The Besnus transition in 4C pyrrhotite revisited

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SUMMARY
Ferrimagnetic, monoclinic 4C pyrrhotite (Fe$_7$S$_8$) is the only iron sulphide with high relevance for palaeomagnetism and rock magnetism that can be identified in rock materials by its characteristic low-temperature anomaly. Despite its relevance in natural magnetism and the many magnetic studies over the last decades, the physics and the crystallography behind this anomaly, also denoted Besnus transition, is a matter of debate. In this study, we analyse the static and dynamic magnetization associated with the Besnus transition in conjunction with low-temperature structural data of 4C pyrrhotite reported in the literature. The correlation between the Fe–Fe bonds causing spin-orbit coupling and the dynamic magnetic properties show that the magnetic characteristics of the Besnus transition stem from the interaction of two magnetocrystalline anisotropy systems triggered by thermally induced structural changes on an atomic level in monoclinic 4C pyrrhotite. This refutes the widespread view that the Besnus transition is caused by a crystallographic change from monoclinic to triclinic.

Key words: Defects; Magnetic properties; Rock and mineral magnetism.

INTRODUCTION
In palaeomagnetism and rock magnetism, the intrinsic low-temperature magnetic anomaly in magnetite (Fe$_3$O$_4$), haematite (Fe$_2$O$_3$) and 4C pyrrhotite (ideal formula Fe$_7$S$_8$) is a key physical property to identify these minerals, which can carry magnetic information in terrestrial and extraterrestrial rock materials for millions of years (Smith & Fuller 1967; Rochette et al. 2018). The Besnus transition in Fe$_7$S$_8$ is still a matter of debate. In the latter study, a key evidence was the occurrence of a fourfold rotational symmetry, which was explained by two easy directions in the basal plane close to 45° and 135° due to changes of the twin-partner distribution associated with the formation of a monoclinic 4C pyrrhotite (Wolfers et al. 2011). Torque measurements by Koulialias et al. (2018a) confirmed the appearance of a fourfold symmetry in $B \approx 0.3$ T below the transition and showed that with increasing applied field the sixfold symmetry becomes more prominent. The simultaneous field-dependent occurrence of a fourfold and sixfold rotational symmetry was alternatively explained by the interaction of two magnetocrystalline anisotropy configurations within the monoclinic 4C pyrrhotite structure (Koulialias et al. 2018a). This interpretation is in accordance with powder neutron diffraction (PND) studies, which show that above and below the Besnus transition 4C pyrrhotite can be refined in the monoclinic C2/c space group (Powell et al. 2004; Koulialias et al. 2018b).

With this in mind the question arises if a triclinic 4C pyrrhotite is required to explain the Besnus transition.

