Fe-S-O system as a function of S and O content at 20 GPa. Dashed lines indicate dynamo regimes reported in Greenwood et al. (2021). Lavender and green bands indicate S+O contents for an Fe-S-O or Fe-S Martian core, respectively (Stähler et al., 2021). Yellow and blue bands indicate Fe-S-C-O and Fe-S-C-O-H compositions (Stähler et al., 2021). These bands provide an upper bound for the light element content of the Martian core. Open circles indicate thermal conductivity values computed with DFT. Open squares indicates experimental thermal conductivity values. Open triangle shows the calculated thermal conductivity of liquid Fe₃S at Martian core conditions (Wagle et al., 2018).

core is controlled by the bulk S and O content, as the expected contributions from C or H alloying are likely smaller (Zhang et al., 2018; Ohta et al., 2019). The thermal conductivity of the Martian core is assumed in Fig. 8 to vary linearly with the S and O content of the core, where it is hypothesized that the effect of both elements on thermal conductivity is the same based on an interpolation between Fe and FeS in an at% basis. In this model, we adopt a value of 45 W/m/K for Fe after recent multianvil electrical studies, which agree with direct thermal conductivity measurements within the latter method's uncertainties (Konôpková et al., 2016; Yong et al., 2019). We apply calculated and experimental thermal conductivity values at Martian core conditions to provide upper and lower bounds on FeS thermal conductivity respectively, and find that this model can reproduce calculated thermal conductivity values for intermediate liquid Fe-S compositions (Wagle et al., 2018). Thermal conductivity estimates reported here are about 33 W/m/K for Fe₃S (25 at% S) and 39 W/m/K for Fe7S (12.5 at% S), while calculated values for liquid Fe-S alloys nearest to the conditions of the Martian core are 40 W/m/K at 27 GPa and 2000 K for Fe₃S, and 38 W/m/K calculated for liquid Fe₇S at 3 GPa and 2000 K (Wagle et al., 2018). The thermal conductivity experiments and calculations presented here, and their comparison with previous literature indicates that the structure of FeS, whether solid or liquid, is not a significant factor for its thermal conductivity variation but rather the metallization of FeS which occurs between 5-10 GPa. Consequently, in this system it is likely more appropriate to compare core thermal conductivity values with mineral parameters at the same temperature rather than within the same structure, unless the structural transition coincides with a significant electronic transition. For Fe, a magnetic transition is reported in liquid iron which enhances thermal conductivity and its pressure evolution (Korell et al., 2019) and may occur in other liquid iron alloys, however here we have demonstrated that FeS adopts a complex spin state which persists over a wide range of pressures and temperatures without significantly altering its thermal or electrical conductivity. Furthermore, the subtle differences between solid and liquid Fe around melting observed in multi-anvil experiments suggest that this magnetic transition is an effect of pressure, rather than structure (Yong et al., 2019; Pommier, 2018). The differing characteristics of end-members Fe and FeS support the view that impurity scattering is the dominant effect in solid and liquid iron-light element alloys (Zhang et al., 2022).

Studies of the thermal evolution of Mars typically employ a wide range of thermal conductivity values owing to the scarcity of data at the conditions of small telluric planets. These values range from 5 W/m/K to 120 W/m/K (Nimmo and Stevenson, 2000; Williams and Nimmo, 2004; Davies and Pommier, 2018; Hemingway and Driscoll, 2021; Greenwood et al., 2021), and have a significant influence on the expected internal dynamics of Mars. As a high thermal conductivity value results in greater heat flux out of the core, it requires a lower mantle viscosity to effectively dissipate heat and satisfy constraints on the cessation time of the Martian magnetic field (Hemingway and Driscoll, 2021). The cessation time of the Martian magnetic field is sensitive to the thermal conductivity of the core-forming alloy, because when heat flux conducted down the core adiabat becomes comparable to the magnitude of conductive heat flux at the core-side of the core-mantle boundary, thermal stratification will occur, and the stratified, conductive layer will begin to screen the magnetic field produced by the interior dynamo (Greenwood et al., 2021). The present study, alongside recent literature on iron demonstrate that the range of thermal conductivity values relevant to the Martian core is smaller than previously thought, at maximum varying between 50 W/m/K to 15 W/m/K for end-members Fe and FeS (Yong et al., 2019; Ohta et al., 2016; Konôpková et al., 2016). A recent thermal evolution study incorporating the effect of thermal stratification explored this range of thermal conductivity values (Greenwood et al., 2021), showing that core conductivity values compatible with observations produce a fully conductive core profile in the present day for values above 23 W/m/K, with values from 15 W/m/K to 23 W/m/K potentially stabilizing a long-lived partial dynamo. Coloured bands shown in Fig. 8 represent upper bounds on the light element content of the Martian core, as recent studies report a higher core density, resulting in a corresponding decrease in light element content (Irving et al., 2023; Le Maistre et al., 2023).

This work demonstrates that the thermal conductivity of Fe-S or Fe-S-O core models are sufficiently high to produce viable Martian dynamo models irrespective of cosmochemical or geochemical permissibility (e.g. Khan et al., 2022; Stähler et al., 2021), owing to the high thermal conductivity of FeS at the conditions of interest for the Martian core as reported here. This is a consequence of the result that FeS is metallic, but a poor metal at Martian core conditions, resulting in a reduced contrast between Fe and Fe-S thermal conductivity at these conditions.

5. Conclusions

We have studied FeS over a wide range of pressures and temperatures using a combination of high pressure experiments and DFT/DMFT computations. The V-IV-Liquid triple point is located at 46(3) GPa and 2300(150) K. The melting temperature of FeS observed here is consistent with the lower bound of existing literature (Boehler, 1992). Firstprinciples calculations demonstrate that FeS exhibits finite magnetic moments at the conditions of the Martian core. The thermal conductivity of FeS is about 15-30 W/m/K at the conditions of the Martian core. With computed electrical resistivity values of about 120-180 $\mu\Omega$ cm, FeS is metallic, but a poor metal at these conditions. These results indicate that sulfur-rich core compositions are compatible with constraints on the cessation time of Mars' early dynamo.

CRediT authorship contribution statement

E. Edmund: Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **T. Bi**: Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Z.M. Geballe:** Writing – review & editing, Methodology, Investigation. K. Brugman: Writing – review & editing, Investigation, Formal analysis. J.-F. Lin: Writing – review & editing, Resources, Conceptualization. S. Chariton: Writing – review & editing, Methodology, Investigation. V.B. Prakapenka: Writing – review & editing, Methodology, Investigation. J. Minár: Software, Methodology. R.E. Cohen: Writing – review & editing, Supervision, Resources, Methodology, Investigation, Funding acquisition. A.F. Goncharov: Writing – review & editing, Supervision, Resources, Methodology, Investigation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.epsl.2024.118959.

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