

Vacancy ordering schemes govern the antiferromagnetism in a modulated pyrrhotite structure

ALEXANDER FIRLUS^{1,*}, JÜRGEN E.K. SCHAWÉ¹, PETER G. WEIDLER², MICHAEL WÖRLE³,
JÖRG F. LÖFFLER¹, AND ANDREAS U. GEHRING^{1,†}

¹Laboratory of Metal Physics and Technology, Department of Materials, ETH Zurich, 8093 Zurich, Switzerland

²Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

³Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland

ABSTRACT

Superstructures with modulated vacancy order are a characteristic trait of the pyrrhotite solid-solution series (Fe_{1-x}S , $0 < x \leq 0.125$), and they strongly affect the magnetocrystalline anisotropy that causes Fe-spin rotation. The effect of a stochastic vacancy order and the resulting structural heterogeneity at the atomic level on the magnetization is not resolved yet in detail. Here, we demonstrate that a thermally tailored antiferromagnetic pyrrhotite made up of fivefold and sixfold stacking modulations with five different Fe-vacancy ordering variants forms two distinct vacancy ordering schemes that govern the spin rotation. A field-dependent thermomagnetic anomaly between 220 and 170 K and a secondary hysteresis loop in the magnetization curve in a field of around 3 Tesla provide compelling evidence for two different Fe-spin rotation patterns. The simultaneous occurrence of the magnetic anomaly and two enthalpy changes link the magnetocrystalline anisotropy to structural distortions of Fe–Fe bonds in the vacancy-ordering schemes, thereby explaining the presence of the two spin rotation patterns. This finding highlights magnetic effects induced by vacancy order and underscores the relevance of its architecture in a key sulfide material extensively used in geoscience and cosmology and with potential for technical applications.

Keywords: Pyrrhotite, fivefold and sixfold modulated stacking, Fe-vacancy ordering variants, XRD, DSC, magnetism

INTRODUCTION

The properties of materials are critically affected by defects and disorder, which can come at different length scales and dimensions and are oftentimes deliberately introduced to improve the material performance or provide novel physical phenomena. Magnetic interactions, in particular, are sensitive to both local defects and their long-range order. Up to now, little attention has been given to the effect of stochastic defect geometry on magnetism, even though defects are omnipresent in materials. To address this fundamental issue, we use an antiferromagnetic pyrrhotite as a testbed, where single vacant atomic sites are subject to order, i.e., they form vacancy-ordering schemes (VOSs).

Pyrrhotite represents an omission solid-solution series (Fe_{1-x}S , $0 < x \leq 0.125$) that comprises a wide variety of mono-sulfide mineral phases ubiquitous in the Earth's crust and extra-terrestrial materials (e.g., chondrites, solar dust) (Berger et al. 2011; Horng 2018; Yang et al. 2018; Schrader et al. 2021; Steele et al. 2023), and is of some interest for technical applications (Boyjoo et al. 2020; Lee et al. 2023; Wang et al. 2023). All pyrrhotite phases are based on a hexagonal NiAs-type structure modified by distortions due to vacant Fe sites in octahedral

interstices of hexagonal closed-packed sulfur atoms (Izaola et al. 2007; Jin et al. 2021; Rezvani et al. 2024). This modification generates superstructures with vacancy ordering in varying stacking modulations of full and defective Fe layers along the *c*-axis, and this in turn determines the magnetic properties that are critically affected by spin rotation (Bin and Pauthenet 1963; Wang and Salveson 2005; Haines et al. 2019). The monoclinic ferrimagnetic end-member Fe_7S_8 , known as 4C pyrrhotite, has a fourfold alternating stacking modulation of full and vacancy sublattices along the *c*-axis. The ferrimagnetism stems from uncompensated sublattices with ferromagnetic in-plane and antiferromagnetic inter-plane coupling with a low-temperature anomaly at $T \approx 32$ K. This is known as the Besnus transition, which is the characteristic trait to unambiguously identify 4C pyrrhotite (Bertaut 1953; Néel 1953; Fillion and Rochette 1988; Gehring et al. 2021; Živković et al. 2021). In the less Fe-deficient members, where the 5C modification (Fe_9S_{10}) is most prominent, the stacking modulations consist of VOSs with an occupation probability distribution, and this in turn leads to antiferromagnetic properties (Elliot 2010; Herbert et al. 2015). All members of the pyrrhotite group reveal a magneto-structural transition above a temperature of about 600 K, where the superstructure breaks down, and a paramagnetic NiAs-type substructure remains (Powell et al. 2004; Herbert et al. 2015; Koulialias et al. 2019a), and at higher temperatures, sulfur is expelled from the structure. By cooling to temperatures below 600 K, superstructures with commensurate or incommensurate stacking modulations are reestablished (Morimoto et al. 1970;

* Co-corresponding author E-mail: alfirlus@ethz.ch Orcid <https://orcid.org/0000-0001-6221-9874>

† Co-corresponding author E-mail: agehring@ethz.ch

‡ Open access: Article available to all readers online under the following license terms: CC BY.

Wang and Salveson 2005; Jin et al. 2021). Such thermal alteration renders it possible to fabricate materials with variable vacancy ordering and to study the effect on their magnetic properties. Here, we tailored a Fe_9S_{10} pyrrhotite with vacancy sites forming VOSs and demonstrate that their interplay produces novel magnetic responses.

MATERIALS AND METHODS

Sample Preparation

The starting material was a nearly stoichiometric 4C pyrrhotite ($\text{Fe}_{6.9}\text{S}_8$) crystal with traces of Ni (377 ppm) and Co (60 ppm) from the Morro Velho mine (Minas Gerais, Brazil) (Vial et al. 2007; Koulialias et al. 2019b). Stoichiometric modification was performed in a thermogravimetric system (TGA 3+, Mettler-Toledo), and this thermally tailored sample was used for all subsequent measurements. To create inert conditions, i.e., to avoid oxidation, the connections to the internal-gas switch unit were disassembled and closed. A reducing gas mixture of Ar with 4% H_2 was connected directly to the protective gas connection. This gas flowed through the balance chamber and the TGA furnace. After floating the system, the gas flow was adjusted to 30 mL min^{-1} to minimize possible turbulence. For these conditions, the temperature of the TGA was calibrated using In, Al, and Au. The 33.3 mg sample was placed into a $30 \mu\text{L}$ aluminum oxide crucible. After equilibration of the measured weight signal, the system was purged for 3 h before starting the measurement. The sample was heated from 473 to 1123 K at 10 K/min, followed by ballistic cooling. The measured curve after blank subtraction is shown in Figure 1. The temperature program was selected after a preliminary test to obtain a mass loss of 2.8%.

