

Changes in Physical Properties of 4C Pyrrhotite (Fe₇S₈) across the 32 K Besnus Transition

Revision 1

Michael W. R. Volk^{a*}, Eric McCalla^{b,c}, Bryan Voigt^b, Michael Manno^b
Chris Leighton^b, Joshua M. Feinberg^a

^aInstitute for Rock Magnetism, Department of Earth Sciences, University of Minnesota,
116 Church Street SE, Minneapolis, MN 55455

^bDepartment of Chemical Engineering and Materials Science, University of Minnesota,
421 Washington Ave. SE, Minneapolis, MN 55455

^cChemistry Department, McGill University, 801 Sherbrooke St. W, Montréal, Québec, Canada, H3A 0B8

Abstract

Pyrrhotite Fe₇S₈ is a common sulfide mineral in the Earth's crust and mantle, as well as in a range of meteorites, and is of interest to a wide variety of disciplines, including economic geology, geophysics, and material science. The 4C variety of pyrrhotite shows a dramatic change in magnetic properties at $T \approx 30$ K, known as the Besnus transition. Although this transition is frequently used to detect pyrrhotite in geologic samples, the underlying mechanism driving the transition has not yet been identified. This study presents a high-resolution view of the changes in heat capacity, magnetic, and electronic properties of a natural single crystal of nearly pure, monoclinic 4C pyrrhotite across the Besnus transition. Contrary to previous studies, *all* of these properties show clear evidence of the Besnus transition, specific heat in particular revealing a clear transition at 32 K, apparently of second order nature. Small-angle neutron scattering data are also presented, demonstrating an unusual change in short-range magnetic scattering at the transition.

*Corresponding author: Michael Volk, Institute for Rock Magnetism, Department of Earth Sciences, University of Minnesota, 116 Church Street SE, Minneapolis, MN 55455x

Email address: mvolk@umn.edu (Michael W. R. Volk)

Preprint submitted to American Mineralogist February 15, 2018

25 Furthermore, a magnetic field dependence of the transition temperature can be seen in both induced
26 magnetization and electrical resistivity. These new observations help narrow the possible nature
27 of the phase transition, clearly showing that interactions between intergrown coexisting 4C and
28 5C* superstructures, as suggested in some literature, are not necessary for the Besnus transition.
29 In fact, the changes seen here in both the specific heat and the electronic transport properties are
30 considerably larger than those seen in samples with intergrown superstructures. To further
31 constrain the mechanism underlying the Besnus transition, we identify five separate potential
32 models and evaluate them within the context of existing observations, thereby proposing
33 experimental approaches that may help resolve ongoing ambiguities.

34 Keywords: Besnus transition, Phase transition, magnetism, heat capacity, resistivity, Sulfide,
35 Pyrrhotite,

36 1 INTRODUCTION

37 Iron mono-sulfides, or pyrrhotites, (Fe_{1-x}S , $0 < x < 0.125$), are commonly occurring iron sulfide
38 minerals that are important to a wide range of scientific disciplines. In the Earth and planetary
39 sciences, 4C pyrrhotite (Fe_7S_8) acts as a recognizable ferrimagnetic phase, and is found in many
40 magmatic and metamorphic rocks (*Dunlop and Özdemir, 1997*), in claystones (*Aubourg and Pozzi,*
41 *2010*), and in limestones (*Muttoni, 1995*). In terrestrial rocks, the remanent magnetization carried
42 by this phase has been used to study polarity reversals of the Earth's magnetic field (e.g.,
43 *Quidelleur et al., 1992*), to examine the nature of magnetization in quartzite clasts from the
44 Precambrian Jack Hills of Western Australia (*Weiss et al., 2015*), and as the basis for a crustal geo-
45 thermometer (*Aubourg and Pozzi, 2010*) or barometer (*Gilder et al., 2011*). Furthermore, 4C
46 pyrrhotite is a major magnetic constituent of several classes of meteorites, most notably in Martian
47 meteorites (*Rochette et al., 2001*). Since pyrrhotite is thermodynamically stable on the surface of

48 Mars, it may also contribute to the Martian magnetic anomalies (*Fegley Jr. et al., 1995*). Moreover,
49 4C pyrrhotite can be found in chondritic meteorites, the most primitive and oldest class of
50 meteorites (*Herndon et al., 1975, Zhang et al., 2008*), and, as such, may possibly record the
51 magnetic fields in the early solar system, as well as transient fields associated with impact events
52 (*Muxworthy et al., 2017*). In general, pyrrhotites are also the most common iron sulfide minerals
53 in certain intrusions, such as the 1.1 Ga Duluth Complex, which hosts economically important
54 quantities of Cu, Ni and Pt group elements. Understanding the oxidation kinetics of pyrrhotite
55 minerals in mine tailings is of critical importance for avoiding water quality degradation due to
56 acid mine drainage (*Lapakko, 2015*). Further, pyrrhotite commonly occurs as inclusions in
57 diamonds, and may provide information about sulfur cycling within the lower mantle (*Sharp,*
58 *1966, Gilder et al. 2011*). Within the material science community, pyrrhotites have been studied
59 as potential candidate materials for anodes in lithium-ion batteries (*Zhang et al., 2015*), and can
60 be used to sequester arsenic contamination in the environment (*Cantu et al., 2016*).

61 Given its importance to geoscience and material science, proper characterization of pyrrhotite
62 within natural and synthetic samples is critical, yet frustratingly difficult. As discussed in more
63 detail below, iron monosulfides can display a wide range of crystallographic symmetries and
64 superstructures based on their composition and growth history, and frequently occur as finely
65 intergrown polycrystalline assemblages. Thus, reflected light and electron microscopy methods
66 are often combined with electron and neutron diffraction to properly determine the structure of
67 small iron monosulfide grains. However, magnetic methods are one of the few techniques that
68 allow researchers to characterize the presence of pyrrhotite in bulk samples. In particular,
69 observations of the low-temperature magnetic transition at approximately 30 K (the “Besnus”
70 transition) of 4C pyrrhotite have been used with increasing frequency as a diagnostic indicator for

71 the presence of pyrrhotite (*Dunlop and Özdemir, 1997*). Low temperature superconducting
72 quantum interference device (SQUID) magnetometers are typically sensitive enough to detect 4C
73 pyrrhotite in natural samples at parts per million concentrations (*Rochette et al. 1990*).

74 Despite the utility of low temperature magnetic methods in detecting the presence of pyrrhotite
75 in natural and synthetic samples, there is remarkably little consensus on the mechanism that
76 underlies this dramatic change in magnetic properties. The aim of this study is to provide a high-
77 resolution view of the physical (heat capacity and resistivity) and magnetic properties (remanence
78 and high- and low-field induced magnetization) across the Besnus transition in a phase-pure
79 specimen of 4C pyrrhotite. Small angle neutron scattering is also presented to help determine the
80 length scales over which the changes in magnetic properties take place. This new data provides
81 the necessary evidence to differentiate between competing models that seek to explain this
82 phenomenon, and will enable researchers to more accurately interpret its magnetic recording on
83 Earth and other planetary bodies.

84 1.1 SUPERSTRUCTURES

85 Pyrrhotite occurs in many polytypes that are often intergrown or show incommensurate
86 chemical composition. Similar to troilite (FeS), these polytypes crystallize in a NiAs-like structure
87 with alternating filled and vacant Fe layers oriented parallel to the *ab* plane containing variably
88 ordered vacancies (*Morimoto et al., 1970*). Within each Fe-layer the spins are coupled
89 ferromagnetically. However, adjacent layers are coupled antiferromagnetically via superexchange
90 through the S atoms, which in turn forms distorted S octahedra around the Fe atoms (*Levinson and*
91 *Treves, 1968*). Ordering of the vacancies gives rise to superstructures, which are referred to using
92 an *NC* notation, where *N* gives the number of stacked NiAs cells along the crystallographic *c*-axis.
93 Four commensurate hexagonal varieties, FeS (2C), Fe₉S₁₀ (5C), Fe₁₀S₁₁ (11C) and Fe₁₁S₁₂ (6C),

Preprint submitted to American Mineralogist February 15, 2018

94 and one monoclinic $\text{Fe}_7\text{S}_8(4\text{C})$ are stable at ambient conditions (*Nakazawa and Morimoto, 1970;*
95 *Morimoto et al., 1970*). The ordering of the vacancies in hexagonal polytypes creates a zero net
96 magnetization, and thus hexagonal pyrrhotites are non-ferro/ferri-magnetic in the bulk, and
97 incapable of retaining a spontaneous magnetization.

98 On the other hand, ordering of vacancies in the most Fe deficient variety of pyrrhotite, Fe_7S_8
99 (4C), creates a small lattice distortion ($\beta \neq 90$), which lowers the mineral's symmetry to monoclinic
100 (*Powell et al. 2004*), and is often referred to as 'pseudo-hexagonal'. Furthermore, the ordered
101 vacancies in 4C pyrrhotite produce a small net magnetization, which gives rise to ferrimagnetism
102 up to its Néel temperature of 598 K (*Powell et al., 2004*). Within the 4C cell, the layers can be
103 labeled as *FAFBFCFD*, where F denotes a filled Fe layer and A-D are four distinct vacancy layers.
104 Each layer with vacancies contains four unique Fe sites (*Bertaut, 1953; Tokonami et al., 1972*). Of
105 these Fe sites, two have no vacancies above or below, while the Fe atoms in the filled (F) layers
106 are adjacent to either one or two vacancies (*Ericsson et al., 1994*). Superexchange coupling
107 through the S atoms is stronger than the direct Fe-Fe coupling (*Levinson and Treves, 1968*).
108 Consequently, sites that do not have vacancies above or below should be largely unaffected by
109 changes in vacancy ordering (*Levinson and Treves, 1968*).

110 **1.2 PHASE TRANSITION**

111 At $T_{\text{Bes}} \approx 30$ K, 4C pyrrhotite undergoes a magnetic phase transition first described by *Besnus*
112 *and Meyer* (1964). The Besnus transition is commonly used to identify pyrrhotite in rocks
113 (*Rochette et al., 2011*). Similar to the Morin transition in hematite (Fe_2O_3) or the Verwey transition
114 in magnetite (Fe_3O_4), the transition is marked by a loss of remanent magnetization on cooling, and
115 a drastic change in fundamental magnetic properties (*Fillion and Rochette, 1988; Dekkers et al.,*
116 *1989; Rochette et al., 1990, Dunlop and Özdemir, 1997*). Furthermore, the anisotropy constants

Preprint submitted to American Mineralogist February 15, 2018

117 and the direction of the magnetic easy axis change during cooling (*Mikami et al.*, 1959; *Bin and*
118 *Pauthenet*, 1963; *Sato et al.*, 1964; *Rochette et al.*, 1990). At room temperature (T_R) the easy axis
119 lies within the basal (a - b) plane of the crystal but this progressively rotates out of the basal plane
120 towards the c axis upon cooling below 205 K (*Bin and Pauthenet*, 1963, *Powell et al.* 2004). While
121 a self-reversal of the magnetization has been observed in very large pyrrhotite crystals (*Fillion and*
122 *Rochette*, 1988), the direction of the remanence vector at room temperature, remains constant upon
123 cycling through T_{Bes} (*Feinberg et al.*, 2015).

124 While the Besnus transition has been known to our community for more than 50 years, the
125 mechanism driving the transition is not well understood. Two prevailing explanations exist.
126 *Wolfers et al.* (2011) measured neutron diffraction and magnetic torque on twinned single crystals.
127 The magnetic torque shows a six-fold symmetry above T_{Bes} , which changes to a four-fold
128 symmetry below the transition. Based on the change in symmetry, *Wolfers et al.* (2011) propose a
129 crystallographic transition from the monoclinic $F2/d$ ($T > T_{Bes}$) to a triclinic $F-1$ ($T < T_{Bes}$) structure.
130 This mechanism is similar to the change from cubic to monoclinic symmetry that occurs within
131 magnetite upon cooling through the Verwey transition at $T \approx 110$ K. The second explanation was
132 proposed by *Charilaou et al.* (2015) and later expanded upon by *Koulialias et al.* (2016, 2018).
133 Here, the change in magnetic properties is explained by changing magnetic interactions between
134 two different coexisting superstructures (4C and 5C*). The proposed 5C* phase in *Charilaou et*
135 *al.* (2015) possesses a different vacancy ordering, but the same overall chemical composition as
136 the 4C structure. Their arguments against a crystallographic phase transition as the basis of the
137 Besnus transition are based in large part on the absence of a transition in the heat capacity $C_p(T)$,
138 and the presence of a second inflection in hysteresis loops at low temperatures ($T < 200$ K). Clearly,
139 this explanation relies on the existence of two distinct coexisting phases of $Fe_{1-x}S$.

Preprint submitted to American Mineralogist February 15, 2018

140 In a previous study, we measured major hysteresis loops in 72 directions within the basal plane
141 of an oriented single crystal of phase-pure 4C pyrrhotite (*Volk et al.*, 2016). The chemical
142 composition and crystallographic orientation of the crystal were determined by Energy-dispersive
143 X-ray spectroscopy (EDX) and Electron backscatter diffraction (EBSD). The experiments were
144 conducted at 21 temperatures spanning the Besnus transition (20-50 K). Several magnetic
145 properties showed a six-fold symmetry above T_{Bes} , including the second hysteresis inflection
146 described by Koulialias *et al.* (2016). However, we found that these magnetic symmetries change
147 from six-fold ($T > T_{\text{Bes}}$) to four-fold ($T < T_{\text{Bes}}$), consistent with the behavior originally observed
148 by *Wolfers et al.*, (2011). Furthermore, the second hysteresis inflection disappeared below T_{Bes} . To
149 better differentiate between the competing models, we present here a detailed study of the
150 structural, magnetic and electronic properties of a second Fe_7S_8 single crystal subsampled from
151 the same piece used in *Volk et al.* (2016) from Morro Velho, Brazil, provided by the Munich
152 Mineralogical State Collection (Mineralogische Staatssammlung München).

