

# 1 **Low-temperature magnetism of alabandite: crucial** 2 **role of surface oxidation**

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25 **Abstract**

26 Manganese(II) monosulphide crystallizes into three different polymorphs (alpha-, beta-, and  
27 gamma-MnS). Out of these, alpha-MnS, also known as mineral alabandite, is considered the  
28 most stable and is widespread in terrestrial materials as well as in extraterrestrial objects such  
29 as meteorites.

30 In this study, the low-temperature antiferromagnetic state of alpha-MnS was investigated  
31 using macroscopic magnetic measurements as induced and remanent field-cooled (FC) and  
32 zero-field-cooled (ZFC) magnetizations and magnetic hysteresis. Both natural alabandite and  
33 synthetic samples show (i) Néel temperatures in a narrow temperature range around 153 K  
34 and (ii) a rapid increase of magnetization around 40 K. The anomalous magnetic behavior  
35 taking place at about 40 K was previously ascribed to a magnetic transition from the high-  
36 temperature antiferromagnetic to low-temperature ferromagnetic state documented for non-  
37 stoichiometric alpha-MnS slightly enriched in manganese. However, our detailed microscopic  
38 observations and in particular, oxidation experiments indicate that the anomalous magnetic  
39 behavior around 40 K is caused by the presence of oxide layer of ferrimagnetic hausmannite  
40 ( $Mn_3O_4$ ) on the surface of alpha-MnS rather than being an intrinsic property of nearly  
41 stoichiometric alpha-MnS.

42

43 **1. Introduction**

44 Alabandite is a manganese sulfide with theoretical composition MnS crystallizing in the cubic  
45 lattice of galena type (PbS). It occurs as an accessory mineral at many localities worldwide,  
46 mainly in epithermal base-metal sulfide veins, in low-temperature manganese deposits  
47 [Doelter, 1926; Hewett and Rove, 1930; Anthony *et al.*, 2012] and also in marine sediments  
48 [Lepland and Stevens, 1998]. Locally, it is an important ore mineral of Mn. Its name is

49 derived from its supposed discovery locality at Alabanda, Turkey. The type locality of  
50 alabandite is Sacarîmb, Romania [Anthony *et al.*, 2012].

51 Apart from terrestrial localities, alabandite is also relatively abundant in certain types of  
52 meteorites, e.g., in E chondrites [Keil, 1968; Zhang *et al.*, 1995; Zhang and Sears, 1996;  
53 Brearley and Jones, 1998] and related achondritic aubrites [Keil and Fredriksson, 1967;  
54 Ryder and Murali, 1987; Lin *et al.*, 1989; Mittlefehldt *et al.*, 1998]. It was also reported in  
55 some ureilites [Fioretti and Molin, 1998] and winonaites [Mason and Jarosewich, 1967].

56 Alabandite is paramagnetic at room temperatures and orders antiferromagnetically below its  
57 Néel temperature,  $T_N \sim 148$  K found out by Heikens *et al.* [1977]. A bit higher  $T_N$  ( $\sim 153$  K)  
58 was later published by Pearce *et al.* [2006]. A structural transition occurs at  $T \sim 130$  K which  
59 is usually interpreted as an abrupt inversion of the rhombohedral distortion of the f.c.c. lattice  
60 along [1 1 1] plane accompanied by a discontinuous change in the magnetic susceptibility  
61 observed on alabandite single crystals [Heikens *et al.*, 1977].

62 The magnetic susceptibility and induced field-cooled and zero-field-cooled magnetization (in  
63 10 mT of external magnetic field) of antiferromagnetic alabandite below its  $T_N$  are low,  
64 typically in the range of  $10^{-7}$  m<sup>3</sup>/kg and 3-4 mA/m<sup>2</sup>/kg, respectively. The substitution of Mn<sup>2+</sup>  
65 ions by Fe<sup>2+</sup> has a pronounced effect on the Néel temperature which increases with increasing  
66 iron content reaching  $\sim 185$  K for the Fe<sub>x</sub>Mn<sub>1-x</sub>S system with  $x = 0.2$  [Petrakovski *et al.*,  
67 2002]. Still, more iron-rich alabandite samples ( $x > 0.25$ ) exhibit ferrimagnetic behavior  
68 above room temperature with Curie temperatures  $T_C$  between 730 K ( $x = 0.27$ ) and 860 K ( $x$   
69 = 0.38) [Loseva *et al.*, 1998; Petrakovski *et al.*, 2002]. However, the magnetization of this  
70 ferrimagnetic-ordered alabandite is weak, close to that of paramagnetic MnS.