The controversy over the Besnus transition in 4C pyrrhotite results mainly from the peculiar structural and magnetic properties (Fig. 1). The monosulphide Fe$_7$S$_8$ derives from a NiAs-type structure with Fe atoms in four different sites (Fe1, Fe2, Fe3 and Fe4), occupying octahedral interstices of hexagonal close-packed sulphur atoms. Every eighth Fe-site is vacant and this in turn results in a monoclinic 4C pyrrhotite superstructure with a fourfold modulated stacking sequence of full and vacancy layers along the c-axis (Bertaut 1953). The sites in the full layers are attributed to Fe1 and Fe3 and those in the vacancy layers to Fe2 and Fe4, where the Fe4-sites are only half-occupied, and their arrangement entails a Kagomé-like sublattice (Fig. 1). The 4C superstructure can be described in the monoclinic space groups F2/d (Tokonami et al. 1972)
antiferromagnetic interlayer coupling (Néel 1953; Wang & Salve-
son 2004). Moreover, 60° twinning perpendicular
to the c-axis is a prominent feature often observed in 4C pyrrhotite
The ferrimagnetism of Fe₇S₈ stems from uncompensated sub-
lattices of ferromagnetically coupled intralayer Fe²⁺ spins and their
antiferromagnetic interlayer coupling (Néel 1953; Wang & Salve-
son 2005; Letard et al. 2007). Moreover, 4C pyrrhotite has a distinct
magneto-crystalline anisotropy with an easy c-plane and a hard c-
axis, which is manifested by an out-of-plane spin rotation at \( T < 200 \text{ K} \) (Weiss 1899; Bin & Pauthenet 1963; Powell 2005; J i n et al. 2007). The anisotropy is caused by the orbital overlap of Fe–Fe bonds with
lengths of less than 3 Å, which generates a pronounced spin-orbit
coupling (SOC) between adjacent sublattices (Goodenough 1963;
Nesbitt et al. 2002). Considering the stacking of the full and va-
cancy sublattices the Fe-sites can be subdivided into two groups,
one (Fe₂, Fe₃, Fe₄) with and the other one (Fe₁) without interlayer
vaccancies as next neighbour (Fig. 1). This arrangement generates
two inherently hexagonal site arrangements in the c-plane displaced
by an angle of 30° (Koulialias et al. 2018a). Based on theoretical
considerations Adachi (1963) postulated that the Fe-sites of the two
groups differ in their local anisotropy. Using Adachi’s phenomeno-
logical statement in conjunction with an experimental and numerical
approach, Koulialias et al. (2018c) in fact found two different out-
of-plane spin rotations with the polar angles \( \theta_{\parallel} \) and \( \theta_{\perp} \) that could be
attributed to the two groups. Given this, 4C pyrrhotite can be seen
as a magnetic system with two anisotropy components.
Numerous magnetic studies in the last decades fostered different
interpretations of the Besnus transition, but their critical evaluation
with structural data is generally fragmentary. Here we present a
structural analysis we took the powder X-ray diffraction data at 300 K
and the powder neutron diffraction (PND) data set published by
Koulialias et al. (2018b), which were obtained from a sister sample of
the crystal used in this study.
All static and dynamic magnetic measurements of this multido-
main 4C pyrrhotite between 5 and 300 K were performed in the
easy c-plane on a MPMS3 SQUID magnetometer using the vibrat-
sample magnetometer (VSM) or the alternating current (AC)
option. The static magnetization was analysed by field-cooling ex-
periments in fields between 0.1 and 3 T from 300 K down to 5 K
and by hysteresis measurements at selected temperatures. The latter
measurements were performed after demagnetization of the sam-
ple at 300 K and cooling it in a zero-field. Furthermore, dynamic
magnetic properties associated with the Besnus transition were ex-
amined by frequency-dependent AC susceptibility measurements
with an amplitude of 1 mT and a parallel 0.1 T direct current (DC)
field bias, in a range of 5–200 Hz at 0.05 K temperature steps.

RESULTS AND DISCUSSION
Structural properties
The Morro Velho 4C pyrrhotite is a pure-phase crystal with unit
lattice parameters \( a = 11.9140 \pm 0.0004 \) Å, \( b = 6.8711 \pm 0.0003 \) Å,
\( c = 12.9082 \pm 0.0005 \) Å and \( \beta = 118.0517 \pm 0.0013 \)°
at 300 K (Koulialias et al. 2018b). For the primitive hexago-
nal NiAs-like substructure (P63/mmc) unit cell parameters of
\( a = b = 3.4371 \pm 0.0003 \) Å and \( c = 5.6977 \pm 0.0007 \) Å were
calculated and they are similar to those reported by Fillion et al.
(1992). In contrast to the numerous X-ray diffraction studies at
300 K, there is only little crystallographic information on Fe-S₈ at
low temperature, which was generally obtained from neutron
diffraction studies (Fillion et al. 1992; Powell et al. 2004; Wolfers
et al. 2011; Koulialias et al. 2018b). In two of these studies, PND
patterns above and below the Besnus transition were refined in
the monoclinic C2/c space group (Powell et al. 2004; Koulialias
et al. 2018b). Haines et al. (2020) used the unit cell parameters
from these PND studies and determined symmetry-breaking shear
strains given by \( \varepsilon = \frac{(a-b)(ab)^{1/2}}{} \) \( \cos \beta \), where \( \beta \) is the reciprocal
lattice angle \( \beta \) of the 4C pyrrhotite in the monoclinic F2/d space
group. They inferred that one of the monoclinic angles changes
from 90° to \( \leq \sim 90°. \) Such a departure is, however, too little to