153 2 RESULTS AND DISCUSSION

154 The chemical composition of the sample was determined by electron microprobe analysis with
155 a JEOL JXA-8900R operated with a beam energy of 20 keV, a current of 20 nA and diameter of
156 5 micron. Detection limits ranged from 0.020 weight percent for Fe $K\alpha$ to 0.022 weight percent
157 for S $K\alpha$ and analytical sensitivity (at the 99% confidence level) ranged from 0.157 percent relative
158 for Fe $K\alpha$ to 0.406 percent relative for S $K\alpha$. Elements were acquired using analyzing crystals
159 LiFH for Fe- α , and PETJ for S- α . The standards were Fe for Fe $K\alpha$, and Pyrite, FeS_2 for S $K\alpha$.
160 The specimen's bulk chemical composition, determined from 12 measurements, is $\text{Fe}_{6.78\pm 0.12}\text{S}_8$
161 ($\text{Fe}_{0.85}\text{S}$, Fe = 45.9 at. %). According to the phase diagram of *Nakazawa and Morimoto* (1971), the
162 sample's measured composition is within in the stability field of 4C pyrrhotite. Significantly, no

Preprint submitted to American Mineralogist February 15, 2018

163 impurities, such as Ni, were detected in any of the 12 measurements (within the limits stated
164 above).

165 In naturally occurring rocks, pyrrhotites are often an intergrown mixture of both the hexagonal
166 and monoclinic phases (*Arnold, 1967*). In our case, it is particularly important to detect the
167 presence of any such hexagonal intergrowths, since one of the proposed mechanisms for the
168 Besnus transition requires the presence of both 4C and 5C* superstructures (*Charilaou et al., 2015*;
169 *Koulialias et al., 2016*). Non-magnetic hexagonal phases transform into a ferrimagnetic
170 phase between 200°C-265°C depending on their iron content (*Schwarz and Vaughan, 1972*). This
171 transformation, due to a rearrangement of vacancies, is identified as a sudden rise in magnetic
172 susceptibility, known as the λ -transition (*Schwarz and Vaughan, 1972*). We measured magnetic
173 susceptibility as a function of temperature using a Geophysica Kappabridge KLY-2 (300 Am⁻¹
174 field at 920 Hz), which is able to detect even small hexagonal impurities. The specimen shows a
175 single Néel temperature (318°C, 591 K) close to the literature value (320°C (*Dunlop and Özdemir,*
176 *1997*)) with no sign of a lambda transition, as shown in Figure S1. This conclusion of the absence
177 of any significant amount of 5C* phase is supported by structure determinations, also, as discussed
178 below.

179 **2.1 POWDER X-RAY DIFFRACTION**

180 To detect possible inclusions (*e.g.*, pyrite FeS₂) in our pyrrhotite sample, or pyrrhotite
181 polytypes (*e.g.*, the 5C* phase discussed above), room temperature powder X-ray diffraction
182 (PXRD) data were acquired with a PANalytical X'Pert PRO X-ray diffractometer equipped with
183 a Co source (0.17909 nm) and an X'Celerator detector. The diffraction patterns were collected
184 from 10°-90° scattering angle in 0.0167° steps with an effective dwell time of 100 s per step.

185 Figure 1 shows the PXRD pattern along with the result of Rietveld refinement with a single
186 phase with a 4C stacking sequence. The software Rietica was used to fit the data using the
187 structural model by *Powell et al. (2004)*. The fitted cell parameters of the monoclinic space group
188 $C2/c$ are $a = 1.1915(1)$ nm, $b = 0.68698(6)$ nm, $c = 1.2907(1)$ nm and $\beta = 118.005(1)^\circ$, with quality
189 parameters of $R_{bragg} = 2.87$ %, $R_P = 2.24$ % and $R_{WP} = 3.51$ %. The lattice parameters agree well
190 with the values for the 4C phase obtained by *Charilaou et al. (2015)*. Furthermore, the composition
191 obtained by PXRD refinement is $Fe_{6.76}S_8$ ($Fe_{0.83}S$), in excellent agreement with the measured
192 chemical composition from electron microprobe analysis. The PXRD results thus indicate that the
193 crystal is pure monoclinic 4C pyrrhotite without any detectable contamination from other minerals
194 (e.g., oxides) or vacancy superstructures. It is important to note that the hexagonal (5C*) phase,
195 which is clearly present in the PXRD data presented by *Charilaou et al. (2015)* (see Fig. 1 inset),
196 is not present here, within the limits of detection.

197 2.2 SMALL ANGLE NEUTRON SCATTERING

198 Small-angle neutron scattering (SANS) from a 4C pyrrhotite single crystal was used to
199 investigate potential structural and/or magnetic changes across the Besnus transition. This
200 powerful method (*Muhlbauer et al., 2018*), which has not yet been applied to pyrrhotite, provides
201 length-scale-dependent information on structural and magnetic inhomogeneities across a wide
202 range. In essence, the neutron scattering cross-section, $d\Sigma/d\Omega$, is measured as a function of the
203 scattering wavevector, Q , revealing information on a length scale $2\pi/Q$. Importantly, in the
204 unpolarized case used here, the inhomogeneities that generate the scattering can be structural (e.g.,
205 long-range defects, twins, twin boundaries) or magnetic (e.g., domains and domain walls, short-
206 range magnetic fluctuations, etc.). The SANS measurements presented were taken on the NG7 30
207 m SANS beamline at the NIST Center for Neutron Research, at 6 temperatures between 5 and 60

Preprint submitted to American Mineralogist February 15, 2018

208 K, i.e., around the Besnus transition. At each temperature, 2D area scans, or Q_x - Q_y intensity maps
209 (see Fig. 2a), were collected in two frames (one at $0.004 \text{ \AA}^{-1} < Q < 0.025 \text{ \AA}^{-1}$ and one at 0.02 \AA^{-1}
210 $< Q < 0.15 \text{ \AA}^{-1}$), resulting in a total covered Q range from 0.004 to 0.15 \AA^{-1} . We thus probe real-
211 space length scales ($2\pi/Q$) from 4 to 160 nm. In such scans the neutron beam is perpendicular to
212 the plane of the detector, the dark region in the center of Fig. 2a is a beam-stop covering the
213 unscattered beam, and displacement outwards from the origin corresponds to increasing Q .

214 Fig. 2 shows the SANS results obtained with a sister specimen to the main crystal studied in
215 this work, oriented with the c -axis approximately parallel to the neutron beam. Panel (a) shows an
216 example 2D area scan (i.e., a Q_x - Q_y intensity map), at 5 K, out to Q_x/Q_y values of 0.02 \AA^{-1} , i.e.,
217 probing real space length scales above 30 nm. The six-fold in-plane symmetry is obvious in the
218 2D scan, and, due to the use of unpolarized neutrons, could arise from structural effects (such as
219 long-range (> 30 nm) defects aligned with high-symmetry in-plane directions) or from magnetic
220 domain formation along specific axes (note that the data were recorded here after nominal zero
221 field cooling). Of high interest in terms of the aforementioned potential explanations for the Besnus
222 transition, the observed six-fold pattern *did not* alter significantly across the 32 K transition
223 temperature. The angular scan in Fig. 2b, which simply shows the cross-section summed over the
224 small range $0.005 \text{ \AA}^{-1} < Q < 0.009 \text{ \AA}^{-1}$ (to improve statistics), was in fact averaged over all
225 temperatures between 5 and 60 K, no significant changes in the angular dependence occurring at
226 any T . Six-fold periodicity is thus clear, but, remarkably, it is not T -dependent across the Besnus
227 transition. If a crystal symmetry change occurs at 32 K, this indicates that the long-range (> 30
228 nm) structural defects or magnetic domains producing the scattering seen here do not change
229 significantly in response.

Preprint submitted to American Mineralogist February 15, 2018

230 There are, however, some subtle changes in the absolute scattering intensity. To illustrate this,
231 Fig. 2c plots $d\Sigma/d\Omega$ vs. the magnitude of Q , acquired by circular averaging of 2D maps of the type
232 shown in Fig. 2(a); the example shown here is at 45 K. As is often the case, $d\Sigma/d\Omega(Q)$ can be fit
233 (solid line through the points) as the sum of two terms: A Porod term (blue dashed line) and a
234 Lorentzian term (red dashed line). The generalized Porod term has the form $d\Sigma/d\Omega = (d\Sigma/d\Omega)_P/Q^n$,
235 where the exponent n provides details on the morphology of the scattering inhomogeneities, and
236 the prefactor $(d\Sigma/d\Omega)_P$ parameterizes the strength of the Porod intensity. In our case $n = 3.3$ (i.e.,
237 somewhat less than 4), as shown in Fig. 2c, indicating that the scattering inhomogeneities (long-
238 range structural defects or magnetic domains) do not have completely smooth surfaces. A value of
239 3.3, however, not far from the generic 4.0 for smooth 3D objects, indicates that the scattering is
240 *not* occurring from clearly one- or two-dimensional objects, such as filaments or lamellae. The
241 Lorentzian term has the form $d\Sigma/d\Omega = (d\Sigma/d\Omega)_L / (Q^2 + \kappa^2)$, where the prefactor $(d\Sigma/d\Omega)_L$
242 parameterizes the strength of the Lorentzian intensity, and κ is a constant. Such scattering is most
243 commonly associated with short-range (nm-scale) magnetic fluctuations, where κ becomes $1/\xi$,
244 the magnetic correlation length. Standard behavior in a ferrimagnet would involve an order-
245 parameter-like turn on of the Porod scattering from magnetic domains below the magnetic ordering
246 temperature, along with a peak in Lorentzian scattering at the ordering temperature due to critical
247 scattering. At $T \leq 60$ K, far below the ordering temperature, Lorentzian scattering should thus be
248 small, and, if present at all, be decreasing on cooling. Not only does Fig. 2c show that the
249 Lorentzian scattering here is non-negligible, but Fig. 2d shows that it has an unusual T dependence.
250 Specifically, $(d\Sigma/d\Omega)_L$ (right axis, red points) decreases on cooling from 60 to 35 K, as might be
251 expected, but then *grows* on further cooling to 5 K. This is unusual in a long-range-ordered ferro-
252 or ferri-magnet far below its ordering temperature. The Besnus transition thus manifests itself in

Preprint submitted to American Mineralogist February 15, 2018

253 some change in short-range (< 10 nm) spin fluctuations/ordering in 4C pyrrhotite, but not
254 obviously so in the angular dependence of long-range (> 30 nm) scattering. We note that the T
255 dependence of $(d\Sigma/d\Omega)_P$ (left axis, black points in Fig. 2d) may provide some evidence of a plateau
256 around the Besnus transition, although much better statistics would be required to reinforce this.
257 Future SANS measurements to probe these findings in more detail could employ a much wider T
258 range (going above the Néel temperature), or polarized neutrons, to better separate magnetic and
259 structural scattering. Both of these approaches are certainly possible.

260 **2.3 HEAT CAPACITY**

261 As discussed above in the Introduction, the existence of an anomaly in specific heat capacity
262 (C_P) at the Besnus transition is important in pyrrhotite, but is not clear from prior experimental
263 work. Specifically, the work of *Grønvold et al.* (1959) indicated a small anomaly around 32 K,
264 while the work on material with mixed 4C/5C* superstructures by *Charilaou et al.* (2015) revealed
265 no such anomaly. In general, first-order phase transitions involve latent heat and result in
266 discontinuities in $C_P(T)$, while second-order transitions involve no latent heat and result in peaks
267 in $C_P(T)$. To probe these issues in our 4C pyrrhotite single crystal, $C_P(T)$ was measured in a
268 Physical Property Measurement System (PPMS) from Quantum Design Inc., from 1.8 K to room
269 temperature. Relaxation calorimetry was employed, using temperature pulses amounting to 2 % of
270 the sample temperature. The crystal was attached to the measurement platform using Apiezon N
271 grease, and the heat capacity of the platform and grease were subsequently subtracted. For all
272 measurements the ratio of sample to addenda heat capacity was maintained at greater than 2.0,
273 safely above the recommended minimum of 0.5 from *Lashley et al.* (2003). Similarly, the thermal
274 coupling parameter between the sample and calorimeter was $> 96\%$, well above the minimum
275 Quantum Design recommendation of 90%.

Preprint submitted to American Mineralogist February 15, 2018

276 Fig. 3 shows our $C_P(T)$ results along with those obtained from *Grønvold et al.* (1959),
277 *Kobayashi et al.* (1999), and *Charilaou et al.* (2015). Fig. 3a shows $C_P(T)$ over the entire T range
278 studied (1.8 - 300 K), *generally* showing good agreement with previous studies over most of the T
279 range. Around the Besnus transition, however (inset to Fig. 3a), the results are substantially
280 different in the various studies. In our work, $C_P(T)$ exhibits a large anomaly at 31.7 K, larger than
281 the one seen by *Grønvold et al.* (1959) (in a synthetic sample), and in contrast to the lack of any
282 anomaly seen by *Charilaou et al.* (2015). In the latter work, multiple stacking sequences (i.e.,
283 coexisting 4C and 5C* phases) were clearly observed in XRD. Here, however, we have a phase-
284 pure 4C pyrrhotite crystal, which apparently results in a clear, well-defined transition in $C_P(T)$,
285 taking the form of a classic “ λ anomaly” expected at a second-order phase transition. (Note that
286 this is not to be confused with the 220 °C “ λ -transition” in hexagonal pyrrhotite, as discussed
287 above). The apparent second-order nature of the transition is supported by the absence of any
288 detectable thermal hysteresis, both in relaxation calorimetry on cooling and warming, and by the
289 use of long-pulse measurements (*Gillard et al.* 2015). The striking differences between our phase-
290 pure 4C natural single crystal and the 4C/5C* natural crystal of *Charilaou et al.* (2015), may well
291 result from the phase-purity with respect to the stacking sequences, and/or trace concentrations of
292 other metals (particularly nickel). It is interesting to note that the 5C polymorph measured later by
293 *Grønvold et al.* (1991) (not shown in Fig. 3) also shows no $C_P(T)$ anomaly, suggesting that the
294 pure 4C structure may be the only form of pyrrhotite that displays a heat capacity anomaly at the
295 Besnus transition, and that any changes in properties across the Besnus transition are intrinsic to
296 4C pyrrhotite.

297 Subtracting a linear T -dependent background from our $C_P(T)$ data around the Besnus transition
298 and then integrating the excess specific heat yields the entropy change across the Besnus transition.

Preprint submitted to American Mineralogist February 15, 2018

299 This gives $2.39 \text{ J mol}^{-1} \text{ K}^{-1}$, or, by mole of Fe, $0.34 \text{ J mol}^{-1} \text{ K}^{-1}$. For comparison, the entropy
300 change across the Verwey transition of magnetite, a first-order structural transition, is
301 approximately $5 \text{ J mol}^{-1} \text{ K}^{-1}$, or by mole of Fe, $1.33 \text{ J mol}^{-1} \text{ K}^{-1}$ (*Shepherd et al.* 1991). Furthermore,
302 the Morin transition of hematite, a first-order spin-flop transition, has an entropy change of 0.43 J
303 $\text{mol}^{-1} \text{ K}^{-1}$, or, per mole of Fe, $0.22 \text{ J mol}^{-1} \text{ K}^{-1}$ (*Pastor et al.* 2012). The entropy change across the
304 Besnus transition in 4C pyrrhotite is thus significant.