Single-Crystal X-ray Diffraction

The structural analysis was performed by single-crystal XRD at about 300 K and at 100 K. Crystals of suitable size and shape were cut from the millimeter-sized thermally treated crystal and mounted on a Mitegen MicroMount. Full-sphere data sets were collected on a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE detector using Mo radiation.

The structures were solved with SHELXT (Sheldrick 2015) using the closest 3D approximants of the incommensurately modulated structures in the non-centrosymmetric space group $P6m2$ (No. 187), and refined with SHELXL (Sheldrick 2008) embedded in Olex2 (Dolomanov et al. 2009) as inversion twins with approximately equal domain size of the two individuals. Any attempt using space groups

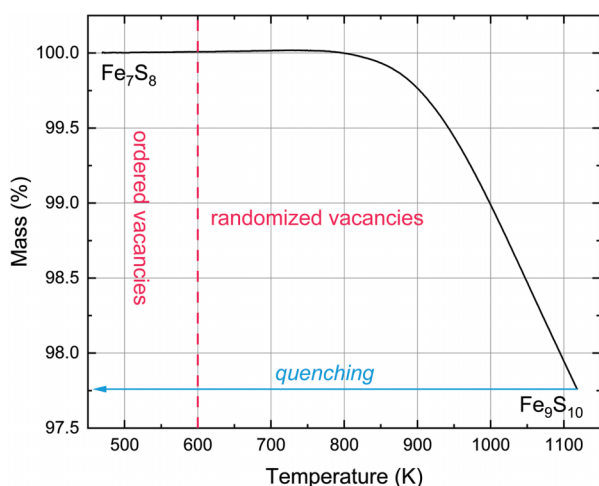


FIGURE 1. TGA mass loss during thermal tailoring of a Fe_7S_8 natural pyrrhotite sample. The sample is chemically stable up to $T \approx 780 \text{ K}$. At $T = 1120 \text{ K}$, the Fe_9S_{10} composition was reached. The material was then quenched to stop further sulfur loss and to reestablish vacancy order.

of lower symmetry and/or twinning did not significantly improve the figures of merit or the model. Crystallographic details for crystals I and II are given in Online Materials¹ Tables S1 and S2.

Magnetometry

The magnetic properties were investigated by vibrating sample magnetometry (VSM) at 15.9 Hz with an MPMS3 device (QuantumDesign). The thermomagnetic curves were measured sequentially in increasing fields with a demagnetization step in-between where the sample was exposed to a slowly oscillating field with diminishing amplitude at 225 K. For measuring the series of $M(B)$ plots at various temperatures the same procedure was used with a demagnetization temperature of 300 K. The cooling curves of the demagnetized samples between the $M(B)$ measurements were recorded and are shown in Online Materials¹ Figure S2. Errors in the measurement of the magnetic moments were confirmed to be <1% with a Pd reference sample, and the temperature controller had an error of less than 5 K, which was confirmed by the Curie temperature of FeNi and pure Ni reference samples.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed using a Mettler-Toledo DSC 3+ with liquid-nitrogen cooling. Enthalpy and temperature were calibrated with water, n-octane, adamantane, and n-heptane. The 28.114 mg sample was encapsulated in a $40 \mu\text{L}$ Al crucible and measured from 130 K to 273 K with a heating rate of 10 K/min.

RESULTS

Thermal Modification

For the fabrication of the monosulfide sample with Fe_9S_{10} stoichiometry, a natural high-quality 4C pyrrhotite crystal (Fe_7S_8) was thermally treated. Thermogravimetric analysis (TGA) reveals that the 4C pyrrhotite starting material is chemically stable up to $T = 780 \text{ K}$. Further heating leads to a steady mass loss due to the release of sulfur, and at $T \approx 1100 \text{ K}$ the pyrrhotite has a Fe/S ratio of 0.88 corresponding to Fe_9S_{10} (Fig. 1). The thermal tailoring of the Fe_9S_{10} material can be considered as a multi-step diffusive process. In a first step, the vacancy ordering in the 4C pyrrhotite starting material breaks down at $T \approx 600 \text{ K}$, and the randomization of the vacancy sites forms a defective NiAs-type structure (Powell et al. 2004; Koulialias et al. 2019a). In a second step, the release of sulfur at $T > 780 \text{ K}$ is controlled by solid-state diffusion, and the linear TGA curve up to $T \approx 1100 \text{ K}$ indicates a zero-order reaction typical for free evaporation, i.e., the diffusion rate of sulfur in the pyrrhotite crystal is larger than the evaporation rate. The overall sulfur loss and the subsequent increase in the Fe/S ratio result in a lesser vacancy density in the NiAs-type structure. Rapid cooling to temperatures below $T \approx 600 \text{ K}$ leads to vacancy ordering in a pyrrhotite phase with a Fe/S ratio of 0.88. Earlier studies reported that such a ratio in pyrrhotite samples generally leads to a superstructure with fivefold modulation (Wang and Salveson 2005; Elliot 2010; Liles and de Villiers 2012; Haines et al. 2020).

Structural Properties

The structural analysis of the thermally treated pyrrhotite was performed by single-crystal XRD at room temperature and at 100 K on two crystallite sister samples referred to as I and II. Both reveal Bragg spots of a well-crystallized incommensurately modulated pyrrhotite that can be described using a classical 3D approximation in the non-centrosymmetric space

group $P\bar{6}m2$ (No. 187). The details of the crystallographic description can be found in Online Materials¹ Tables S1 and S2.