MATERIAL AND METHODS
A 4C pyrrhotite crystal from the Morro Velho gold mine in Brazil
(Vial et al. 2007) was used. The structural and magnetic properties
of samples from this locality have been extensively studied over
more than a century (e.g. Weiss 1905; Buerger 1947; Volk et al.
2016; Koulialias et al. 2018b, 2019; Haines et al. 2020). For struct-
ural analysis we took the powder X-ray diffraction data at 300 K
and the powder neutron diffraction (PND) data set published by
Koulialias et al. (2018b), which were obtained from a sister sample
of the crystal used in this study.

Figure 1. Left: stacking sequence of 4C pyrrhotite (sulphur atoms omitted for clarity) with full (F) and vacancy (V) layers. Middle: view perpendicular to a F-layer with alternating Fe1 and Fe3 sites in rows parallel to the a- and b-axes. Right: view on the V-layer forming a Kagomé-like sublattice with alternating rows of Fe2 and Fe4 sites parallel to the a- and b-axes, where one half of the Fe4-sites is vacant.

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unambiguously support symmetry lowering at the Besnus transition, also considering that Tokonami et al. (1972) found an angle $\beta$ of 90.43° for 4C pyrrhotite at 300 K. Nevertheless, we use here the PND data by Koulialias et al. (2018b) for a detailed inspection in a wide $d$-spacing range in order to evaluate the possibility of a crystallographic change at low temperature (Fig. 2). The $d$-spacing range is critically affected by extinction rules that in turn depend on the mineral’s space group. For monoclinic 4C pyrrhotite, the (111) crystallographic peak has the highest spacing with $d = 5.71 \AA$ and it is superimposed by the strongest magnetic peak (Powell et al. 2004; Koulialias et al. 2018b). An additional weak peak at $d \approx 6.7 \AA$ in the PND pattern may be attributed to (010) in a triclinic $P\overline{1}$ structure or to a magnetic peak (Fig. 2). Because this single peak is detectable over the whole temperature range a triclinic 4C pyrrhotite can be excluded. Given this and considering the minor release of shear strain at the Besnus transition, as reported by Haines et al. (2020), the structural changes in monoclinic 4C pyrrhotite at low temperature must be on the atomic level.

The unit cell parameters $a$ and $c$ of the hexagonal superstructure (Fillion et al. 1992) and $a$, $b$, and $c$ of the monoclinic superstructure (Koulialias et al. 2018b) continuously decrease upon cooling to about 50 K and exhibit little changes at lower temperature. It is worth noting that the thermal contraction is anisotropic with a slight expansion in $b$ direction at $T < 50$ K. Simultaneously, the angles of the six Fe–S–Fe super-exchange paths in 4C pyrrhotite become more regular upon cooling and tend towards $135^\circ$ (Koulialias et al. 2018b). Such a value is characteristic of an undistorted NiAs-type structure with antiferromagnetic interactions (Goodenough 1963). With this in mind the change towards an angle of 135° within the 4C pyrrhotite lattice suggests a decrease in distortion and subsequently a release of shear strain associated with the Besnus transition. It is worth noting that for a Morro Velho 4C pyrrhotite sample such release coincides with a peak in the heat capacity (Volk et al. 2018; Haines et al. 2020).

Thermal contraction also affects the Fe–Fe bond lengths, which again determine the SOC, that is the magnetocrystalline anisotropy. At low temperature four Fe–Fe bonds with lengths of less than 3 Å contribute to the SOC of 4C pyrrhotite (Fig. 3). Three of them are interlayer bonds and one is an intra-layer bond. Moreover, the Fe3-sites are those with no vacancy as next neighbour, and therefore they have lesser freedom to be yielded by stress/strain in the crystallographic lattice (Fig. 1). The structural changes that affect the anisotropic properties in the 4C pyrrhotite are best manifested in the Fe3–Fe2 and Fe3–Fe4 bond lengths, which converge in conjunction with the Besnus transition (Fig. 3).