305 Further analysis was performed on the low T specific heat (Fig. 3b), which can be used to
306 extract electronic and lattice contributions, in turn allowing for determination of the density-of-
307 states at the Fermi level and the Debye temperature, respectively. (As discussed later in this work,
308 pyrrhotite is an electronic conductor). As shown in Fig. 3b, our $C_p(T)$ in this region is in excellent
309 agreement with that of *Kobayashi et al.* (1999), but again rather different to the mixed phase
310 4C/5C* crystal of *Charilaou et al.* (2015). Our data were fit following the standard procedure,
311 using $C_p(T) = \gamma T + \beta T^3 + \alpha T^5$, where the first term is the electronic contribution and the latter two
312 are from lattice dynamics. The T^3 term is the standard low-temperature expansion in the Debye
313 model, while the T^5 term is the next order term, as often needed to adequately describe
314 experimental data. Two fitting procedures were employed, the first considering all data up to 10
315 K, comparable to that used by *Kobayashi et al.* (1999). This resulted in a poor fit, with an
316 unphysically large αT^5 term. The second fitting approach acknowledges the clear upturn in the data
317 at $T^2 < 30 \text{ K}^2$, and fits only at $T^2 > 30 \text{ K}^2$, resulting in the good fit shown in Fig. 3b. Considering
318 the electronic contribution first, the results give $\gamma = 95 \text{ mJ mol}^{-1} \text{ K}^{-2}$, a substantial value.
319 Theoretical values from the density-of-states at the Fermi level calculated from density functional
320 theory suggest $\sim 46.5 \text{ mJ mol}^{-1} \text{ K}^{-2}$, however (*Shirai et al.*, 1996; *Shimada, et al.*, 1998),
321 corresponding to only a modest effective mass enhancement of ~ 2 , in good agreement with

Preprint submitted to American Mineralogist February 15, 2018

322 *Shimada et al.* (1998) and *Kobayashi et al.* (1999). With respect to lattice contributions, the
323 extracted β was used to determine the Debye temperature, Θ_D , yielding 278 K. This is in reasonable
324 agreement with the value of *Kobayashi et al.* (1999) ($\Theta_D = 313$ K), who, we note, did not include
325 the higher order αT^5 term used here. We add that in our case the αT^5 term is indeed almost an order
326 of magnitude smaller than the βT^3 term, even at the highest T , as would be expected. Finally, with
327 respect to the excess specific heat at $T^2 < 30$ K² (i.e., below 5.5 K, as also seen in *Kobayashi et al.*
328 (1999)) we note only that upturns on $C_P(T)$ vs. T^2 plots at the lowest T are not at all uncommon in
329 solid-state systems, and can derive from Schottky anomalies, for example (*Rosenberg*, (1963);
330 *Gopal*, (1966)). The latter occur due to any mechanism that produces a manifold of low-lying
331 states, and can result from all manner of origins; further study at temperatures well below 1 K
332 could clarify this.

333 2.4 MAGNETIC PROPERTIES

334 2.4.1 REMANENT AND INDUCED MAGNETIZATION

335 In paleomagnetism, the Besnus transition is associated with a loss in remanent magnetization
336 on cooling. We measured the temperature dependence of a room temperature saturation isothermal
337 magnetization (RTSIRM) with a Quantum Design MPMS-XL (Magnetic Property Measurement
338 System) on cooling and warming. The specimen acquired a RTSIRM in a 2.5 T magnetic field at
339 300 K applied along two arbitrarily chosen directions in the basal plane of the crystal (Φ_1 , Φ_2),
340 both roughly perpendicular to the [001] c -axis. The temperature dependence of the RTSIRM was
341 measured twice, firstly spanning the full temperature range from 300-10 K (5K/min) and secondly
342 in high resolution (0.5 K/min) spanning the transition (20-50 K).

343 The cooling path (Fig. 4 insets) of the RTSIRM ($\Phi_1 = 1.5$, $\Phi_2 = 1.9$ Am²/kg) shows a gradual
344 decrease in magnetization to ≈ 45 % at 110-150 K, where it plateaus. Characteristic of the Besnus

345 transition (*Dekkers et al.*, 1989), the remanence drops sharply in the narrow temperature range of
346 35-25 K (fig. 4). Estimates of the transition from the maximum dM/dT , yield a slightly higher
347 temperature (34 K) than the peak in specific heat (31.7 K). While the shapes of the cooling paths
348 in Φ_1 and Φ_2 are comparable, the warming paths (path 4 in Fig. 4a,b)) are quite different in the
349 vicinity of T_{Bes} , when measured in high-resolution (0.5 K steps). The recovery of magnetization
350 by warming back through the Besnus transition is strongly dependent on the grain-size of the
351 sample and should be low for large grains (*Dekkers et al.*, 1989). Along Φ_1 (Fig. 4a) a small portion
352 ($\approx 5\%$) of the RTSIRM is recovered on warming from 10 K back to 40 K. In contrast, the
353 measurement along direction Φ_2 (Fig. 4b) shows a zig-zag behavior at T_{Bes} , with a local minimum
354 centered exactly at the specific heat peak. Furthermore, Φ_2 shows little remanence recovery.
355 Finally, the remaining remanence decays further with warming and only $20 \pm 4\%$ of the initial
356 RTSIRM remains at room temperature.

357 *Dekkers et al. (1989)* showed that cycling to 4.2 K changes the median destructive field (MDF)
358 of the sample. Similarly, the second high resolution cooling/warming cycle (path 3,4) shows that
359 the newly acquired RTSIRM(50 K) is slightly larger than the first one. This indicates that the
360 changes occurring across the Besnus transition may not be entirely reversible. Furthermore, the
361 changes in MDF are grain-size-dependent (*Dekkers et al., 1989*), with the biggest increases
362 occurring in larger particles. Thus, the configuration of domain walls in large, multi-domain grains
363 may be altered after cycling through the Besnus transition. A possible rearrangement of vacancies
364 at the transition could change the defect structure of the crystal and lead to different pinning of
365 domain walls and consequently a hardening of MDF and increased remanence ratio (Table 1).

366 The application of DC magnetic fields can modify the precise temperature of some magnetic
367 transitions, or even influence crystallographic changes during transitions in magnetic materials.

368 For example, in magnetite the orientation of the monoclinic c -axis below the Verwey transition
369 can be strongly controlled by the application of a DC magnetic field during cooling, where the
370 monoclinic c -axis is selected from the cubic a -axis that is closest to the orientation of the applied
371 field (*Li, 1932, Kasama et al., 2010*). To look for field-dependent effects at the Besnus transition,
372 we performed in-field cooling (FC) (5 K/min) in 0.5, 1, 1.5, 2 and 3 T ($B \perp [001]$) followed by zero-
373 field warming (5 K/min) of the low temperature remanence (LTSIRM) that was acquired in the
374 respective field at 10 K (Fig. 5). The saturation magnetization determined from field cooling
375 ($M(300\text{K}, 3\text{T}) = 20.2 \text{ Am}^2/\text{kg}$, see table 1) is well within the range of reported values (18.3-21.2
376 Am^2/kg) (*O'Reilly et al., 2000; Kind et al., 2013*). As the sample cools in a field (Fig. 5a), the
377 magnetization increases to a local maximum at $T \approx 180 \text{ K}$ ($M(180 \text{ K}, 3 \text{ T}) = 21.7 \text{ Am}^2/\text{kg}$). The
378 maximum is located close to where the magnetic anisotropy constant K_4 is also at a maximum and
379 where K_3 changes sign from positive to negative (*Bin and Pauthenet, 1963*).

380 Cooling in fields lower than $\approx 1.5 \text{ T}$ causes a sharp increase of magnetization at the Besnus
381 transition. By comparison, in strong fields ($B > 1.5 \text{ T}$), the Besnus transition is only visible as a
382 slight bump in the magnetization, which has been reported in several studies (*Besnus and Meyer,*
383 *1964; Dekkers et al., 1989; Kind et al., 2013; Charilaou et al., 2015; Koulialias et al., 2016*). The
384 changing crystalline anisotropy causes the spins, which are lying in the basal plane at room
385 temperature, to rotate out of the plane with decreasing temperature (*Bin and Pauthenet, 1963;*
386 *Powell et al. 2004*). Thus, the increase in magnetization could be related to a change in spin
387 configuration at the transition.

388 We can compare the directional dependence of the magnetization with data from magnetic
389 hysteresis loops (*Volk et al., 2016*), which were measured as a function of orientation (Φ) and
390 temperature on a single crystal sister specimen from the same sample studied here. Consequently,

391 each magnetization value can be expressed as a function of field, orientation and temperature M
392 (B , T , Φ) and used to determine quasi “FC”. Figure 5b shows the magnetization in a 500 mT field
393 in different crystallographic orientations as a function of temperature. Similar to the MPMS
394 measurements along Φ_1 and Φ_2 (Fig. 5a), the quasi FC data shows orientation-dependent
395 magnetization. However, these measurements show a clear directional dependence of the shape
396 and magnitude of the Besnus transition. Moreover, the standard deviation of the induced moment
397 is about 2.6 times greater for $T = 50$ K than for $T = 20$ K. The decrease in variability at lower
398 temperature suggests changes in magneto-crystalline anisotropy as the crystal is cooled through
399 the transition.

400 To check for possible thermal hysteresis, we repeated the FC experiment (500 mT, Φ_2) at a
401 higher resolution (0.5 K). While hysteretic behavior is typical for first-order transitions, no such
402 behavior is expected for second-order ones, as noted above. The fact that both cooling and
403 warming curves are perfectly aligned, completely reversible, and show no hysteresis (inset in Fig.
404 5b), further underlines the second-order character of the Besnus transition, consistent with our
405 specific heat data.

406 The remanence acquired in the field-cooling experiments at 10 K (LTSIRM, Fig. 5c) was
407 measured on warming back to room temperature in zero field. The absolute magnetization is the
408 same for all fields used, which drops by 90 % at T_{Bes} and further decays to only $\approx 2\%$ at room
409 temperature. While the LTSIRM is about 7 times stronger than the RTSIRM (tab. 1) at low
410 temperature, the two are comparable after a full cooling-warming circle. There was no field
411 dependence observed in the warming of LTSIRM for pure 4C pyrrhotite.

412

Preprint submitted to American Mineralogist February 15, 2018

413 The $M(B, T, \Phi)$ data (Fig. 5b) from the hysteresis loops, as described earlier, allow for the
414 extraction of T_{Bes} as a function of Φ (in the basal plane) and applied field. We define $T_{\text{Bes}}(B, \Phi)$ as
415 the maximum change in magnetization ($\max(dM/dT)$) on cooling. $T_{\text{Bes}}(B, \Phi)$ is determined from
416 a cubic spline interpolation of the smoothed data. Figure 6a shows that the mean $T_{\text{Bes}}(\Phi)$ is field
417 dependent, and increases from ~ 30 to ~ 34 K as applied field increases from 0 to 1 T. The most
418 prominent change is visible in the first 100 mT (see inset in Fig. 6a), where T_{Bes} changes by ≈ 2 K
419 from 30 K to 32 K. As the field is further increased, T_{Bes} rises linearly until it saturates at 750 mT
420 and 34 K. In our previous study (Volk *et al.*, 2016), we were not able to explain how the coercivity
421 of remanence (B_{cr}) of the single crystal could be lower than its coercivity (B_{c}) for temperatures
422 < 30 K. However, the field dependence of the transition can explain this phenomenon. When B_{cr}
423 is measured in zero field, the crystal is above T_{Bes} and consequently the coercivity of remanence
424 is low. B_{c} , on the other hand, is measured *in* a magnetic field, which raises T_{Bes} . The measurement
425 is therefore done below the transition temperature. B_{c} is greatly enhanced for $T < T_{\text{Bes}}$ which leads
426 to the unusual $B_{\text{cr}} < B_{\text{c}}$. Furthermore, the mean $T_{\text{Bes}}(B)$ shows a directional dependence (Fig. 6b).
427 Parallel to the crystallographic a -axes (determined using EBSD (see Volk *et al.*, 2016)), we find
428 the maximum T_{Bes} , while minima lie between axes, coinciding with orientations whose hysteresis
429 loops most strongly show a second inflection. Finally, combining the field and directional
430 dependence (Fig. 6c) shows the minimum (dark color) of T_{Bes} (30.1 K) located close to the
431 projection of the c -axis onto the basal plane with a transition temperature close to the peak in heat
432 capacity. Thus, the highest Besnus transition temperatures occur when a field is applied parallel to
433 one of the a -axis directions, while the lowest T_{Bes} occurs in between these directions and closest
434 to the projection of the c -axis. It appears as though the application of DC magnetic fields in

435 between the a -axes, or even potentially along the c -axis, stabilizes the $T > T_{\text{Bes}}$ phase, requiring
436 lower temperatures to ultimately bring about the Besnus transition.

437 **2.4.2 ALTERNATING CURRENT SUSCEPTIBILITY**

438 Measurements of low-field AC susceptibility as a function of temperature can provide
439 important information about the mobility of domain walls as a mineral's intrinsic magnetic
440 anisotropy changes, as the pinning energies of vacancies change, or as a mineral undergoes a
441 crystallographic transition. Low field in-phase (χ') and out of phase (χ'') AC susceptibility
442 between 10 K and 300 K (see table 2) was collected at 5 field amplitudes (0.02 - 0.3 mT, 5K/min)
443 on cooling and subsequent warming along the sample's [001] axis (χ_{\parallel}) as well as perpendicular to
444 it (χ_{\perp} , Φ_2). The AC susceptibility (Fig. 7) in the basal plane (χ_{\perp}) shows a gradual decline during
445 cooling until it drops sharply at ≈ 34 K. There is a strong amplitude dependence in both the in-
446 phase (Fig. 7a) and the out-of-phase components (Fig. 7b) of χ_{\perp} . While the amplitude dependence
447 of χ_{\perp} is approximately constant down to 35 K, it increases dramatically at T_{Bes} and then drops to
448 close to zero below the transition. The measurement of χ_{\parallel} , on the other hand, shows a vastly
449 different behavior. Here, both χ_{\parallel} and its amplitude dependence decrease with increasing
450 temperature. The maximum of χ_{\parallel} ($17\text{-}24 \times \chi_{\parallel}(T_k)$) is reached close to the Besnus transition. Similar
451 to χ_{\perp} , χ_{\parallel} evidences a sharp change at T_{Bes} . While the measurements in this study come from a
452 multidomain single crystal, *Kind et al.* (2013) measured similar changes in susceptibility for a
453 natural Fe_7S_8 powder. They interpret the decrease in susceptibility during cooling across the
454 Besnus transition as a reduction in domain wall mobility at lower temperatures, an explanation
455 which would only apply to predominantly MD samples. *Bezaeva et al.*, (2016) also reported a drop
456 in susceptibility across the Besnus transition for predominantly single-domain 4C pyrrhotite,

Preprint submitted to American Mineralogist February 15, 2018

457 which suggests instead that something about the intrinsic magnetic anisotropy energy of the
458 material has changed below T_{Bes} .