At room temperature, the diffraction pattern of crystal I can be indexed with a unit cell of hexagonal metric [$a = 6.9032(2)$ Å, $c = 28.8312(9)$ Å], which corresponds to a fivefold superstructure along the c -axis and a twofold superstructure along the a -axis compared to the underlying NiAs-structure type, namely $a = 2 \cdot a_{\text{NiAs}}$ and $c = 5 \cdot c_{\text{NiAs}}$. A close inspection of the intensity distribution and positions of the superstructure reflections, however, suggests that their positions in the pattern are even better described by an incommensurately modulated structure with $a = 6.9041(17)$ Å, $c = 5.766(3)$ Å, and a modulation vector $q = 0$ 0 0.1938(8). Incommensurate modulations are well known for pyrrhotite, e.g., 5.5C pyrrhotite (Yamamoto and Nakazawa 1982). For crystal I, the description as an incommensurately modulated structure is very close to the commensurate modulation (q -vector component along the c^* -axis of almost 0.2), requiring a quintupling of the c -axis in the classical 3D description. Given this, the 3D fivefold superstructure approximation was chosen to describe crystal I, and the figures of merit indicate that this is a valid approximation (see Online Materials¹ Table S1).

Crystal II reveals slightly different features with respect to the superstructure/satellite reflections, even though it was cut from the same parent crystal. An indexing analogous to crystal I as an incommensurately modulated structure leads to $a = 6.9054(10)$ Å, $c = 5.7743(11)$ Å, and a modulation vector $q = 0$ 0 0.1770(13). With this q -vector, the satellite reflections are located close to the positions expected for a sixfold superstructure in the classical 3D description. Therefore, the description as a 3D approximant with hexagonal lattice constants of $a = 6.9084(3)$ Å and $c = 34.6477(17)$ Å was chosen for the structure solution and refinement. It should still be noted that neither description can account for some weak additional superstructure reflections. This could be accomplished with an incommensurately modulated unit cell with $a = 11.9426(7)$ Å, $c = 11.5757(12)$ Å, and $q = 0$ 0 0.3590(19), which is obtained by applying the transformation matrix $\begin{bmatrix} 1 & -1 & 0 & 1 & 2 & 0 & 0 & 2 \end{bmatrix}$ to the setting with the lattice constants $a = 6.9054(10)$ Å, $c = 5.7743(11)$ Å, and $q = 0$ 0 0.1770(13). The classical approximant for this larger cell then requires a tripling of the cell volume and massively increases the number of parameters, which leads to large correlation matrix elements during the refinement. This, in turn, renders a model with increased complexity less significant. Because the superstructure reflections are weak, it can be assumed that the main features of the crystal structure are already reflected by the description in the smaller cell.

It is worth noting that coexisting five- and sixfold modulations were recently reported from a pyrrhotite crystal in a regolith sample of the Ryugu asteroid, and their formations were explained by a diffusive sulfur loss from a 4C pyrrhotite caused by space weathering (Harries et al. 2024). The two crystals I and II of the present study, both refined in the $P\bar{6}m2$ space group, however, have nearly identical unit-cell parameters a and b , whereas the c parameters differ by 20% due to intercalated layers with full occupancy of the Fe positions (see Fig. 2a).

In both crystals, the vacancy layers can be subdivided into two Fe-deficient building blocks that are different in their VOSs

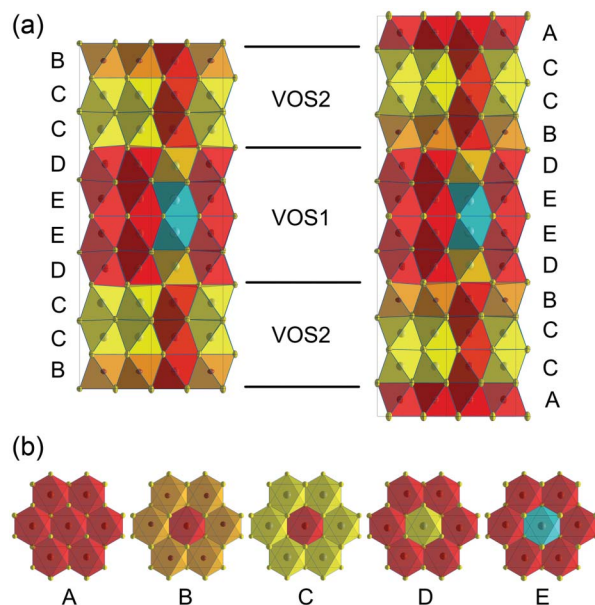


FIGURE 2. Atomic structure of the thermally tailored sample. **(a)** The structures of crystal I (left) and crystal II (right) in the viewing direction $[-1 \ -1 \ 0]$ with two VOSs. The unit cells are shown as stacking of layers of edge-sharing FeS_6 -octahedra colored according to the occupancy factors of the Fe sites grouped in intervals of 1 (red), 0.91–0.94 (orange), 0.84–0.90 (yellow), and 0.58–0.62 (blue). The stacking modulation consists of five Fe-vacancy ordering variants A–E. **(b)** The five Fe-vacancy ordering variants within individual layers. Variant A represents full layers; in B and C, the vacancies are in a six-ring, and in D and E, they are in the center of a six-membered ring.

(Fig. 2a). VOS1 consists of four layers where the vacancy sites are in the center of the fully occupied six-membered Fe rings (Fig. 2b). This configuration with the variants D and E leads to relatively high vacancy order in strings along the c -axis and to a hexagonal array in the Fe rings in the basal plane similar to the vacant layers in the 4C pyrrhotite end-member (Firlus et al. 2022). VOS2 with the variants B and C comprises fully occupied Fe sites in the center of partially occupied Fe rings (Fig. 2b). In this case, the fully occupied Fe site has, on average, fewer than six neighboring cations within the layer, i.e., the local hexagonality is broken. Moreover, for VOS2, the variation of occupation factors in variants B and C (0.91–0.94 and 0.84–0.90, respectively) is relatively low for the defect sites, whereas in VOS1, the variation of the occupation factors in variants D and E is significant (0.84–0.90 and 0.58–0.62, respectively) (Fig. 2b).