71 It was reported that iron-free MnS samples with a slight excess of Mn show antiferro- to  
72 ferromagnetic transition at  $T \sim 40$  K [Petrakovski *et al.*, 2001]. This transition manifests itself  
73 in a sharp, two orders of magnitude, increase of induced magnetization on cooling. Such a

74 sharp change in magnetic properties can significantly increase magnetic response of  
75 alabandite at low temperatures and can potentially contribute to low-temperature magnetic  
76 properties of extraterrestrial bodies [Kohout *et al.*, 2010]. Similar low-temperature magnetic  
77 transition is observed in troilite (FeS) [Kohout *et al.*, 1997; Cuda *et al.*, 2011]. Moreover,  
78 Gattacceca *et al.* [2011] recently reported that chromite with Curie temperature in 40–80 K  
79 range exist in certain meteorites and may significantly modify their low-temperature magnetic  
80 properties. Therefore, verification, interpretation and quantification of this magnetic  
81 phenomenon in alabandite samples and its comparison to low-temperature magnetic  
82 properties of troilite and chromite is required and is subject of this study.

83

## 84 **2. Materials and methods**

85 Basic characteristics of our samples are summarized in the Table 1. Natural polycrystalline  
86 sample of alabandite (NA) comes from Broken Hill, N.S.W., Australia; sample Bm 1972,  
87 294, kindly provided by Natural History Museum, London. Additionally, nearly  
88 stoichiometric alpha-MnS was synthesized adopting two alternative procedures

89 SA1 sample was prepared using a slightly modified solvothermal process of *Biswas and*  
90 *Chaudhuri* [2007]. First, manganese acetate [(CH<sub>3</sub>CO<sub>2</sub>)Mn·4H<sub>2</sub>O, purity >99.0%, Sigma  
91 Aldrich] and thiourea [CH<sub>4</sub>N<sub>2</sub>S, purity >99.0%, Sigma Aldrich] was mixed in molar ratio of  
92 1:3 with water solvent, loaded into ace pressure tube (Sigma Aldrich) and placed into a  
93 furnace at 190°C for 17 hours. Then, the dried product was annealed in helium atmosphere at  
94 temperatures up to 450°C.

95 SA2 sample was synthesized by direct thermal fusion of sulfur (purity >98.0%, Sigma  
96 Aldrich) and manganese (purity >99.0%, Sigma Aldrich) powders in stoichiometric molar  
97 ratio. The precursors were annealed twice in a sealed quartz tube under vacuum for 12 hours  
98 at 700°C including sample homogenization between two subsequent runs.



99 Measurements of the macroscopic magnetic response such as induced and remanent field-  
100 cooled (FC) and zero-field-cooled (ZFC) magnetizations and magnetic hysteresis  
101 measurements were carried out at the Institute for Rock Magnetism, University of Minnesota  
102 and at the Regional Centre of Advanced Technologies and Materials, Palacky University  
103 Olomouc, using MPMS5S and MPMS XL-7 (both Quantum Design) SQUID magnetometers.  
104 Details of FC and ZFC measurement procedure are provided in auxiliary material.

105 X-Ray Diffraction (XRD) patterns of all samples were recorded with a PANalytical X'Pert  
106 PRO MPD diffractometer (iron-filtered  $\text{CoK}\alpha$  radiation:  $\lambda = 0.178901$  nm, 40 kV and 30 mA)  
107 in the Bragg-Brentano geometry. Details of the XRD measurement procedure are provided in  
108 auxiliary material.

109 The bulk chemical composition of the SA2 sample was determined using quantitative X-ray  
110 wavelength dispersive spectral analysis on a MICROSPEC 3PC X-ray wavelength dispersive  
111 system (WDS) on a CamScan 3200 scanning electron microscope (SEM) at the Czech  
112 Geological Survey. The analyses were performed using an accelerating voltage of 20 kV,  
113 25 nA beam current, 1  $\mu\text{m}$  beam size and ZAF correction procedures. The counting times  
114 were 30 s for all analyzed elements. A combination of natural and synthetic standards was  
115 used for calibration.

116 SEM TESCAN VEGA 3XM at Institute of Geology, Academy of Sciences of the Czech  
117 Republic has been used to document surface features of the natural alabandite (NA sample).  
118 To avoid potential deterioration of the sample, the specimen has not been coated and the SEM  
119 has been operated at low-vacuum mode. Energy dispersive x-ray (EDX) spectra of individual  
120 phases observed on the surface of the studied specimen have been acquired with a Bruker  
121 XFlash detector attached to the SEM. Subsequently, part of the sample has been polished and  
122 analyzed with an electron microprobe (EMPA) CAMECA SX-100 instrument at Institute of

123 Geology, Academy of Sciences of the Czech Republic to determine the stoichiometry of the  
124 sample interior.

125

### 126 **3. Results and discussion**

#### 127 **3.1. Characterization and low-temperature magnetic properties of alpha-MnS**

128 XRD patterns of a natural alabandite (NA) and of two synthetic alpha-MnS (SA1 and SA2)  
129 samples are depicted in Figure 1a, 1b, and 1c. They perfectly correspond to the cubic structure  
130 of alpha-MnS (PDF No. 01-088-2223). In the NA sample, some amount of elemental sulfur  
131 (16% by Rietveld refinement) and hausmannite (see below) has been found in addition to the  
132 alabandite main phase. The presence of sulfur on NA sample surface was also confirmed by  
133 SEM/EDX (Figure S1 of the auxiliary material). In contrast EMPA of NA sample interior did  
134 not reveal any presence of sulfur or hausmannite. The SEM-WDS analysis of SA2 sample  
135 show similar results. Based on information provided above, all three studied samples can be  
136 considered as a representative of alabandite sample with only minor presence of other phases  
137 limited to surface of the individual grains.