459 To gain a better understanding of how susceptibility changes at the transition, we also
460 measured the frequency dependence of AC susceptibility (χ_{\perp} and χ_{\parallel}) at high resolution (0.5 K
461 steps) for 7 frequencies (1 - 1000 Hz) spanning T_{Bes} (from 20-40 K). There is no frequency
462 dependence in the in-phase data (Fig. 6a) for either χ_{\perp} or χ_{\parallel} . There is a slight frequency dependence
463 in the out-of-phase data (Fig. 6b), however, the main drop of χ_{\parallel} occurring at temperatures ≈ 1 K
464 warmer than χ_{\perp} in both in-phase and out-of-phase measurements. This shift is reproducible and is
465 likely not an instrumental artifact. Furthermore, close inspection of the data of *Koulialias et al.*
466 (2016) reveals a similar shift, which seems to decrease with increasing frequency.

467 A prominent secondary peak is visible at ≈ 32 K (see inset in Fig. 7a) in χ_{\perp}' and less expressed
468 in χ_{\perp}'' , while χ_{\parallel} does not show it at all. Similar features were reported by *Koulialias et al.* (2016)
469 in their natural single crystal and *Kind et al.* (2013) in Fe_7S_8 powder. To resolve this feature, data
470 must be collected at sufficiently high resolution (here, 0.5 K steps). Thus, the feature is not visible
471 in the lower resolution amplitude dependence measurements (2.5 K steps). It is noteworthy that
472 this secondary peak is located directly at the temperature of the specific heat peak discussed above.
473 This indicates that the peak is directly related to the transition. Consequently, a Besnus transition
474 temperature, determined from the decay of susceptibility may be overestimating T_{Bes} .

475 The strong anisotropy of susceptibility in 4C pyrrhotite is reflected in the vastly different
476 susceptibilities that are measured parallel and perpendicular to [001]. At room temperature, χ_{\perp} is
477 ~ 170 times larger than χ_{\parallel} . As temperatures approach T_{Bes} , however, χ_{\parallel} increases while χ_{\perp} decreases,
478 which results in a linear decrease of their ratio ($\chi_{\perp}/\chi_{\parallel}$) when plotted logarithmically (Fig. 8). This

479 linearity is broken at T_{Bes} , where the ratio shows a discontinuity, again well-aligned with the
480 specific heat peak (see inset Fig. 7). We interpret this change a consequence of the rotation of the
481 easy axis of the crystal during cooling. *Powell et al.* (2004) showed that as Fe_7S_8 is cooled, the
482 easy axis rotates out of the (001) plane, consistent with increasing susceptibility in [001]. Similarly,
483 the sudden increase in $\chi_{\perp}/\chi_{\parallel}$ could be caused by an abrupt rotation of the easy axis towards the
484 basal plane and back out, towards [001].

485 Finally, below T_{Bes} , χ_{\perp} decreases to <1% of its room temperature value (Table 2); χ_{\parallel} on the
486 other hand is only reduced to about 50%. Consequently, below the transition both susceptibilities
487 are comparable ($\chi_{\perp} \approx 2 \times \chi_{\parallel}$). Thus, the anisotropy of the crystal is greatly reduced below T_{Bes} . The
488 sample in study has a platelet shape, and therefore shape anisotropy may play a role. If one were
489 to correct for the shape of our sample, the sense of the correction would lower the susceptibility
490 within the basal plane, and therefore it is possible that susceptibility parallel to [001] could be even
491 closer to, if not larger than, χ_{\perp} .

492 2.5 ELECTRICAL RESISTIVITY

493 To gain an understanding of the electronic property changes that take place across the Besnus
494 transition, we performed temperature- and magnetic-field-dependent measurements of resistivity
495 (ρ) from 4 to 300 K, using a home-built Janis cryostat with a 9 T superconducting magnet. Silver
496 paste contacts were employed in a 4-wire van der Pauw configuration (*van der Pauw*, 1958), using
497 a Lakeshore 370 13.7 Hz AC bridge to measure 4-terminal resistances. Checks for Ohmicity,
498 contact resistance, and self-heating were made at 4 and 300 K.

499 As shown in Fig. 9a, the ρ in the basal plane of our 4C pyrrhotite single crystal exhibits clearly
500 metallic behavior ($d\rho/dT$ is metallic-like (i.e., positive) over almost the entire temperature range,
501 with finite apparent conductivity as $T \rightarrow 0$), with a large anomaly visible at 32 K, where the

502 resistivity drops significantly. We note that the peak in the ratio of $\chi_{||} / \chi_{\perp}$, this resistivity anomaly,
503 and the peak in specific heat are all located at the same temperature. This highlights the
504 reproducibility and precision of T_{Bes} in our measurements, in addition to its clear, recognizable
505 effect on diverse properties (magnetic, electronic, and thermodynamic). In contrast to the Verwey
506 transition in magnetite, which displays a sharp drop in resistivity on warming (e.g., *Kuipers and*
507 *Brabers, 1979*), the resistivity change here is continuous, again consistent with second-order
508 character of the Besnus transition (there is also no thermal hysteresis in $\rho(T)$ on heating/cooling).
509 The room temperature resistivity ($\rho_{300\text{ K}}$) of the crystal measured here is 0.32 m Ω cm, which
510 compares well with the $\rho_{300\text{ K}}$ of 0.41 m Ω cm originally obtained by *Besnus and Meyer (1964)*,
511 being considerably lower than the 2.1 m Ω cm obtained by *Charilaou et al. (2015)*. This
512 consistency with the original work, and the lower values than those obtained by *Charilaou et al.*
513 (2015), again highlight the quality of this phase-pure natural single crystal, and reinforce the clear
514 expression of the Besnus transition in this phase-pure sample. Consistent with this, the temperature
515 dependence of ρ is also stronger in this crystal. For example, the residual resistivity ratio (RRR),
516 defined as $\text{RRR} = \rho_{300\text{ K}} / \rho_{5\text{ K}}$, is 4.04 in this work, compared to ~ 2.9 in *Besnus and Meyer (1964)*,
517 and 1.34 in *Charilaou et al. (2015)*. This indicates not only lower defect densities in our phase-
518 pure crystal, but also a stronger decrease in $\rho(T)$ below T_{Bes} . With a RRR of above 4, and also
519 given the absolute magnitudes of the resistivities, this pyrrhotite crystal can be considered a “bad”
520 or “dirty” metal or semimetal. In terms of constraining the *origin* of the Besnus transition, we note
521 that any explanation for it must be able to explain a substantial *decrease* in resistivity on cooling.

522 Fig. 9b shows the magnetic field dependence of ρ vs. T around the Besnus transition, with the
523 field applied along a random direction in the basal plane. As the field increases from 0 T to 0.5 T,
524 progressive smearing of the sharp anomaly in ρ vs. T and a weak negative magnetoresistance (MR)

525 is seen, meaning that the apparent T_{Bes} increases monotonically with field, consistent with
526 magnetization data shown in Fig. 6a. In this field orientation, there is no significant additional field
527 dependence above 0.5 T. This can be seen in the inset to Fig. 9c, where the magnetoresistance (MR
528 = $(\rho(H) - \rho(0)) / \rho(0)$) as a function of magnetic field at 32 K only shows negative MR out to ~ 1
529 T. Application of larger fields then causes an inversion in the slope of the MR and a slight increase
530 in magnitude, saturating at high fields. The main panel of Fig 9c shows MR(9 T) as a function of
531 temperature. Upon warming, positive MR at low T gives way to a slight negative MR around T_{Bes} ,
532 with the peak negative MR being $\sim -2\%$ at T_{Bes} . Above the transition, the MR goes positive again,
533 and remains relatively constant past 60 K at about $\sim 0.5\%$. In this field orientation, MR effects are
534 thus small, the typical growth of positive MR on cooling, as expected in a metal, being interrupted
535 at T_{Bes} with only a small negative MR effect. This small negative MR saturates quickly with
536 increasing field.

537 Fig. 9d displays the magnetic field dependence of ρ vs. T around the Besnus transition, this
538 time with the field applied *out* of the basal plane, i.e., parallel to the c -axis. In this case, a clear
539 decrease in the apparent transition temperature is observed as the out-of-plane magnetic field is
540 increased from 0 to 9 T. The apparent transition temperature shift is monotonic, with an overall
541 shift of ~ 2 K with 9 T of applied field, which is relatively small. The presence of an out-of-plane
542 field thus apparently favors the $T > T_{\text{Bes}}$ phase. Importantly, this is consistent with the remanence
543 and hysteresis data (§2.4.1) (Fig. 6c) in that when the applied field is along, or parallel to, the c -
544 axis, the lowest T_{Bes} values are observed. Specifically, it appears that fields applied parallel to the
545 c -axis pull the spins out-of-plane near the transition, which allows the phase above the transition
546 to persist to lower T . One way to rationalize this is in terms of Zeeman energy stabilization. The T
547 $> T_{\text{Bes}}$ phase has a larger component of magnetization along the c -axis than the $T < T_{\text{Bes}}$ phase (see

Preprint submitted to American Mineralogist February 15, 2018

548 *Charilaou et al. (2015)*), allowing the $T > T_{\text{Bes}}$ phase to be stabilized when a field is applied along
549 the c -axis, lowering T_{Bes} as larger fields are applied. Naturally, and as shown in the expanded view
550 in Fig. 9d, the lowering of the apparent transition temperature with out-of-plane field combines
551 with the positive dp/dT to generate positive MR. This is shown as a function of magnetic field at
552 30 K in the inset to Fig. 9e, where positive MR up to 7.5 % is seen, not saturating even at 9 T. Fig.
553 9e shows that this positive MR is found at all temperatures between 5 – 60 K when the field is
554 applied parallel to the c -axis. The positive MR effect associated with the Besnus transition turns
555 on near T_{Bes} , reaches a sharp peak, and then gradually decreases towards 5 K.

556 3 DISCUSSION

557 This study represents one of the most exhaustive studies of the Besnus transition to date,
558 performed on a high purity, phase-pure, 4C pyrrhotite single crystal specimen. While the precise
559 mechanism(s) driving the transition still remain elusive, it is possible to now better constrain
560 potential explanations by considering all of the phenomena that have been observed to accompany
561 the transition. Ultimately, a comprehensive theory for the Besnus transition must explain:

- 562 1. An entropy change at T_{Bes} resulting from an apparently second-order phase transition in
563 specific heat (this study, *Grønvold et al., 1959*)
- 564 2. Loss of remanent magnetization upon cooling (RTSIRM) and warming (LTSIRM) through
565 the transition.
- 566 3. Changing rock magnetic properties (B_c , B_{cr} , M_{rs}), while M_s remains constant
- 567 4. Irreversible changes after cycling through T_{Bes} , represented as increases in remanence and
568 MDF (this study, *Dekkers et al., 1989*)
- 569 5. The disappearance of the second inflection phenomenon in hysteresis loops at T_{Bes} (appears
570 at $\approx 200\text{K}$, aligned with crystal structure) (*Volk et al., 2016, Koulialias et al., 2016*)

Preprint submitted to American Mineralogist February 15, 2018

- 571 6. Symmetry changes of rock magnetic properties from 6-fold above the transition to 4-fold
572 below the transition (*Wolfers et al., 2011, Volk et al., 2016, Koulialias et al., 2018*)
- 573 7. Field dependence of $T_{\text{Bes}} \perp [001]$, as determined from magnetic data and resistivity
- 574 8. Field dependence of T_{Bes} in resistivity $\parallel [001]$
- 575 9. Different magnetoresistive behavior when applied fields are within the basal plane or
576 parallel to the c -axis
- 577 10. A distinct decrease in resistivity on cooling through T_{Bes}
- 578 11. Splitting of Fe sites (4 unique \rightarrow 5 unique) below T_{Bes} , as determined by Mössbauer
579 spectroscopy (*Jeandey et al., 1991, Oddou et al., 1992*)
- 580 12. The anomaly seen in short-range magnetic scattering seen in SANS data.

581 Unfortunately, no single mechanism appears capable of simply explaining all of the observed
582 behaviors across the transition, although existing observations do allow us to rule out some
583 proposed mechanisms, which ultimately helps constrain the nature of the transition. All of the
584 mechanisms proposed thus far are discussed in turn below in addition to several new ones.

585 **3.1 The role of interacting superstructures.** The specimen studied here is purely 4C pyrrhotite
586 and contains *no additional superstructures*, as supported by powder X-ray diffraction, microprobe
587 analysis, heat capacity measurements, a single magnetic ordering temperature, the absence of a
588 magnetic λ -transition, the M_s value, and the RRR value. Nevertheless, we clearly observe the
589 Besnus transition in all physical properties studied. The specific heat shows a clear peak at ≈ 31.7
590 K, in agreement with the transition temperature determined from resistivity measurements to
591 within one kelvin at zero field. This agrees well with that of the synthetic specimen studied by
592 *Grønvold et al. (1959)*. The transition temperatures in the magnetic susceptibility, RTSIRM,
593 LTSIRM, and FC curves ($\approx 32 - 34$ K) are slightly higher than the C_p peak, but agree well with

Preprint submitted to American Mineralogist February 15, 2018

594 most published data (*Dekkers et al.*, 1989; *Rochette et al.*, 1990; *Fillion and Rochette*, 1988; *Kind*
595 *et al.*, 2013). On the other hand, the 26 K transitions described by *Charilaou et al.* (2015) and
596 *Koulialias et al.* (2016) deviate markedly. *Baranov et al.* (2014) showed that Ti substitution can
597 induce changes in vacancy ordering, which results in a change from 4C to 3C in Fe₇S₈.
598 Consequently, it seems possible that the 0.5 % Ni substitution in their sample may be responsible
599 for the additional 5C* structure, and may explain the shifted transition temperature and the
600 suppressed specific heat peak. More substantial Ni substitution results in an entirely new iron
601 sulfide mineral Smythite (Fe,Ni)₉S₁₁ with a trigonal structure, that is often found associated with
602 pyrrhotite. We conclude that the Besnus transition is intrinsic to the 4C phase, and is not caused
603 by interactions of different superstructures as proposed by *Koulialias et al.* (2016, 2018).