Taking into account that for a fivefold-modulated pyrrhotite a low-temperature Morin-like spin rotation associated with an endothermic peak in the heat capacity was postulated (Haines et al. 2020), we analyzed the structure of crystals I and II at $T = 100$ K with the same approach as used for room temperature. As can be seen in Online Materials¹ Tables S1 and S2, the structures remain the same, and the unit-cell parameters reveal only minor thermal contractions. The sixfold modulation sequence shortens in the parameters a and b by 0.6% and expands in parameter c by 0.1%, whereas in the fivefold modulation, the a and b parameters shorten by 0.1% and the c parameter remains

constant. The occupation factors in both schemes exhibit no significant variations, and this, in turn, means that no cation diffusion took place within the tailored pyrrhotite upon cooling. Moreover, the Fe–Fe distances in the basal plane are longer than 3 Å, whereas in the *c*-direction of both crystals, they are shorter than 3 Å, with a mean value of 2.88 ± 0.07 Å at 300 K and 2.89 ± 0.08 Å at 100 K. In NiAs-type sulfides, Fe–Fe distances that are shorter than 3 Å have an orbital overlap that causes spin-orbit coupling (SOC), and this in turn determines the uniaxial magnetocrystalline anisotropy (MCA) (Goodenough 1963). The SOC generated by Fe–Fe bonds causes spin rotations out of the basal plane, and their angles are critically affected by the vacancy arrangement (Adachi 1963; Powell et al. 2004; Koulialias et al. 2018b). Detailed magnetic torque studies on 4C pyrrhotite provided clear evidence that Fe spins at sites next to a vacancy in the *c*-direction differ in their out-of-plane tilting compared to those with intact cation surroundings, resulting in two MCA subsystems (Koulialias et al. 2018a, 2018c). Given this, it can be supposed that the vacancy architecture of the VOSs generates different spin rotation patterns. The pattern in VOS2 then has a higher heterogeneity because the vacancies break the hexagonal, local symmetry of the ring formed by the six FeS₆ octahedra around the fully occupied Fe-site (Fig. 2b).

In summary, the thermally tailored sample can be described as a modulated pyrrhotite structure made of two well-defined VOSs associated with intermediate full layers that form five Fe-vacancy ordering variants (Fig. 2b); this structure is neither a fivefold nor a sixfold pyrrhotite as described in the literature (e.g., Elliot 2010; Liles and de Villiers 2012).

Magnetic and Thermodynamic Properties

The magnetization (*M*) vs. magnetic field (*B*) of the thermally tailored pyrrhotite, roughly measured in the *c*-plane at *T* = 300 K, is characteristic of a canted antiferromagnet far from saturation (Fig. 3a). The magnetization curve reveals a bending formed by two nearly linear branches with an inflection at about *B* = 3 T, which indicates the contribution of two magnetization regimes.

The bending is most likely caused by localized SOC, i.e., MCA, in the VOSs, which results in different spin rotation patterns (Koulialias et al. 2018c). Considering the structural data, VOS2 has a more heterogeneous vacancy order than VOS1 because of the broken local hexagonality. The increase in magnetization at low fields (*B* < 3 T) can then be explained by the reduction of spin rotation heterogeneities, preferentially in VOS2. This also makes the ferromagnetic coupling of nearest-neighbors in the *c*-plane more relevant to the magnetization mechanism. Consequently, at higher fields (*B* > 3 T), the linear magnetization increase stems from an apparent collective spin rotation in both VOSs. This change of the dominant magnetization mechanism from individual to apparent collective spin rotation gives rise to the bending, generating two slopes in the *M*(*B*) curves.

At 100 K, the *M*(*B*) plot is linear, and the contributions of the different VOSs and local disorder effects to the magnetization are no longer detected (Fig. 3b), i.e., they show an apparent collective spin rotation. Surprisingly, the cooling curve to 100 K of the demagnetized sample reveals a sudden increase in magnetization at *T* ≈ 200 K (inset to Fig. 3b; Online Materials¹ Fig. S2).

Such anomalous behavior is also found between 200 and 170 K in the field-cooling (FC) magnetization curves (Fig. 4). This anomaly, however, generates a field-dependent step function with positive as well as negative slopes in the *M*(*T*,*B*) curves, with the maximum change in magnetization being about 15% (Fig. 4a). This behavior unlikely comes from a Morin-type spin transition as postulated for 5C pyrrhotite by Haines et al. (2019). The field-induced changes of *M*(*T*), however, can be visualized by the comparison of the magnetization curves at 170 and 200 K extracted from the FC curves (Fig. 4b). At 200 K, the *M*(*B*) curve extracted from FC is bent, whereas at *T* = 170 K the bending has disappeared. The difference $\Delta M = M_{170\text{K}} - M_{200\text{K}}$ has two zero points and shows a maximum at *B* ≈ 3 T, which is indicative of the transition from an individual spin rotation to an apparent collective one. At *B* < 3 T, ΔM mirrors an individual spin rotation, as also indicated by the

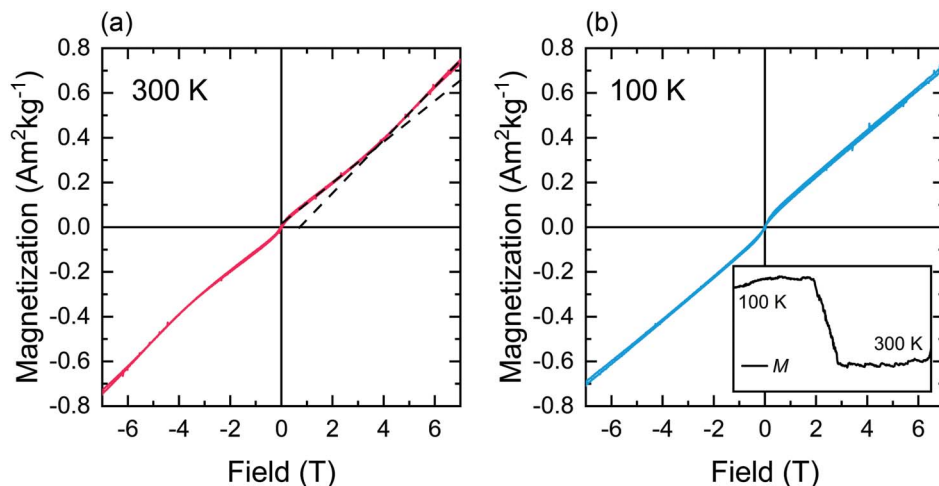


FIGURE 3. Magnetization loop of the thermally tailored pyrrhotite. (a) The *M*(*B*) plot at *T* = 300 K reveals two nearly linear branches, as indicated by the dashed lines, with an inflection at *B* = 3 T. (b) At *T* = 100 K, the magnetization curve shows no bending. The inset displays the shape of the zero-field cooling magnetization down to 100 K of the sample demagnetized at 300 K.