**Magnetic properties**

At 300 K a field of $B = 2$ T in the $c$-plane results in a magnetization $M_{2T} = 21.2 \text{ Am}^{-2} \text{ kg}^{-1}$ (Fig. 4), which is near the theoretical value for 4C pyrrhotite estimated by Néel (1953). Saturation, however, is not reached due to slight spin tilting, which is caused by the high anisotropy field of about 13 T at 300 K (Koulialias et al. 2018c). Upon cooling the $M_{2T}$ curve reveals a concave shape between 300 K and 50 K followed by a discontinuity indicating the low-temperature transition. The field-cooled magnetization is implicitly related to the total free energy of the system ($E_{\text{tot}}$), given as the superposition of the Zeeman ($E_Z$) and the magnetocrystalline anisotropy ($E_{\text{an}}$) energy contributions: $E_{\text{tot}} = E_Z + E_{\text{an}}$. The temperature-dependent quantities that enter this equation are the magnetocrystalline anisotropy constants within $E_{\text{an}}$ and the absolute value of the net magnetization vector within $E_Z$. Considering the work of Bin & Pauthenet (1963), the absolute value of the magnetization exhibits a steady increase of about 3 per cent between 300 and 150 K and becomes nearly constant at lower temperature, whereas at $T < 200$ K the change in sign of one of the three magnetocrystalline anisotropy constants ($K_1$) leads to a gradual out-of-plane spin rotation, which was experimentally confirmed by PND studies (Powell et al. 2004; Koulialias et al. 2018b). The onset of the gradual spin rotation coincides with the drop of the intra-layer Fe3–Fe2 bond lengths below the critical value of 3 Å and this in turn indicates an additional contribution to the overall SOC in 4C pyrrhotite (Koulialias et al. 2018b). Taking the above, the thermal behaviour of $M_{2T}$ mirrors the interplay between $E_Z$ and $E_{\text{an}}$, and the maximum in the field-cooled magnetization curve at $T \approx 170$ K marks the onset of a prevailing contribution of $E_{\text{an}}$ (Fig. 4). This effect is also seen at lower fields in the $M_{0.1T}$ curve. Both the $M_{2T}$ and $M_{0.1T}$ curves can be described with a second-order polynomial fit down to $T \approx 50$ K, and this in turn suggests that the concave shapes are critically affected by the out-of-plane spin rotation (Fig. 4). The shallowing with a local minimum at $T = 44$ K marks the change in the spin rotation regime with respect to the (001) plane of the 4C pyrrhotite. This temperature accords with the onset of a pronounced SOC change, as indicated by the Fe3–Fe2 and Fe3–Fe4 bonds (Fig. 3). Theoretically, the spin rotation has two degrees of freedom, parallel to the (001) plane and in/out of the easy plane. It can be assumed that in a 2 T field the spins are aligned in the $c$-plane and the effects of domains and twins are negligible. Based on this the spins of the two groups of Fe-sites only differ in the polar angles $\theta_1$ and $\theta_2$ and the increase in $M_{2T}$ associated with the Besnus transition is caused by the reversed in-plane rotation of the angle $\theta_2$ (Koulialias et al. 2018c). The peak in the $M_{2T}$ curve then indicates the minimum in $\theta_1$ and the return to coherent out-of-plane spin rotations in the two groups at lower temperature. The relative increase in the magnetization curves in the temperature range between 44 K and 31 K is field-dependent with 1.4 per cent in $M_{2T}$ and 17.9 per cent in $M_{0.1T}$, respectively. Because of the hard uniaxial anisotropy, the more pronounced jump in the $B = 0.1$ T field points to prevailing azimuthal spin rotation in the easy plane due to a change in the SOC. Considering the fourfold symmetry in the in-plane torque experiments in relatively low fields (Wolffers et al. 2011; Koulialias et al. 2018a), the jump in $M_{0.1T}$ can mainly be attributed to an interaction onset of the two anisotropy systems in 4C pyrrhotite. With this in mind the field-dependent magnetization jump associated with the Besnus transition reveals the formation of a system with interacting anisotropies that are dominated by the uniaxiality of the 4C pyrrhotite.