604 **3.2 The role of twinning.** Pyrrhotite is prone to the formation of stacking faults and twins when
605 there are local perturbations in the superstructure (*Bin and Pauthenet*, 1963). Thus, one could
606 imagine that even subtle changes to the unit cell across the Besnus transition may induce twinning
607 at the nanometer scale (*Wolfers et al.*, 2011). The formation of such features could also reconfigure
608 the distribution of dislocations, vacancies, and pinning sites for domain walls within the material.
609 Consequently, the magnetic interactions between these twins would change, as well as the mobility
610 of domain walls, and thus, the bulk magnetic properties would also change. Nanometer-scale
611 twinning may explain the irreversible changes (e.g., enhanced remanence and coercivity) seen after
612 low temperature cycling. Twinning is also consistent with the length scale of the
613 structural/magnetic changes observed in our high Q SANS data (Figure 2(c,d)), but is somewhat
614 inconsistent with the significant decrease in resistance observed below the transition. The
615 decreasing resistivity can perhaps only be explained by a reduction in the number of twins.
616 Furthermore, twinning is not able to explain the splitting of the occupancy of Fe sites observed in

617 the Mössbauer data. The orientation of twinning in other magnetic minerals, such as magnetite,
618 can be influenced by applied fields, and if this were the case for pyrrhotite, it could explain the
619 field dependence of the transition. Depending on the orientation of the twin boundaries, it is
620 possible that the symmetry of the magnetic properties may change from 6-fold to 4-fold below the
621 transition. As a mechanism, twinning could thus potentially explain many of the phenomena
622 observed below the Besnus transition.

623 **3.3 The role of crystallographic transitions.** Wolfers *et al.* (2011) not only proposed a change
624 in twinning schemes, but a true crystallographic transition, with a lowering of the symmetry from
625 monoclinic to triclinic. This is consistent with the changes in the symmetry of rock magnetic
626 properties from 6-fold symmetry above T_{Bes} to 4-fold symmetry below T_{Bes} (Volk *et al.*, 2016).
627 Confusingly, however, our SANS data show a clear six-fold symmetry, even at 5 K. While this is
628 not conclusive evidence against a crystallographic transition, it indicates that any crystallographic
629 changes, if they occur, could be weak. It is worth reiterating in this regard that the 4C monoclinic
630 superstructure at room temperature is only 0.26° different from a perfect hexagonal unit cell
631 (Wolfers *et al.*, 2011). Hence, any additional subtle distortions may not be easily detectable, and
632 will require further high-resolution crystallographic study.

633 A crystallographic change, where the monoclinic unit cell is subtly distorted to form a
634 different, also monoclinic unit cell is another possible mechanism. Such an *isostructural* or
635 *isomorphic* transformation would be difficult to detect with SANS. However, such a transition
636 could explain many of the phenomena described above. The changing crystal structure could
637 explain the second-order transition indicated by specific heat, but only if the phase transition is
638 truly second-order, or only very weakly first-order. A change in crystal structure would result in
639 changes in the band structure of the material, which would affect electronic transport, *i.e.*, the

640 resistivity and MR. Therefore, the differences in electronic transport (specifically dp/dT) above
641 and below T_{Bes} could potentially be explained. Furthermore, the newly created twins could change
642 the domain structure and pin magnetic domain walls at twin boundaries. Consequently, the
643 changing unit cell and rearrangement of domains would lead to a loss of the remanent
644 magnetization. Pinning of domain walls, on the other hand, would increase the coercivity of the
645 crystal. If the changes are small enough, the saturation magnetization should not be affected.
646 Finally, the generation of twins that accompanies an isostructural transformation could explain
647 irreversible changes on cycling through the transition.

648 **3.4 The role of changing crystalline anisotropy.** Several studies have investigated the
649 crystalline anisotropy of pyrrhotite (*Mikami et al. 1959; Bin and Pauthenet, 1963; Sato et al.,*
650 *1964*). Bin and Pauthenet (*1963*) showed that the crystalline anisotropy of pyrrhotite changes upon
651 cooling. The K_4 anisotropy constant, which dominates, shows a maximum, while the K_3 constant
652 changes sign and becomes negative at ≈ 200 K. The changing anisotropy causes the spins to rotate
653 out of the basal plane, which was confirmed by neutron diffraction data by Powell *et al. (2004)*.
654 These changes in magnetic anisotropy may be able to explain the Besnus transition. In this
655 scenario, the magnetic easy axis switches to a different crystallographic direction. Consequently,
656 the remanent magnetization would be lost and domain wall orientation as well as the fundamental
657 magnetic properties would change. However, the measurements of Bin and Pauthenet (*1963*) were
658 done on an obviously twinned crystal. Furthermore, the authors were not able to determine the
659 anisotropy from measurements in the basal plane at temperatures < 60 K, as the magnetic easy axis
660 seemed to switch when a magnetic field is applied. As the second inflection in magnetic hysteresis
661 loops appears at ≈ 180 K, it is likely related to this presumed easy axis switching.

Preprint submitted to American Mineralogist February 15, 2018

662 On balance, it seems unlikely that the Besnus transition is solely caused by a changing
663 anisotropy. Given that the low temperature behavior of the crystalline anisotropy is not well
664 known, the main changes seem appear at 200 K. However, the remanence is unaffected, as are the
665 magnetic properties. Furthermore, the model fails to explain the changes seen in resistivity,
666 Mössbauer, and high Q (Lorentzian) SANS. On the other hand, it seems likely that the anisotropy
667 would change as a byproduct of even a subtle crystallographic transition.

668 **3.5 The role of exchange inversion within NiAs structures.** Kittel (1960) predicted a
669 phenomenon called exchange inversion in materials with a NiAs crystal structure. Since then it
670 has been found in Mn₂Sb and other Mn-Sb compounds with substitutions (e.g. *Bither et al., 1962*).
671 At the phase transition, the formerly ferromagnetic coupling between spins switches, and becomes
672 antiferromagnetic. The spins within each Fe plane in pyrrhotite couple ferromagnetically, while
673 the spins between layers couple antiferromagnetically. It seems possible for exchange inversion to
674 take place at T_{Bes} . This would change the coupling within a plane to become antiferromagnetic,
675 becoming ferromagnetic to the adjacent plane. The changing spin orientation would remove most
676 of the remanent magnetization, without affecting the bulk saturation magnetization. The field
677 dependence of the transition could also be explained, as strong magnetic fields could exert force
678 on the spins and hinder their reorganization. Furthermore, a reorientation of spins was found to
679 change electronic properties in a pyrrhotite analogue Fe₇Se₈ with a 4C NiAs structure (*Li et al.,*
680 *2016*). While being able to explain several phenomena, this scenario fails to explain the splitting
681 of the iron sites in Mössbauer spectroscopy. Furthermore, a spin reorganization should be visible
682 in neutron diffraction data. Powell *et al.* (2004) did not observe such a transition in their neutron
683 study. However, in their work only one scan was taken below T_{Bes} .

684 **3.6 Future research.** In light of the above, this study clearly emphasizes the need for further
685 research along at least three lines: High-resolution structural characterization, laboratory synthesis
686 of single phase pyrrhotite, and linking single crystal observations to bulk sample behavior. The
687 observations in this study and previous work suggest that nanometer-scale twinning within
688 pyrrhotite across the Besnus transition may explain many of the magnetic and physical properties
689 observations. However, it is not clear which mechanism(s) may be driving the twinning. To
690 distinguish between subtle crystallographic transitions or fundamental changes in the exchange
691 coupling, further research is required. Wolfers *et al.* (2011) proposed that fine low temperature X-
692 ray diffraction experiments could be used to obtain a detailed description of any crystallographic
693 change near the 32 K transition. If such an approach is meant to differentiate between monoclinic-
694 triclinic and isostructural transitions, then these diffraction experiments may only be possible using
695 synchrotron facilities. Similarly, synchrotron-based X-ray absorption near-edge structure
696 (XANES) analyses may shed light on the changes in Fe site occupancy across the transition
697 originally observed with Mössbauer spectroscopy. Finally, powder neutron diffraction, similar to
698 Powell *et al.* (2004) at temperatures spanning the transition would further show changes in spin
699 structure as well as possible structural changes.

700 Magnetic methods may also help constrain the importance of twinning in mixed phase
701 (hexagonal and monoclinic) crystals. If nanometer-scale twinning does occur across the Besnus
702 transition, then vacancies may reorder on warming, and the distribution of pyrrhotite
703 superstructures at room temperature may change after cycling through the Besnus transition. If so,
704 then there should be observable changes in the nature of the lambda transition near 220°C in
705 susceptibility measurements. Given the field dependence of the Besnus transition observed here,
706 it is possible that fields applied along different crystallographic directions may lead to different

Preprint submitted to American Mineralogist February 15, 2018

707 ratios of superstructures at room temperature. However, if no lambda transition is observed near
708 220°C after cycling through the Besnus transition, then perhaps the role of twinning may need to
709 be re-evaluated.

710 **4 IMPLICATIONS**

711 Many open questions also remain regarding the influence of the Besnus transition on the full-
712 vector remanence held by pyrrhotite in natural samples. While the magnitude of magnetization
713 decreases after cycling through the Besnus transition, the direction of a laboratory-induced
714 isothermal remanent magnetization in a single crystal of pyrrhotite is stable (Feinberg *et al.*, 2015).
715 This observation may have important implications for paleomagnetic studies of terrestrial and
716 meteoritic samples containing pyrrhotite. Similar to the ways in which low-temperature treatments
717 that cycle through the Verwey transition in magnetite are used to reduce the remanence held by
718 large multidomain grains and give a more unfettered view of the remanence held by well-behaved,
719 single-domain-like grains, cycling through the Besnus transition may be useful isolating high
720 coercivity remanence in pyrrhotite. Single-domain-like grains also express a Besnus transition, but
721 no observations exist regarding the directional stability of their magnetization across the transition.

722 The high purity of the 4C single crystal sample in this study is particularly unusual but was
723 essential for demonstrating the intrinsic nature of the Besnus transition and its directional
724 dependence. However, this sample is limited in mass, and, given the numerous ongoing questions
725 about pyrrhotite, there is a clear need to develop dependable synthesis methods (metastability is
726 often a problem) for pyrrhotite that control the resulting superstructures. Many existing synthesis
727 methods are time consuming, require repeated annealing steps (which only partially control the
728 ratio of resulting superstructures), and are limited to only producing fine grained samples. Methods

Preprint submitted to American Mineralogist February 15, 2018

729 capable of producing large single crystals of well-characterized pyrrhotite would be especially
730 beneficial to future research.

731 In addition, due to our improved ability to detect pyrrhotite in natural samples, it is becoming
732 increasingly important to identify how this mineral influences or records numerous geophysical,
733 environmental, and planetary science processes. Similarly, the mineral and its superstructures are
734 important to the materials science community. A deeper understanding of the nature of the Besnus
735 transition will only improve our interpretations regarding pyrrhotite, and we hope this study makes
736 a convincing case for the need for further research that combines high-resolution structural
737 characterization with carefully controlled rock magnetic experiments on natural and synthetic bulk
738 samples.

739 **5 ACKNOWLEDGMENTS**

740 We would like to thank Anette von der Handt for acquiring electron microprobe data and
741 Jeanette Voelz for help in measuring powder X-ray diffraction data. Furthermore, we would like
742 to thank Rupert Hochleitner and the Bavarian Mineralogical State Collection for providing the
743 sample material and for their kind support. EM, BV, MM and CL acknowledge support from the
744 DOE through the UMN Center for Quantum Materials under DE-FG02-06ER46275 and DE-SC-
745 0016371. We acknowledge the support of the National Institute of Standards and Technology, US
746 Department of Commerce, in providing the neutron facilities used in this work; the assistance of
747 John Barker is gratefully acknowledged in that regard. The Institute for Rock Magnetism is a U.S.
748 National Multiuser Facility supported through the NSF-EAR Instrumentation and Sciences
749 Program and by funding from the University of Minnesota. This is IRM publication (#1710).

750

751 **6 REFERENCES**

752 Arnold, R.G. (1967) Range in composition and structure of 82 natural terrestrial pyrrhotites.
753 The Canadian Mineralogist, 9, 31–50.

754 Aubourg, C., and Pozzi, J.-P. (2010) Toward a new <250°C pyrrhotite–magnetite
755 geothermometer for claystones. Earth and Planetary Science Letters, 294, 47–57.

756 Baranov, N.V., Ibrahim, P.N.G., Selezneva, N.V., Kazantsev, V.A., Volegov, A.S., and
757 Shishkin, D.A. (2014) Crystal structure, phase transitions and magnetic properties of pyrrhotite-
758 type compounds $\text{Fe}_{7-x}\text{TixS}_8$. Physica B: Condensed Matter, 449, 229–235.

759 Bertaut, E.F. (1953) Contribution à l'étude des structures lacunaires: la pyrrhotine. Acta
760 Crystallographica, 6, 557–561.

761 Besnus, M.J., and Meyer, A.J. (1964) Nouvelles données expérimentales sur le magnétisme de
762 la pyrrhotine naturelle. Proc. Int. Conf. Mag., 20, 507–511.

763 Bezaeva, N.S., Chareev, D.A., Rochette, P., Kars, M., Gattacceca, J., Feinberg, J.M., Sadykov,
764 R.A., Kuzina, D.M., and Axenov, S.N. (2016) Magnetic characterization of non-ideal single-
765 domain monoclinic pyrrhotite and its demagnetization under hydrostatic pressure up to 2 GPa with
766 implications for impact demagnetization. Physics of the Earth and Planetary Interiors, 257, 79–90.

767 Bin, M., and Pauthenet, R. (1963) Magnetic Anisotropy in Pyrrhotite. Journal of Applied
768 Physics, 34, 1161–1162.

769 Bither, T.A., Walter, P.H.L., Cloud, W.H., Swoboda, T.J., and Bierstedt, P.E. (1962) New
770 Modified Mn_2Sb Compositions Showing Exchange Inversion. Journal of Applied Physics, 33,
771 1346–1347.

Preprint submitted to American Mineralogist February 15, 2018

772 Cantu, J., Gonzalez, L.E., Goodship, J., Contreras, M., Joseph, M., Garza, C., Eubanks, T.M.,
773 and Parsons, J.G. (2016) Removal of arsenic from water using synthetic Fe₇S₈ nanoparticles.
774 Chemical Engineering Journal, 290, 428–437.