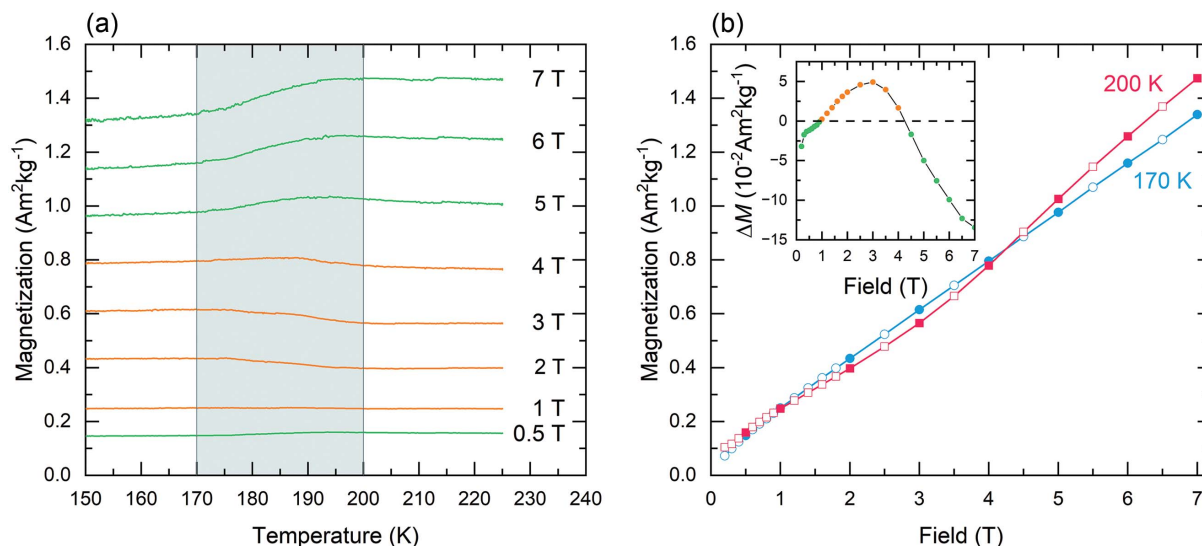


FIGURE 4. Thermomagnetic curves of the thermally tailored pyrrhotite. (a) The thermomagnetic curves show a field-dependent anomaly at 170–200 K. The magnetization decreases during cooling at high and low fields (green lines) but increases at intermediate fields (orange lines). (b) The implied magnetization curves at 170 K (blue line) and 200 K (red line) have a similar shape to the magnetization loops in Figure 3. The field-dependent change in magnetization ΔM shows a maximum at around 3 T (see inset).

bending. The positive slope of ΔM is due to the fact that the susceptibility at 170 K of the apparently collective system is higher than that of the individual system at 200 K (Fig. 4b). The decline of ΔM at $B > 3$ T occurs in a field range where the spin rotation is apparently collective at both temperatures. Here, the susceptibility decreases upon cooling due to changes in the MCA during the transition. Hence, the local maximum in ΔM is a consequence of different responses of spin rotation in the VOSs to an external field.

Further insight into the interplay of the spin rotations in the VOSs can be obtained from the $M(B)$ plots recorded at different temperatures. At $T = 170$ K, the $M(B)$ curve is like that at $T = 100$ K (Fig. 3b and 5) and shows a linear increase in magnetization. At $T = 200$ K, the $M(B)$ curve resembles that at $T = 300$ K (Fig. 3a and 5), but a secondary hysteresis at around $B = 3$ T associated with the inflection is observed.

The hysteretic behavior occurs exactly in the field range of the transition from an individual to an apparent collective spin rotation in the VOSs and marks an energy barrier. The (in-plane) energy landscape stems from an interplay between the isotropic ferromagnetic coupling, the external field, and the heterogeneous SOC due to the vacancy distribution. At high fields, the lowest energy is at a configuration where the spins are parallelly aligned because the contributions generated by the external field and ferromagnetic coupling are stronger than the SOC generated by the heterogeneous vacancy distribution. By contrast, in low fields, the dominant SOC-energy contribution generates a heterogeneous spin rotation. The transition to such rotation goes through intermediate states, where the ferromagnetic coupling is violated, and this in turn gives rise to an energy barrier. Moreover, the hysteretic behavior is temperature dependent and cannot be detected at $T > 270$ K (see Online Materials¹ Fig. S1). The major change in SOC, i.e., MCA, however, is associated with the magnetic anomaly between 170 and 200 K. XRD

reveals no crystallographic changes down to 100 K but thermodynamic changes in this range can be detected by DSC (Fig. 6). The transition exhibits an endothermic enthalpy change of $\Delta H = 120 \text{ mJ g}^{-1}$ upon heating, which can be fitted with two Gaussians. A similar value for ΔH is extracted from the heat capacity vs. temperature curve associated with the Morin-type spin transition in 5C pyrrhotite, reported by Haines et al. (2020), which shows a peak at $T = 154$ K and a shoulder at a lower temperature. Such features indicate two contributions to the heat capacity, and this is similar to the DSC measurements (Fig. 6). Grönvold et al. (1991) found no low-temperature peak for a synthetic 5C pyrrhotite, and this in turn suggests that the two contributions most likely stem from variations in stacking modulation. Haines et al. (2020), however, reported that in a field of $B = 9$ T the heat capacity curve shifts to lower temperature but the shape remains unchanged. This implies that ΔH associated with the postulated Morin-type transition is unaffected by the magnetic field, in contrast to the entropy change ΔS , which becomes larger in high fields. Such behavior is consistent with an in-field spin rotation upon heating, also found in the $M(B)$ curves (Haines et al. 2020). In our DSC measurements, performed in the absence of a magnetic field, the two endothermic enthalpy components are well resolved, and their temperature range corresponds to that of the anomaly in the zero-field cooling magnetization curves (Fig. 6; Online Materials¹ Fig. S2). One component between 170 and 180 K is characterized by a minimum at 177.5 K and an enthalpy change of $\Delta H = 42.1 \text{ mJ g}^{-1}$, and the other has a minimum at 183.9 K with $\Delta H = 76.7 \text{ mJ g}^{-1}$. The corresponding entropy changes are $\Delta S = 0.24 \text{ mJ g}^{-1} \text{ K}^{-1}$ and $\Delta S = 0.42 \text{ mJ g}^{-1} \text{ K}^{-1}$, respectively. The two peaks provide clear evidence that the magnetic anomaly is associated with the VOSs. The peak at lower temperature is assigned to VOS2 with its heterogeneous spin rotation pattern generated by the broken local hexagonality caused by the