Fig. 5 shows the in-phase $\chi'$ and the out-of-phase $\chi''$ susceptibility in a 0.1 T DC bias field. The in-phase, which mirrors the slope of the field-cooled magnetization curve, shows at $T = 31.5$ K a peak with a weak frequency dependence on the low-temperature side (Fig. 5a). The out-of-phase susceptibility is indicative of dissipative processes and reveals changes in a range of about 10 K flanking the Besnus transition, with two local maxima at 34 K and 30 K and a local minimum at $T \approx 31.5$ K (Fig. 5b). The latter two exhibit a frequency dependence. At low frequency, the minimum is associated with a shoulder and with increasing frequency the two features merge to a relatively flat one (Fig. 5b). This conversion in $\chi''$ at $T \approx 31.5$ K coincides with the maximum in $\chi'$, a peak in the heat capacity of a Morro Velho pyrrhotite (Volk et al. 2018), and with a distortion decrease in the NiAs-like substructure (Koulialias et al. 2018b). With this in mind the frequency dependence of $\chi''$ at $T \approx 31.5$ K is most likely a dissipative effect due to the change from incoherent to coherent spin rotation and the interaction onset of the...
two anisotropy systems at the Besnus transition. Moreover, the peak at $T = 30$ K, which can be regarded as the lower limit of the scope of the transition manifested in $B = 0.1$ T (Fig. 4, inset), exhibits a shift to higher temperature with increasing frequency $f$. Taking the Arrhenius-Néel equation $f(T) = f_0 \exp(-\Delta E/k_B T)$ into account, where $f$ is the excitation frequency, $f_0$ is the attempt frequency, $\Delta E$ is the energy barrier, $k_B$ is the Boltzmann constant and $T$ is the temperature, an activation energy $\Delta E = 1.7$ eV ($2.72 \times 10^{-19}$ Joule) is obtained from the $f$ versus $1/T$ plot (Fig. 5c). Considering the energy levels of the Fe orbitals in pyrrhotite (Sakkopoulos et al. 1984; Nesbitt et al. 2002), such $\Delta E$ can be assigned to changes in the spin structure and the electron correlation, respectively, presumably due to a coupling of itinerant spins to localized spins. Evidence for such a change in 4C pyrrhotite is a decrease in resistivity (Besnus & Meyer 1964), an electronic contribution to the specific heat (Kobayashi et al. 1999), and higher-order terms in the anisotropic magnetic resistivity (Charilaou et al. 2015).

Above the Besnus transition the hysteresis loops recorded in the basal plane show the typical properties of a multidomain 4C pyrrhotite (e.g. Dekkers et al. 1989; Volk et al. 2016). The hysteresis parameters at 300 K are coercivity $B_c = 1.9$ mT, magnetization at 3 T field $M_{3T} = 21.4$ Am$^2$ kg$^{-1}$, remanence magnetization $M_r = 1.0$ Am$^2$ kg$^{-1}$, and a squareness ratio $M_r/M_{3T} = 0.05$. At $T = 50$ K, the parameters are nearly the same, but the hysteresis curve exhibits
Figure 4. Field-cooling magnetization curves, where the dashed black line marks the lower limit of the polynomial fitting (red). The dash-dotted red line marks the inflection point in the $B = 0.1$ T differential curve (inset) and the local maximum in the $B = 2$ T curve.

Figure 5. Highly resolved AC susceptibility with an amplitude of 1 mT and a parallel DC bias field of 0.1 T in a frequency range between 5 and 200 Hz: (a) the in-phase signal $\chi'$ shows a weak frequency dependence at around 30 K and (b) the out-of-phase signal $\chi''$ reveals a frequency dependence at $T \approx 31.5$ and 30 K, respectively. (c) Arrhenius–Néel plot of the frequency dependence of $\chi''$ at 30 K (peak of $\chi''$ in panel b).