775 Charilaou, M., Kind, J., Koulialias, D., Weidler, P.G., Mensing, C., Loffler, J.F., and Gehring,
776 A.U. (2015) Magneto-electronic coupling in modulated defect-structures of natural Fe_{1-x}S.
777 Journal of Applied Physics, 118, 083903–6.

778 Dekkers, M.J. (1988) Magnetic properties of natural pyrrhotite Part I: Behaviour of initial
779 susceptibility and saturation-magnetization-related rock-magnetic parameters in a grain-size
780 dependent framework. Physics of the Earth and Planetary Interiors, 52, 376–393.

781 Dekkers, M.J., Mattéi, J.-L., Fillion, G., and Rochette, P. (1989) Grain-size dependence of the
782 magnetic behavior of pyrrhotite during its low-temperature transition at 34 K. Geophysical
783 Research Letters, 16, 855–858.

784 Dunlop, D.J. (2002) Theory and application of the Day plot (M_s versus H_c/H_c) 1.
785 Theoretical curves and tests using titanomagnetite data. Journal of Geophysical Research: Solid
786 Earth, 107, 2056.

787 Dunlop, D.J., and Özdemir, Ö. (1997) Rock Magnetism. Cambridge University Press,
788 Cambridge.

789 Erd, R.C., Evans, H.T., and Richter, D.H. (1957) Smythite, a New Iron Sulfide, and Associated
790 Pyrrhotite From Indiana. American Mineralogist, 42, 309–333.

791 Ericsson, T., Amcoff, Ö., and Nordblad, P. (1994) Vacancy ordering in Fe₇Se₈-Fe₇S₈ solid
792 solutions studied by Mössbauer, X-ray and magnetization techniques. Hyperfine Interactions, 90,
793 515–520.

Preprint submitted to American Mineralogist February 15, 2018

794 Fegley, B., Jr., Lodders, K., Treiman, A.H., and Klingelhöfer, G. (1995) The Rate of Pyrite
795 Decomposition on the Surface of Venus. *Icarus*, 115, 159–180.

796 Feinberg, J.M., Solheid, P.A., Swanson-Hysell, N.L., Jackson, M.J., and Bowles, J.A. (2015)
797 Full vector low-temperature magnetic measurements of geologic materials. *Geochemistry,*
798 *Geophysics, Geosystems*, 16, 301–314.

799 Fillion, G., and Rochette, P. (1988) The Low Temperature Transition In Monoclinic Pyrrhotite.
800 *Le Journal de Physique Colloques*, 49, C8–907–C8–908.

801 Gilder, S.A., Egli, R., Hochleitner, R., Roud, S.C., Volk, M.W.R., Le Goff, M., and de Wit,
802 M. (2011) Anatomy of a pressure-induced, ferromagnetic-to-paramagnetic transition in pyrrhotite:
803 Implications for the formation pressure of diamonds. *Journal of Geophysical Research: Solid*
804 *Earth*, 116, B10101.

805 Gillard, T.M., Phelan, D., Leighton, C., and Bates, F.S. (2015) Determination of the Lamellae-
806 to-Disorder Heat of Transition in a Short Diblock Copolymer by Relaxation Calorimetry.
807 *Macromolecules*, 48, 4733–4741.

808 E. S. R. Gopal (1966) *Specific Heats at Low Temperatures*, Plenum Press, New York

809 Grønvold, F., Stølen, S., Labban, A.K., and Westrum, E.F. (1991) Thermodynamics of iron
810 sulfides I. Heat capacity and thermodynamic properties of Fe₉S₁₀ at temperatures from 5 K to 740
811 K. *The Journal of Chemical Thermodynamics*, 23, 261–272.

812 Grønvold, F., Westrum, E.F., and Chou, C. (1959) Heat Capacities and Thermodynamic
813 Properties of the Pyrrhotites FeS and Fe_{0.877}S from 5 to 350°K. *The Journal of Chemical Physics*,
814 30, 528–531.

Preprint submitted to American Mineralogist February 15, 2018

815 Halgedahl, S.L., and Fuller, M.D. (1981) The dependence of magnetic domain structure upon
816 magnetization state in polycrystalline pyrrhotite. *Physics of the Earth and Planetary Interiors*, 26,
817 93–97.

818 Herndon, J.M., Rowe, M.W., Larson, E.E., and Watson, D.E. (1975) Origin of magnetite and
819 pyrrhotite in carbonaceous chondrites. *Nature*, 253, 516–518.

820 Jeandey, C., Oddou, J.L., Mattéi, J.-L., and Fillion, G. (1991) Mössbauer investigation of the
821 pyrrhotite at low temperature. *Solid State Communications*, 78, 195–198.

822 Kasama, T., Church, N.S., Feinberg, J.M., Dunin-Borkowski, R.E., and Harrison, R.J. (2010)
823 Direct observation of ferrimagnetic/ferroelastic domain interactions in magnetite below the
824 Verwey transition. *Earth and Planetary Science Letters*, 297, 10–17.

825 Kind, J., Garcia-Rubio, I., Charilaou, M., Nowaczyk, N.R., Loffler, J.F., and Gehring, A.U.
826 (2013) Domain-wall dynamics in 4C pyrrhotite at low temperature. *Geophysical Journal*
827 *International*, 195, 192–199.

828 Kittel, C. (1960) Model of Exchange-Inversion Magnetization. *Physical Review*, 120, 335–
829 342.

830 Kobayashi, H., Nozue, T., Matsumura, T., Suzuki, T., and Kamimura, T. (1999) The low-
831 temperature specific heat of FeS and M_{0.875}X (M = Fe, Co; X = S, Se) with a NiAs-like structure.
832 *Journal of Physics: Condensed Matter*, 11, 8673–8679.

833 Koulialias, D., Charilaou, M., Schäublin, R., Mensing, C., Weidler, P.G., Loffler, J.F., and
834 Gehring, A.U. (2018) Ordered defects in Fe_{1-x}S generate additional magnetic anisotropy
835 symmetries. *Journal of Applied Physics*, 123, 033902–11.

Preprint submitted to American Mineralogist February 15, 2018

- 836 Koulialias, D., Kind, J., Charilaou, M., Weidler, P.G., Loffler, J.F., and Gehring, A.U. (2015)
837 Variable defect structures cause the magnetic low-temperature transition in natural monoclinic
838 pyrrhotite. *Geophysical Journal International*, 204, 961–967.
- 839 Kuipers, A.J.M., and Brabers, V.A.M. (1979) Electrical transport in magnetite near the Verwey
840 transition. *Physical Review B*, 20, 594–600.
- 841 Lapakko, K.A. (2015) Preoperational assessment of solute release from waste rock at proposed
842 mining operations. *Applied Geochemistry*, 57, 106–124.
- 843 Lashley, J.C., Hundley, M.F., Migliori, A., Sarrao, J.L., Pagliuso, P.G., Darling, T.W., Jaime,
844 M., Cooley, J.C., Hults, W.L., Morales, L., and others (2003) Critical examination of heat capacity
845 measurements made on a Quantum Design physical property measurement system. *Cryogenics*,
846 43, 369–378.
- 847 Levinson, L.M., and Treves, D. (1968) Mössbauer study of the magnetic structure of Fe₇S₈.
848 *Journal of Physics and Chemistry of Solids*.
- 849 Li, C.H. (1932) Magnetic Properties of Magnetite Crystals at Low Temperature. *Physical*
850 *Review*, 40, 1002–1012.
- 851 Li, G., Zhang, B., Baluyan, T., Rao, J., Wu, J., Novakova, A.A., Rudolf, P., Blake, G.R., de
852 Groot, R.A., and Palstra, T.T.M. (2016) Metal–Insulator Transition Induced by Spin Reorientation
853 in Fe₇Se₈ Grain Boundaries. *Inorganic Chemistry*, 55, 12912–12922.
- 854 Mikami, I., Hirone, T., Watanabe, H., Maeda, S., Adachi, K., and Yamada, M. (1959) On the
855 Magnetic Anisotropy of a Pyrrhotite Crystal. *Journal of the Physical ...*, 14, 1568–1572.
- 856 Morimoto, N., Nakazawa, H., Nishigucmi, K., and Tokonami, M. (1970) Pyrrhotites:
857 Stoichiometric Compounds with Composition Fe_n–1Sn (n≥8). *Science*, 168, 964–966.

Preprint submitted to American Mineralogist February 15, 2018

858 Muhlbauer, S., Honecker, D., Perigo, E., Bergner, F., Disch, S., Heinemann, A., Erokhin, S.,
859 Berkov, D., Leighton, C., Eskildsen, M., and others (2018) Magnetic Small-Angle Neutron
860 Scattering. *Reviews of Modern Physics*, submitted.

861 Muttoni, G. (1995) “Wasp-waisted” hysteresis loops from a pyrrhotite and magnetite-bearing
862 remagnetized Triassic limestone. *Geophysical Research Letters*, 22, 3167–3170.

863 Muxworthy, A.R., Bland, P.A., Davison, T.M., Moore, J., Collins, G.S., and Ciesla, F.J. (2017)
864 Evidence for an impact-induced magnetic fabric in Allende, and exogenous alternatives to the core
865 dynamo theory for Allende magnetization. *Meteoritics & Planetary Science*, 112.

866 Nakazawa, H., and Morimoto, N. (1970) Pyrrhotite Phase Relations below 320°C. *Proceedings*
867 *of the Japan Academy*, 46, 678–683.

868 O'Reilly, W., Hoffmann, V., Chouker, A.C., Soffel, H.C., and Menyeh, A. (2000) Magnetic
869 properties of synthetic analogues of pyrrhotite ore in the grain size range 1-24 μm . *Geophysical*
870 *Journal International*, 142, 669–683.

871 Oddou, J.L., Jeandey, C., Mattéi, J.-L., and Fillion, G. (1992) Mössbauer study of the low-
872 temperature transition in pyrrhotite. *Journal of Magnetism and Magnetic Materials*, 104-107,
873 1987–1988.

874 Pastor, J.M., Pérez-Landazábal, J.I., Gómez-Polo, C., Recarte, V., Larumbe, S., Santamarta,
875 R., Fernandes Silva, M., Gómez Pineda, E.A., Winkler Hechenleitner, A.A., and Lima, M.K.
876 (2012) Entropy change linked to the magnetic field induced Morin transition in Hematite
877 nanoparticles. *Applied Physics Letters*, 100, 063102.

878 Powell, A.V., Vaqueiro, P., Knight, K.S., and Chapon, L.C. (2004) Structure and magnetism
879 in synthetic pyrrhotite Fe₇S₈: A powder neutron-diffraction study. *Physical Review B*.

Preprint submitted to American Mineralogist February 15, 2018

880 Quidelleur, X., Valet, J.-P., and Thouveny, N. (1992) Multicomponent magnetization in
881 paleomagnetic records of reversals from continental sediments in Bolivia. *Earth and Planetary*
882 *Science Letters*, 111, 23–39.

883 Rochette, P., Fillion, G., and Dekkers, M.J. (2011) Interpretation of Low-Temperature Data
884 Part IV: The Low-Temperature Magnetic Transition of Monoclinic Pyrrhotite. *The IRM Quarterly*,
885 21, 1–11.

886 Rochette, P., Fillion, G., Mattéi, J.-L., and Dekkers, M.J. (1990) Magnetic transition at 30–34
887 Kelvin in pyrrhotite: insight into a widespread occurrence of this mineral in rocks. *Earth and*
888 *Planetary Science Letters*, 98, 319–328.

889 Rochette, P., Lorand, J.P., Fillion, G., and Sautter, V. (2001) Pyrrhotite and the remanent
890 magnetization of SNC meteorites: a changing perspective on Martian magnetism. *Earth and*
891 *Planetary Science Letters*, 190, 1–12.

892 H. M. Rosenberg (1963) *Low Temperature Solid State Physics*, Oxford University Press, New
893 York,

894 Sato, K., Yamada, M., and Hirone, T. (1964) Megnetocrystalline Anisotropy of Pyrrhotite.
895 *Journal of the Physical Society of Japan*, 19, 1592–1595.

896 Schwarz, E.J., and Vaughan, D.J. (1972) Magnetic Phase Relations of Pyrrhotite. *Journal of*
897 *geomagnetism and geoelectricity*, 24, 441–458.

898 Sharp, W.E. (1966) Pyrrhotite: a Common Inclusion in South African Diamonds. *Nature*, 211,
899 402–403.

Preprint submitted to American Mineralogist February 15, 2018

900 Shepherd, J.P., Koenitzer, J.W., Aragón, R., Spalek, J., and Honig, J.M. (1991) Heat capacity
901 and entropy of nonstoichiometric magnetite $\text{Fe}_3(1-\delta)\text{O}_4$: The thermodynamic nature of the
902 Verwey transition. *Physical Review B*, 43, 8461–8471.

903 Shimada, K., Mizokawa, T., Mamiya, K., Saitoh, T., Fujimori, A., Ono, K., Kakizaki, A., Ishii,
904 T., Shirai, M., and Kamimura, T. (1998) Spin-integrated and spin-resolved photoemission study
905 of Fe chalcogenides. *Physical Review B*, 57, 8845–8853.

906 Shirai, M., Suzuki, N., and Motizuki, K. (1996) Electronic band structure and photoemission
907 spectra of Fe_7S_8 . *Journal of Electron Spectroscopy and Related Phenomena*, 78, 95–98.

908 Tokonami, M., Nishiguchi, K., and Morimoto, N. (1972) Crystal structure of a monoclinic
909 pyrrhotite (Fe_7S_8). *American Mineralogist*, 57, 1066–1080.

910 van der Pauw, L.J. (1958) A method of measuring the resistivity and Hall coefficient on
911 lamellae of arbitrary shape, *Philips Tech. Rev.* **20**, 220

912 Volk, M.W.R., Gilder, S.A., and Feinberg, J.M. (2016) Low-temperature magnetic properties
913 of monoclinic pyrrhotite with particular relevance to the Besnus transition. *Geophysical Journal*
914 *International*, 207, 1783–1795.

915 Weiss, B.P., Maloof, A.C., Tailby, N., Ramezani, J., Fu, R.R., Hanus, V., Trail, D., Bruce
916 Watson, E., Harrison, T.M., Bowring, S.A., and others (2015) Pervasive remagnetization of detrital
917 zircon host rocks in the Jack Hills, Western Australia and implications for records of the early
918 geodynamo. *Earth and Planetary Science Letters*, 430, 115–128.

919 Wolfers, P., Fillion, G., Ouladdiaf, B., Ballou, R., and Rochette, P. (2011) The Pyrrhotite 32
920 K Magnetic Transition. *Solid State Phenomena*, 170, 174–179.