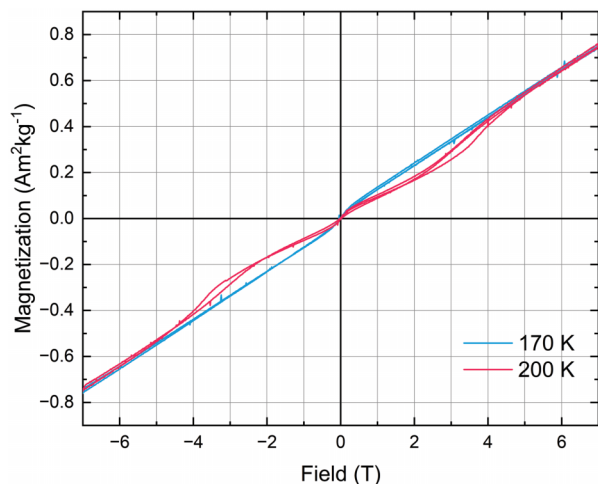


FIGURE 5. Magnetization loops of the thermally tailored pyrrhotite at 170 and 200 K. The $M(B)$ plots at 170 and 200 K are similar to those at 100 and 300 K shown in Figure 3, respectively. However, at 200 K, a secondary hysteresis centered at around ± 3 T develops.

vacancies in the Fe rings (Fig. 2). The higher-temperature peak is due to VOS1, where the vacancy arrangement leads to a less heterogeneous spin rotation pattern.

The crystal structures I and II exhibit no crystallographic change with temperature, and this, in turn, is consistent with the relatively low value of ΔH (Figs. 2 and 6). Given this, ΔH most likely stems from changes in local structural distortions on the atomic level. Such distortions along the c -axis change the Fe–Fe bond lengths, the SOC, and subsequently the MCA that determines spin rotation (Goodenough 1963; Koulialias et al. 2018a, 2018b). Hence, the changes in spin rotation, manifesting the magnetic anomaly, are triggered by local structural distortions. An apparent collective spin rotation response can then be enforced either by a high external magnetic field to suppress the heterogeneities or by temperature.

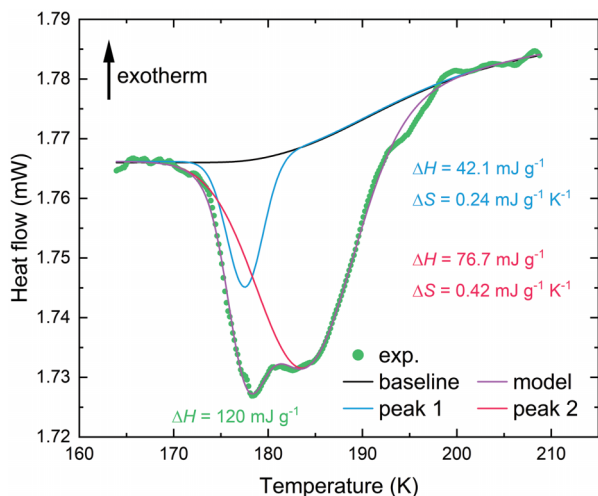


FIGURE 6. DSC curve of the thermally tailored pyrrhotite. The anomaly between 170 and 200 K is endothermic and appears as two distinct thermal events.

IMPLICATIONS

Our study demonstrates the importance of considering not only the type of defects but also their arrangement in a material. Magnetism is particularly sensitive to the defect geometry and can bring forth complex responses to external variables such as the magnetic field or temperature. The pyrrhotite omission series, with its simple chemistry, well-defined layered structure, and tunable vacancy geometry, is an ideal material to provide closer insight into the interplay of vacancy order and magnetism. Even though the tailored pyrrhotite sample has stacking modulations with two distinct stochastic VOSs, single-crystal properties remain intact. The magnetic response of the two VOSs detected by field-dependent thermomagnetometry and secondary hysteresis loops provides compelling evidence that the magnetization properties are governed by the different sublattice architectures in the pyrrhotite. This unexpected behavior illustrates the potential of vacant atomic sites to manipulate physical properties in crystalline solids, and this, in turn, may be beneficial in tailoring the functionality of materials. Furthermore, the members of the pyrrhotite omission series are important information carriers in Earth and planetary sciences to decipher the mineral-chemical and paleomagnetic history of rock bodies. Our findings that the chemical composition does not unambiguously determine the vacancy architecture can thus be crucial when studying the robustness of the information obtained from pyrrhotite phases. The consideration of the vacancy architecture and its effect on the magnetic properties is especially vital for extraterrestrial materials, such as chondrites, solar dust, or materials returned from asteroids, where pyrrhotite phases with different stacking modulations and VOSs generally coexist. Finally, the complementation of the structural and magnetic VOS analysis with thermodynamic information presents a holistic experimental approach that appears to be invaluable in multidisciplinary scientific fields, where crystallographic defects are effective in determining the material properties.

DATA AVAILABILITY

The data sets generated and analyzed during the current study are available in the ETH Research collection: Data sets to “Vacancy ordering schemes govern the antiferromagnetism in a modulated pyrrhotite structure,” <https://doi.org/10.3929/ethz-b-000702003>. CSD 2393289–2393292 contains the supplementary crystallographic data for this paper (see Online Materials¹). These data can be obtained free of charge from FIZ Karlsruhe via <https://www.ccdc.cam.ac.uk/structures>.

ACKNOWLEDGMENTS AND FUNDING

This work was supported by an ETH Research Grant (No. ETH-47 17-1).