Below the Besnus transition the second inflection vanishes again (Fig. 6b). Associated with this transition, the appearance of a fourfold rotational symmetry has been reported (Volk et al. 2018; Koulialias et al. 2018a). Taking the structural properties of the monoclinic 4C pyrrhotite into account, this fourfold symmetry points to an interaction of the two hexagonal anisotropy systems displaced by $30^\circ$. The simultaneous increase of the hysteresis parameters in the multidomain 4C pyrrhotite, with $B_c = 135.3$ mT and $M_r/M_T = 0.8$ at 10 K (Fig. 6b), is then most likely caused by a gain in domain-wall (DW) energy triggered by the interacting anisotropy systems, that is the remagnetization becomes harder. Moreover, the magnetization of the initial curve at 10 K is somewhat lagged with a nearly zero increase up to 50 mT (Fig. 6b, inset). This 50 mT field can be taken as a measure for the energy barrier to be overcome in order to initiate DW movement. With this in mind the characteristic

the characteristic second inflection (Fig. 6a) that was first described by Koulialias et al. (2016). Volk et al. (2016) demonstrated that this effect has an angular dependence and is most pronounced if the external field has a $30^\circ$ angle to the a-axis of the 4C pyrrhotite. These authors interpreted the second inflection as a field-induced easy axis flipping. Based on crystallographic considerations, Koulialias et al. (2018a), however, explained this hysteresis effect as a response of two superimposed, hexagonal anisotropy systems caused by the vacancy order in the stacking sequence of full and Kagomé-like sublattices (Figs 1b and c). The easy c-plane exhibits a sixfold rotational symmetry as it is expected for the hexagonal NiAs-type substructure (Koulialias et al. 2016; Volk et al. 2016). Given this, the two anisotropy systems inferred by Koulialias et al. (2018a) must also have a sixfold rotation symmetry with no interactions.
increase in the hysteresis parameters below the Besnus transition (e.g. Dekkers et al. 1989; Charilaou et al. 2015; Volk et al. 2016.) can be explained by the growth of the DW thickness due to the interacting magnetocrystalline anisotropy systems. Such change of the DW properties in multidomain 4C pyrrhotite accords well with the loss of the amplitude dependence in AC susceptibility below the Besnus transition (Kind et al. 2013).

**SUMMARY AND CONCLUSIONS**

The powder neutron diffraction data by Koulialias et al. (2018b) provide no evidence for a monoclinic to triclinic symmetry change associated with the Besnus transition. The change of the monoclinic angle $\beta$ from 90° to $\sim$90.06°, as calculated by Haines et al. (2020) from these diffraction data, may indicate a lowering of the crystallographic symmetry below the Besnus transition. The analysis of the structural properties in the temperature range between 298 and 10 K, however, reveals a different picture. Thermal contraction associated with the Besnus transition leads to a more regular NiAs-like substructure and this in turn suggests that the distortion in the 4C superstructure decreases.

In fact, the very minor departure of the monoclinic angle $\beta$ reported by Haines et al. (2020) can be explained by structural changes on an atomic level within the C2/c space group. Such change governs the variation of the Fe–Fe bonds with lengths of less than 3 Å, which critically affect the spin-orbit coupling in NiAs-like structures and therefore the magnetocrystalline anisotropy in 4C pyrrhotite. The highly ordered vacancies in the 4C superstructure generate two anisotropy systems, where the onset of their interactions marks the Besnus transition and can explain the changes in the magnetic properties at low temperature. In conclusion, the magnetic anomaly of the Besnus transition stems from the magnetocrystalline anisotropy of a crystal structure with ordered vacancies in a Kagomé-like Fe sublattice, which is a characteristic trait of monoclinic 4C pyrrhotite.

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**DATA AVAILABILITY**

The data underlying this paper will be shared on reasonable request to the corresponding author.

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