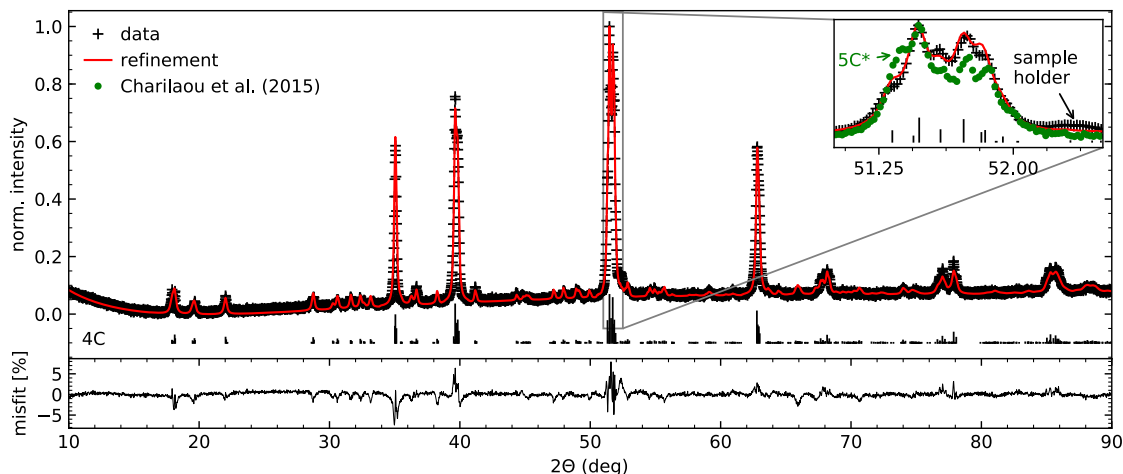
Preprint submitted to American Mineralogist February 15, 2018

921 Zhang, Kailong, Zhang, T., Liang, J., Zhu, Y., Lin, N., and Qian, Y. (2015) A potential
922 pyrrhotite (Fe₇S₈) anode material for lithium storage. RSC Advances, 5, 14828–14831.

923 Zhang, Ke, Zheng, H., Wang, J., and Wang, R. (2008) Transmission electron microscopy on
924 iron monosulfide varieties from the Suizhou meteorite. Physics and Chemistry of Minerals, 35,
925 425–432.

926

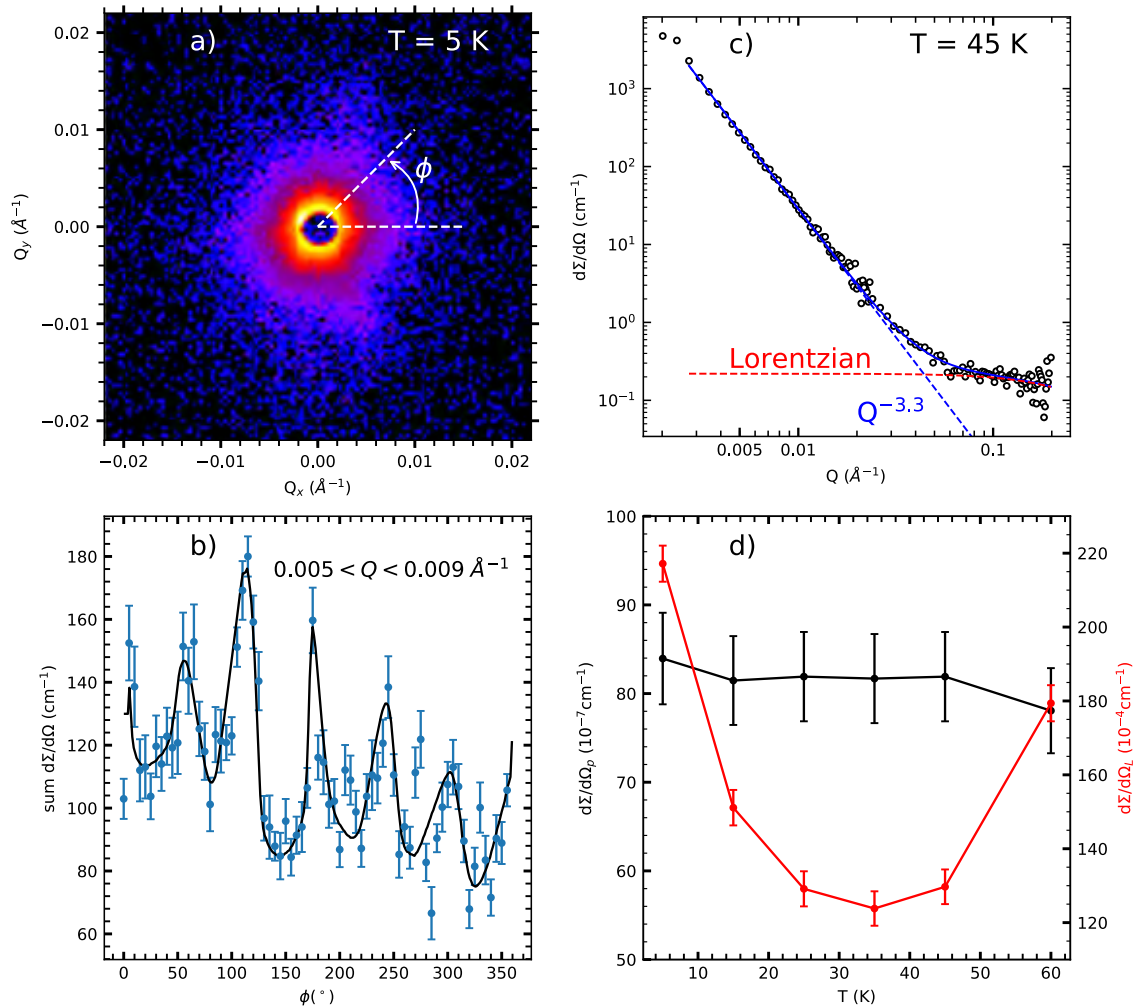
Preprint submitted to American Mineralogist February 15, 2018



927

928 **Figure 1:** Powder X-ray diffraction (room temperature) of a sister specimen using Co
929 radiation. The red line shows the fit obtained with Rietveld refinement. The inset shows an
930 expanded view of the most prominent peak, in comparison with data from Charilaou et al. (2015)
931 in green. The misfit is between the refinement and data.

Preprint submitted to American Mineralogist February 15, 2018



932

933 **Figure 2:** SANS results obtained with a 4C pyrrhotite crystal. a) The low Q 2D scattering
934 pattern (Q_x - Q_y map) obtained at 5 K (the brightness/color of each pixel indicates the differential
935 scattering cross-section). b) The sum of scattering cross-sections over the indicated low Q range
936 ($0.005 \text{ \AA}^{-1} < Q < 0.009 \text{ \AA}^{-1}$) as a function of the in-plane angle, ϕ , as defined in panel (a). These
937 data were averaged over all 6 temperatures probed (from 60 to 5 K), due to the absence of any
938 significant temperature dependence of the angular dependence. c) A representative ($T = 45 \text{ K}$)
939 scattering cross-section ($d\Sigma/d\Omega$) vs. Q scan obtained by circular integration of the 2D scattering
940 patterns. The fit (solid blue line) is the sum of a Porod term (blue dashed line) and a Lorentzian
941 term (red dashed line), as discussed in the text. These two terms are defined by $d\Sigma/d\Omega =$

Preprint submitted to American Mineralogist February 15, 2018

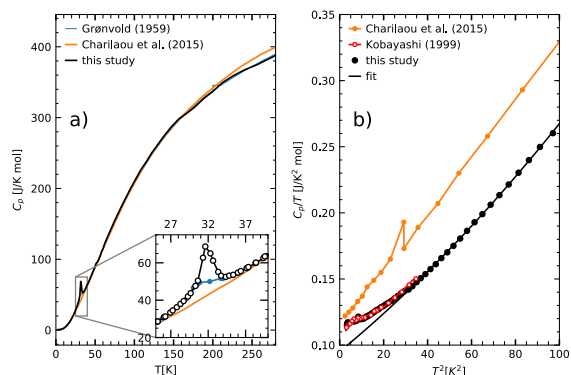
942 $(d\Sigma/d\Omega)_P/Q^n + (d\Sigma/d\Omega)_L/(Q^2 + \kappa^2)$, where “P” and “L” subscripts are for Porod and Lorentzian, n

943 is the generalized Porod exponent, and κ is defined in the text. d) The temperature (T) dependence

944 of the Porod (black) and Lorentzian (red) cross-sections, .

945

946



947

948 **Figure 3:** Heat capacity measurements obtained in this study along with those from previously

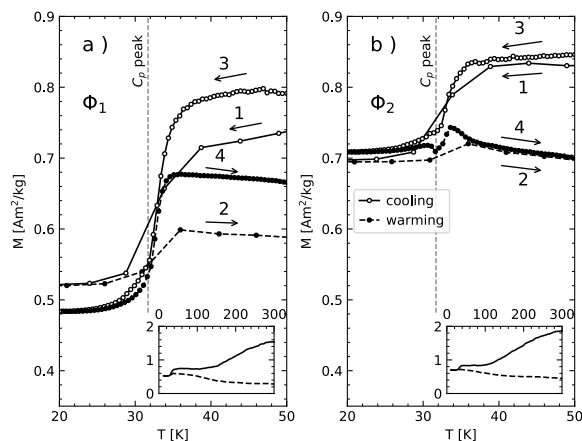
949 published studies. (a) C_p as a function of temperature (T), with the inset focusing on the Besnus

950 transition at 32 K. The solid lines are simple linear segments connecting data points. (b) C_p/T as a

951 function of T^2 at low temperature. The solid black line is a fit to the data as described in the text.

952

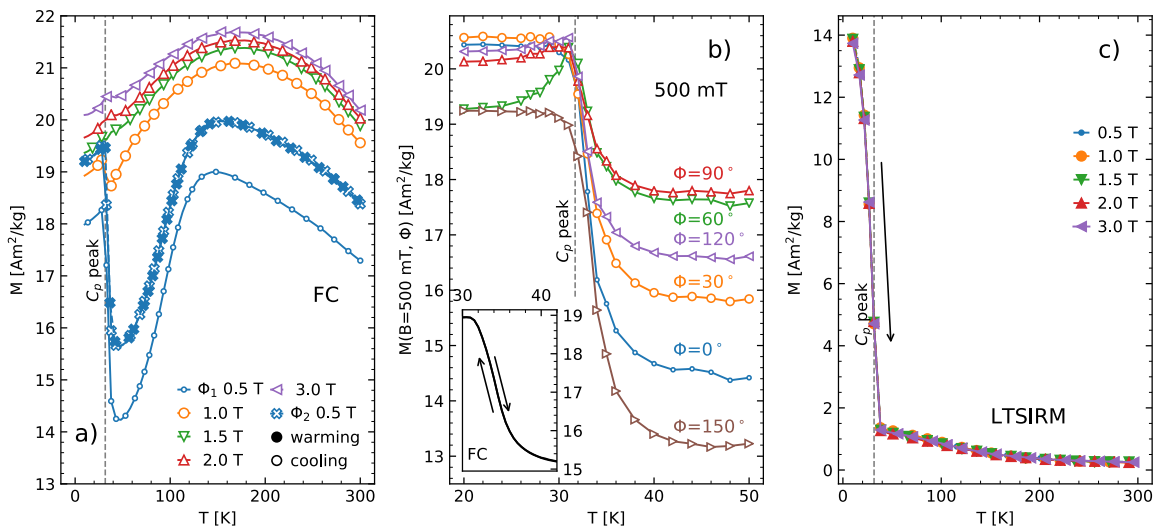
953



954

955 **Figure 4:** Zero field low-temperature cycling of a room temperature SIRM moment acquired
956 in a 2.5 T field in the basal (a-b) plane. a) and b) show different orientations of the single crystal.
957 The experiment was repeated twice for each orientation, where the first experiment was measured
958 using a larger temperature interval (every 5 K) than the second experiment (every 0.5 K). The
959 magnetization in the second experiment is usually higher than in the first, suggesting a slight
960 hardening after the first thermal cycling. Arrows show cooling or warming, numbers indicate the
961 measurement sequence. Dashed lines denote the temperature of the heat capacity peak. Insets in
962 both (a) and (b) are SIRM moments over the entire temperature range measured, with solid lines
963 being the cooling paths and dashed lines warming.

Preprint submitted to American Mineralogist February 15, 2018

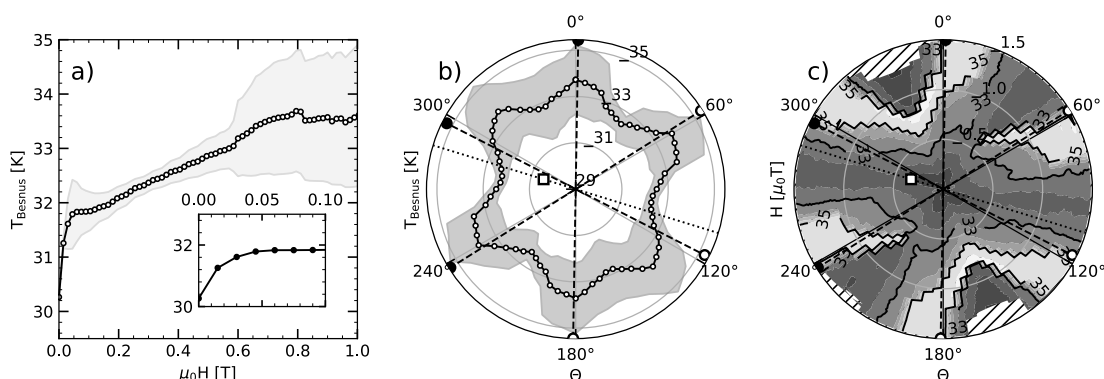


964

965 **Figure 5:** Field cooling (FC) experiments in different fields a). FC in 500 mT was measured
 966 along two arbitrary, perpendicular directions in the basal plane (Φ_1 , Φ_2). Crosses mark direction Φ_1
 967 on cooling and warming (filled marker). b) shows $M(B = 500 \text{ mT}, T, \Phi)$ determined from
 968 hysteresis loops (see text) at selected orientations within the basal plane of an oriented single
 969 crystal of Fe_7S_8 . Inset in b) demonstrates the lack of hysteresis of a high-resolution (0.5 K) FC
 970 measurement (see a)) in a 500 mT field (Φ_1) on warming and cooling. c) shows warming of a low-
 971 temperature SIRM acquired by cooling in field (a) to 10 K.