REFERENCES CITED

- Adachi, K. (1963) Origine de l'énergie d'anisotropie magnétocristalline de la pyrrhotine. *Journal de Physique et le Radium*, 24, 725–731, <https://doi.org/10.1051/jphys:019630024010072500>.
- Berger, E.L., Zega, T.J., Keller, L.P., and Lauretta, D.S. (2011) Evidence for aqueous activity on comet 81P/Wild 2 from sulfide mineral assemblages in Stardust samples and CI chondrites. *Geochimica et Cosmochimica Acta*, 75, 3501–3513, <https://doi.org/10.1016/j.gca.2011.03.026>.
- Bertaut, E.F. (1953) Contribution à l'étude des structures lacunaires: La pyrrhotine. *Acta Crystallographica*, 6, 557–561, <https://doi.org/10.1107/S0365110X53001502>.

- Bin, M. and Pauthenet, R. (1963) Magnetic anisotropy in pyrrhotite. *Journal of Applied Physics*, 34, 1161–1162, <https://doi.org/10.1063/1.1729413>.
- Boyjoo, Y., Shi, H., Olsson, E., Cai, Q., Wu, Z., Liu, J., and Lu, G.Q. (2020) Lithium-sulfur batteries: Molecular level design of pyrrhotite electrocatalyst decorated hierarchical porous carbon spheres as nanoreactors for lithium-sulfur batteries. *Advanced Energy Materials*, 10, 2070092.
- Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., and Puschmann, H. (2009) OLEX2: A complete structure solution, refinement and analysis program. *Journal of Applied Crystallography*, 42, 339–341, <https://doi.org/10.1107/S0021889808042726>.
- Elliot, A.D. (2010) Structure of pyrrhotite 5C (Fe₉S₁₀). *Acta Crystallographica Section B*, 66, 271–279, <https://doi.org/10.1107/S0108768110011845>.
- Fillion, G., and Rochette, P. (1988) The low temperature transition in monoclinic pyrrhotite. *Le Journal de Physique Colloques*, 49, C8-907–C8-908.
- Firlus, A., Schawe, J.E.K., Weidler, P.G., Charilaou, M., Löffler, J.F., and Gehring, A.U. (2022) Anisotropy-induced spin disorder in intergrown, ferrimagnetic Fe₇S₈ polytypes. *Applied Physics Letters*, 121, 154103, <https://doi.org/10.1063/5.0111498>.
- Gehring, A.U., Firlus, A., Koulialias, D., Weidler, P.G., and Löffler, J.F. (2021) The Besnus transition in 4C pyrrhotite revisited. *Geophysical Journal International*, 228, 1724–1730, <https://doi.org/10.1093/gji/ggab430>.
- Goodenough, J.B. (1963) *Magnetism and the Chemical Bond*, 393 p. Wiley.
- Grønvold, F., Stølen, S., Labban, A.K., and Westrum, E.F. Jr. (1991) Thermodynamics of iron sulfides I. Heat capacity and thermodynamic properties of Fe₉S₁₀ at temperatures from 5 K to 740 K. *The Journal of Chemical Thermodynamics*, 23, 261–272, [https://doi.org/10.1016/S0021-9614\(05\)80184-3](https://doi.org/10.1016/S0021-9614(05)80184-3).
- Haines, C.R.S., Howard, C.J., Harrison, R.J., and Carpenter, M.A. (2019) Group-theoretical analysis of structural instability, vacancy ordering and magnetic transitions in the system troilite (FeS)-pyrrhotite (Fe_{1-x}S). *Acta Crystallographica Section B, Structural Science, Crystal Engineering and Materials*, 75, 1208–1224, <https://doi.org/10.1107/S2052520619014197>.
- Haines, C.R.S., Lampronti, G.I., Klooster, W.T., Coles, S.J., Dutton, S.E., and Carpenter, M.A. (2020) Morin-type transition in 5C pyrrhotite. *American Mineralogist*, 105, 1404–1411, <https://doi.org/10.2138/am-2020-7266>.
- Harries, D., Matsumoto, T., Langenhorst, F., Noguchi, T., Miyake, A., Igami, Y., Haruta, M., Seto, Y., Miyahara, M., Tomioka, N., and others. (2024) Incipient space weathering on asteroid 162173 Ryugu recorded by pyrrhotite. *Meteoritics & Planetary Science*, 59, 2134–2148, <https://doi.org/10.1111/maps.14176>.
- Herbert, F.W., Krishnamoorthy, A., Yildiz, B., and Van Vliet, K.J. (2015) Diffusion-limited kinetics of the antiferromagnetic to ferrimagnetic λ -transition in Fe_{1-x}S. *Applied Physics Letters*, 106, 092402, <https://doi.org/10.1063/1.4913201>.
- Hong, C.-S. (2018) Unusual magnetic properties of sedimentary pyrrhotite in methane seepage sediments: Comparison with metamorphic pyrrhotite and sedimentary greigite. *Journal of Geophysical Research: Solid Earth*, 123, 4601–4617, <https://doi.org/10.1002/2017JB015262>.
- Izaola, Z., González, S., Elcoro, L., Perez-Mato, J.M., Madariaga, G., and García, A. (2007) Revision of pyrrhotite structures within a common superspace model. *Acta Crystallographica Section B*, 63, 693–702, <https://doi.org/10.1107/S0108768107037275>.
- Jin, L., Koulialias, D., Schnedler, M., Gehring, A.U., Pósfai, M., Ebert, P., Charilaou, M., Schäublin, R.E., Jia, C.-L., Löffler, J.F., and others. (2021) Atomic-scale characterization of commensurate and incommensurate vacancy superstructures in natural pyrrhotites. *American Mineralogist*, 106, 82–96, <https://doi.org/10.2138/am-2020-7479CCBY>.
- Koulialias, D., Charilaou, M., Schäublin, R., Mensing, C., Weidler, P.G., Löffler, J.F., and Gehring, A.U. (2018a) Ordered defects in Fe_{1-x}S generate additional magnetic anisotropy symmetries. *Journal of Applied Physics*, 123, 033902, <https://doi.org/10.1063/1.5007830>.
- Koulialias, D., Canévet, E., Charilaou, M., Weidler, P.G., Löffler, J.F., and Gehring, A.U. (2018b) The relation between local structural distortion and the low-temperature magnetic anomaly in Fe₇S₈. *Journal of Physics: Condensed Matter*, 30, 425803, <https://doi.org/10.1088/1361-648X/aad54>.