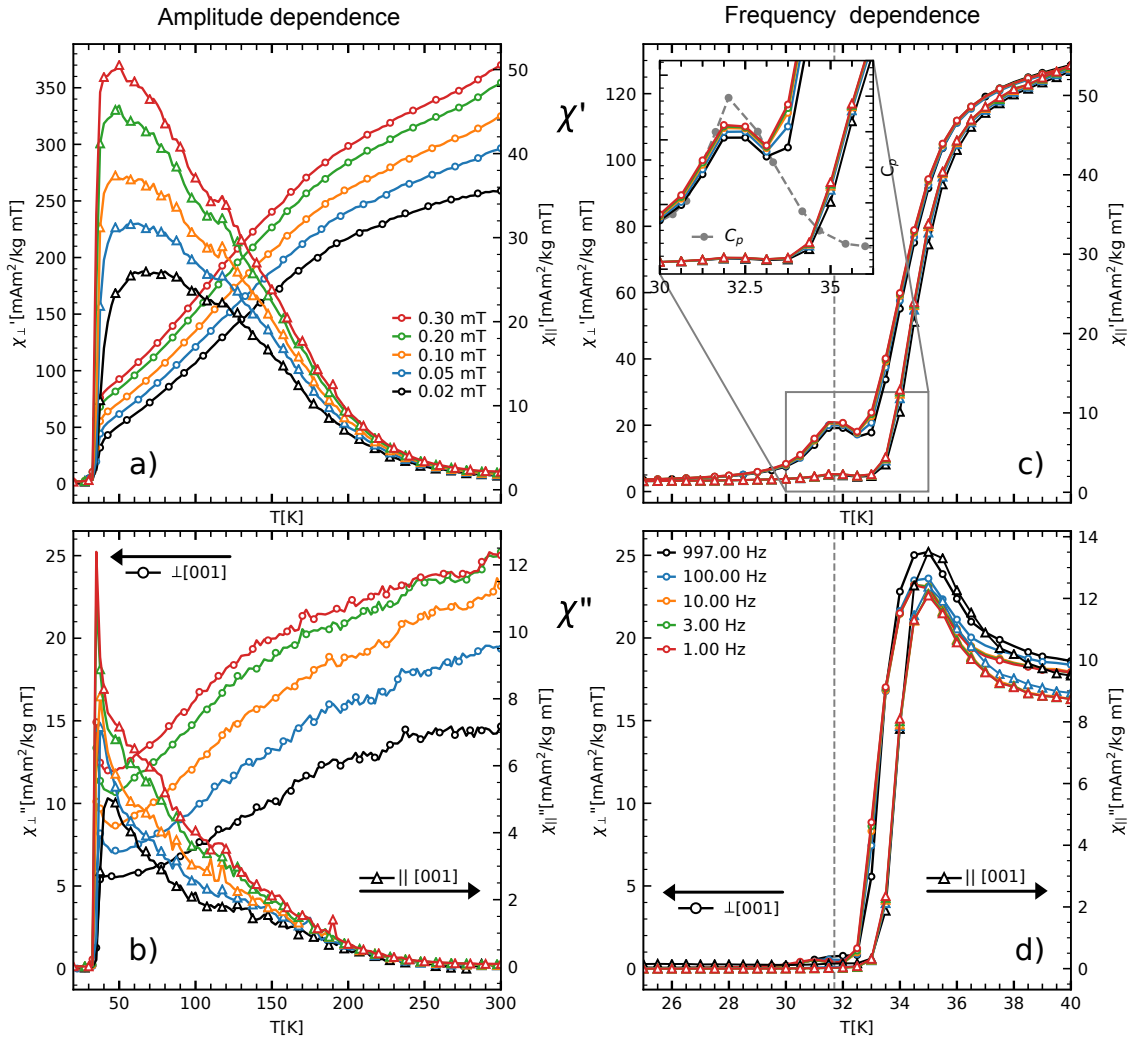
972

973



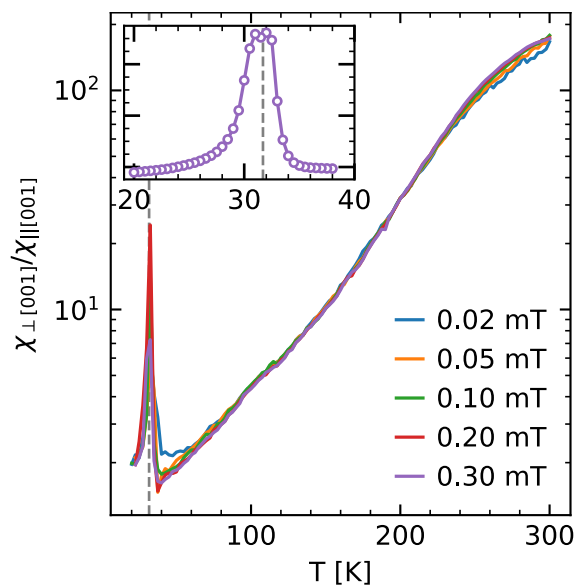
974 **Figure 6:** Transition temperature calculated from the maximum of dM/dT of the positive
975 ascending branch of the hysteresis loop for all orientations and fields. a) Average transition
976 temperature with one standard deviation (shaded region) for all orientations as a function of
977 magnetic field. The inset shows a zoomed-in view of the first 100 mT b) Directional dependence
978 of the mean transition temperature over all applied fields. A data point's distance from the center
979 of the plot corresponds to the T_{Bes} for that orientation and varies between 29 and 35K. The shaded
980 region shows 1σ uncertainty. c) Contour plot for all fields (radius) and orientation (angle), dark =
981 low, light = high transition temperature. Hashed regions show the area where T_{Bes} could not be
982 calculated. Solid lines in b) and c) show the crystallographic axis as determined by EBSD. The
983 dashed line is the projection of the c-axis onto the plane.

984



985

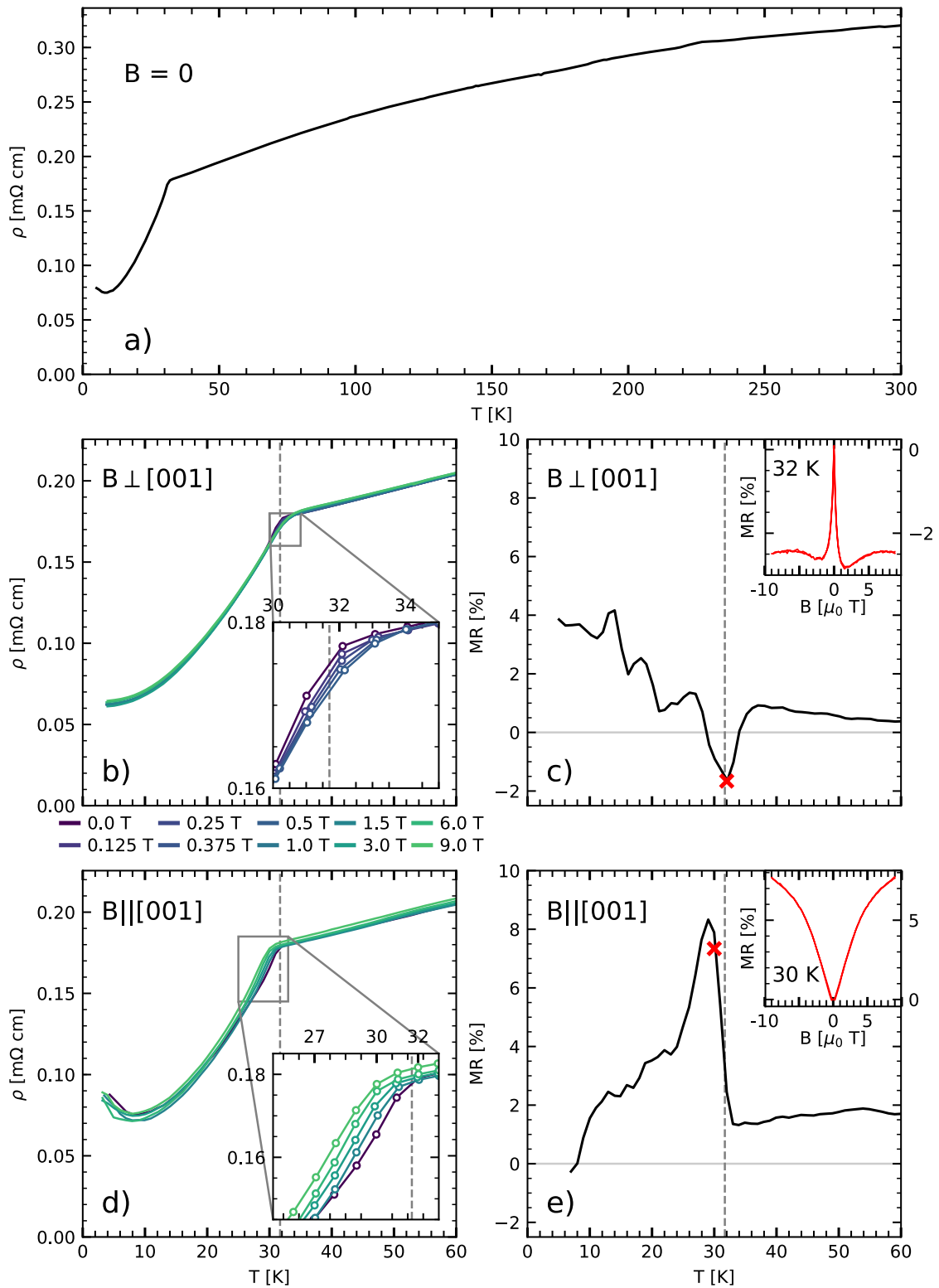
986 **Figure 7:** Mass-normalized in-phase (χ') and out-of-phase (χ'') susceptibility as a function of
 987 temperature in different field amplitudes (a, b) (frequency = 100 Hz, marker every 4th
 988 measurement) and frequencies (c, d) (amplitude = 0.30 mT). Circles show measurements within
 989 the basal plane (χ_{\perp}) of the crystal, while triangles show measurements done along the
 990 crystallographic c-axis (χ_{\parallel} , secondary y-axis). Dashed vertical lines show the maximum from the
 991 heat capacity measurement. Inset shows a zoom into the secondary peak overlaid with specific
 992 heat data (see. fig. 2) in arb. units. The background in specific heat was removed by polynomial
 993 interpolation.



994

995 **Figure 8:** Ratios of in-plane over out-of-plane susceptibilities ($\chi_{\perp}/\chi_{\parallel}$) as a function of
996 temperature for different field amplitudes. The inset shows the ratio determined from high-
997 resolution AC susceptibility data (100 Hz, 0.3 mT). The dashed line shows the transition
998 temperature determined from specific heat.

Preprint submitted to American Mineralogist February 15, 2018



999

1000

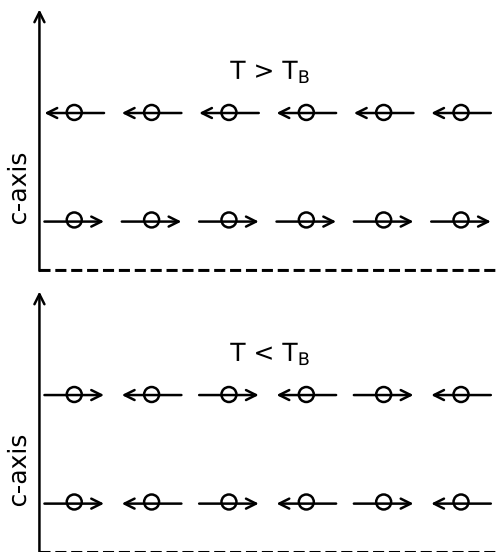
1001

Figure 9: 4C pyrrhotite single crystal electrical resistivity measured via the van der Pauw method as a function of temperature and magnetic field. (a) a-b plane resistivity (ρ) as a function

Preprint submitted to American Mineralogist February 15, 2018

1002 of temperature (T) upon warming from 4 K to 300 K in zero field (B). (b-d) show expanded views
1003 of transport and magnetotransport properties in the T_{BS} region. (b) ρ vs. T as a function of B (from
1004 0 – 0.5 T) applied in the basal plane. (c) Corresponding magnetoresistance (MR) as a function of
1005 T at 9 T. The inset shows the B dependence of the MR at 32 K. (d) ρ vs. T as a function of B (from
1006 0 - 9 T) applied along [001]. (e) Corresponding MR as a function of T at 9 T. The inset shows the
1007 B dependence of the MR at 30 K. Red crosses in (c) and (e) mark the measurement temperature
1008 for the MR(B) traces shown in the insets.
1009

Preprint submitted to American Mineralogist February 15, 2018



1010

1011 **Figure 10:** Schematic representation of exchange inversion. Arrows indicate the spins of the
1012 atoms.

1013

Preprint submitted to American Mineralogist February 15, 2018

1014 **Table 1:** Mean saturation magnetization ($M_s(\theta_1, \theta_2)$) determined from in-field cooling in a 3 T
1015 field and saturation remanence (M_{rs}) at 10 (LTSIRM) and 300 K (RTSIRM).

	$M_{rs} [Am^2/kg]$	$M_s [Am^2/kg]$	M_{rs}/M_s
<i>10 K</i>	13.85	20.09	0.69
<i>300 K</i>	1.67	20.19	0.08

1016

1017

Preprint submitted to American Mineralogist February 15, 2018

1018 **Table 2:** Amplitude dependence of susceptibility above (300 K) and below (20 K) T_{Bes} .

1019 Absolute values of the susceptibility are given in $\text{mAm}^2\text{kg}^{-1}\text{mT}^{-1}$

<i>Amplitude in mT</i>	<i>0.2</i>	<i>0.5</i>	<i>1.0</i>	<i>2.0</i>	<i>3.0</i>
$\chi_{\parallel}(300\text{ K})$	1.55	1.68	1.82	2.04	2.15
$\chi_{\parallel}(20\text{ K})$	0.97	0.97	0.95	0.96	0.96
$\chi_{\parallel}(20\text{ K} / 300\text{ K}) [\%]$	62.26	57.72	52.09	47.22	44.74
$\chi_{\perp}(300\text{ K})$	258.96	296.64	324.94	354.51	370.13
$\chi_{\perp}(20\text{ K})$	1.84	1.82	1.84	1.83	1.83
$\chi_{\perp}(20\text{ K} / 300\text{ K}) [\%]$	0.71	0.61	0.57	0.52	0.50
$\chi_{\perp}/\chi_{\parallel}(300\text{ K})$	166.86	176.60	178.43	174.15	172.55
$\chi_{\perp}/\chi_{\parallel}(20\text{ K})$	1.91	1.87	1.94	1.91	1.91

1020

1021