- Koulialias, D., Charilaou, M., Mensing, C., Löffler, J.F., and Gehring, A.U. (2018c) Torque analysis of incoherent spin rotation in the presence of ordered defects. *Applied Physics Letters*, 112, 202404, <https://doi.org/10.1063/1.5023886>.
- Koulialias, D., Weidler, P.G., Charilaou, M., Löffler, J.F., and Gehring, A.U. (2019a) Cation diffusion patterns across the magneto-structural transition in Fe₇S₈. *Physical Chemistry Chemical Physics*, 21, 13040–13046, <https://doi.org/10.1039/C9CP01387C>.
- Koulialias, D., Lesniak, B., Schwotzer, M., Weidler, P.G., Löffler, J.F., and Gehring, A.U. (2019b) The Besnus Transition in single domain 4C pyrrhotite. *Geochemistry, Geophysics, Geosystems*, 20, 5216–5224, <https://doi.org/10.1029/2019GC008627>.
- Lee, J.-J., Chu, Y.-H., Yen, Z.-L., Muthu, J., Ting, C.-C., Huang, S.-Y., Hofmann, M., and Hsieh, Y.-P. (2023) Vacancy-plane-mediated exfoliation of submonolayer 2D pyrrhotite. *Nanoscale Advances*, 5, 4074–4079, <https://doi.org/10.1039/D3NA00263B>.
- Liles, D.C. and de Villiers, J.P.R. (2012) Redetermination of the structure of 5C pyrrhotite at low temperature and at room temperature. *American Mineralogist*, 97, 257–261, <https://doi.org/10.2138/am.2012.3887>.
- Morimoto, N., Nakazawa, H., Nishigucmi, K., and Tokonami, M. (1970) Pyrrhotites: Stoichiometric Compounds with Composition Fe_{n-1}S_n (n ≥ 8). *Science*, 168, 964–966, <https://doi.org/10.1126/science.168.3934.964>.
- Néel, L. (1953) Some new results on antiferromagnetism and ferromagnetism. *Reviews of Modern Physics*, 25, 58–63, <https://doi.org/10.103/RevModPhys.25.58>.
- Powell, A.V., Vaqueiro, P., Knight, K.S., Chapon, L.C., and Sánchez, R.D. (2004) Structure and magnetism in synthetic pyrrhotite Fe₇S₈: A powder neutron-diffraction study. *Physical Review B*, 70, 014415, <https://doi.org/10.1103/PhysRevB.70.014415>.
- Rezvani, A., Raji, F., Liu, Q., and Peng, Y. (2024) Identification and quantification of pyrrhotite superstructures in base metal sulfide ore samples: A critical review. *Minerals Engineering*, 218, 108975, <https://doi.org/10.1016/j.mineng.2024.108975>.
- Schrader, D.L., Davidson, J., McCoy, T.J., Zega, T.J., Russell, S.S., Domanik, K.J., and King, A.J. (2021) The Fe/S ratio of pyrrhotite group sulfides in chondrites: An indicator of oxidation and implications for return samples from asteroids Ryugu and Bennu. *Geochimica et Cosmochimica Acta*, 303, 66–91, <https://doi.org/10.1016/j.gca.2021.03.019>.
- Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica Section A*, 64, 112–122, <https://doi.org/10.1107/S0108767307043930>.
- (2015) SHELXT—integrated space-group and crystal-structure determination. *Acta Crystallographica Section A*, 71, 3–8, <https://doi.org/10.1107/S2053272314026370>.
- Steele, S.C., Fu, R.R., Volk, M.W.R., North, T.L., Brenner, A.R., Muxworthy, A.R., Collins, G.S., and Davison, T.M. (2023) Paleomagnetic evidence for a long-lived, potentially reversing martian dynamo at ~3.9 Ga. *Science Advances*, 9, eade9071, <https://doi.org/10.1126/sciadv.ade9071>.
- Vial, D.S., DeWitt, E., Lobato, L.M., and Thorman, C.H. (2007) The geology of the Morro Velho gold deposit in the Archean Rio das Velhas greenstone belt, Quadrilátero Ferrífero, Brazil. *Ore Geology Reviews*, 32, 511–542, <https://doi.org/10.1016/j.oregeorev.2004.12.008>.
- Wang, H. and Salveson, I. (2005) A review on the mineral chemistry of the non-stoichiometric iron sulphide, Fe_{1-x}S (0 ≤ x ≤ 0.125): Polymorphs, phase relations and transitions, electronic and magnetic structures. *Phase Transitions*, 78, 547–567, <https://doi.org/10.1080/01411590500185542>.
- Wang, H., Fu, S., Choi, C., Zhong, Y., and Schaefer, S. (2023) Exploring the potential of natural pyrrhotite mineral for electrochemical energy storage. *Energy Storage Materials*, 54, 421–429, <https://doi.org/10.1016/j.ensm.2022.10.058>.
- Yamamoto, B.Y.A. and Nakazawa, H. (1982) Modulated Structure of the NC-type (N = 5.5) Pyrrhotite, Fe_{1-x}S*. *Acta Crystallographica Section A*, 38, 79–86, <https://doi.org/10.1107/S0567739482000151>.
- Yang, T., Dekkers, M.J., and Chen, J. (2018) Thermal alteration of pyrite to pyrrhotite during earthquakes: New evidence of seismic slip in the rock record. *Journal of Geophysical Research: Solid Earth*, 123, 1116–1131, <https://doi.org/10.1002/2017JB014973>.
- Živković, A., King, H.E., Wolthers, M., and de Leeuw, N.H. (2021) Magnetic structure and exchange interactions in pyrrhotite end member minerals: Hexagonal FeS and monoclinic Fe₇S₈. *Journal of Physics: Condensed Matter*, 33, 465801, <https://doi.org/10.1088/1361-648X/ac1cb2>.

MANUSCRIPT RECEIVED MARCH 28, 2025

MANUSCRIPT ACCEPTED JANUARY 21, 2026

ACCEPTED MANUSCRIPT ONLINE FEBRUARY 4, 2026

MANUSCRIPT HANDLED BY SARAH JO BROWNLEE

Endnotes:

¹Deposit item AM-26-89847. Online Materials are free to all readers. Go online, via the table of contents or article view, and find the tab or link for supplemental materials. The CIF has been peer-reviewed by our Technical Editors.