138 Temperature dependences of induced FC and ZFC magnetizations at 10 mT (Figure 2) as well  
139 as remanent FC and ZFC magnetizations (imprinted by 2.5 T at 5 K, Figure 3) yield Néel  
140 temperatures ( $T_N$ ) for natural and synthetic samples in the narrow temperature range around  
141 153 K as expected for alabandite [*Pearce et al.*, 2006]. Néel temperature manifests itself in  
142 peaks on the induced magnetization curves, and in merging of FC and ZFC remanent  
143 magnetization curves at  $T_N$ .

144 In all the alabandite samples, we further observe magnetic feature at ~40 K manifested by a  
145 rapid increase of magnetic response with decreasing temperature (Figure 2 and 3). The  
146 enhanced magnetic response is also seen in hysteresis properties at 5 K, namely, an S-shaped

147 hysteresis loop and a tendency to saturation in a high external magnetic field (Figure 4). Such  
148 behavior is typical for ferro/ferrimagnetic materials rather than for an antiferromagnetic one.  
149 The enhanced magnetic response below 40 K is similar to that reported for iron-free alpha-  
150 MnS samples slightly enriched in Mn with respect to stoichiometric alpha-MnS and  
151 interpreted as antiferro- to ferromagnetic transition at 40 K upon cooling [*Petrakovski et al.*  
152 2001]. However, in our case, both NA and SA2 samples are highly stoichiometric examples  
153 of alabandite (Table 1). According to our measurements, the enhanced magnetic response at  
154 40 K occurs in all studied samples and its amplitude does not correlate with Mn/S ratio. Thus,  
155 the question arises whether such low-temperature behavior is limited to alabandite samples  
156 slightly enriched in Mn as reported by *Petrakovski et al.* [2001], or it is a general phenomenon  
157 occurring also in stoichiometric or Mn-depleted alabandite samples. Alternatively, a presence  
158 of small amounts of another phases on alabandite grain surfaces identified above may be  
159 responsible for the observed low-temperature magnetic behavior and will be evaluated in  
160 following section.

161

### 162 **3.2. Effects of surface oxidation on low-temperature magnetic properties of alpha-MnS**

163 In order to confirm or exclude the role of manganese oxides on magnetic response of alpha-  
164 MnS (sulfur should not significantly influence the low-temperature magnetic properties of  
165 alabandite), we artificially oxidized the SA1 sample by hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). About  
166 20 mg of SA1 material was briefly submerged in hydrogen peroxide and air-dried at room  
167 temperature for 20 hours (sample labeled as SA1\_OX). Subsequently, XRD and magnetic  
168 measurements were carried out following the same procedures as for other samples (Figures  
169 1d and 5).

170 Upon hydrogen peroxide treatment, surface of MnS was partially oxidized into manganese  
171 oxide phases and thus the ratio of alabandite to manganese oxides in the SA1\_OX sample

172 changed compared to original SA1 sample. Presence of Manganese oxide  $Mn_3O_4$ , known also  
173 as mineral hausmannite, was confirmed by XRD analysis in the SA1\_OX sample (Figure 1d).  
174 Hausmannite has Curie temperature  $T_C \sim 41-43$  K [Dwight and Menyuk, 1960; Robie and  
175 Hemingway, 1985]. It is very close to the temperature where enhanced magnetic response of  
176 alabandite is observed upon cooling, making hausmannite a meaningful candidate to explain  
177 the observed low-temperature magnetic behavior of alabandite. Other phases identified in the  
178 XRD pattern are bixbyite ( $\alpha$ - $Mn_2O_3$ , antiferromagnetic below 80 K [Robie and  
179 Hemingway, 1985] or 90 K [Mukherjee et al., 2006]) and sulfur (diamagnetic [O'Handley,  
180 2000; Blundell, 2001]). These phases do not have any magnetic transitions around 40 K which  
181 would be explained observed magnetic behavior at this temperature.

182 The oxidized SA1\_OX sample shows a significant (by a factor of eight) increase in its  
183 magnetic response below  $\sim 40$  K compared to the unoxidized  $\alpha$ -MnS sample (insets in  
184 Figure 5). The dependence of magnitude of the 40 K magnetic response on the amount of  
185 manganese oxides including hausmannite suggests that the low-temperature behavior  
186 observed in studied alabandite samples is not an intrinsic property of alabandite itself, but  
187 rather hausmannite governs the low-temperature magnetic response below 40 K. A similar  
188 example was described for antiferromagnetic MnO nanoparticles with  $Mn_3O_4$  surface layers  
189 [Berkowitz et al., 2008].

190 The low-temperature saturation magnetization ( $M_S$ ) of SA1\_OX sample (i.e., after oxidation)  
191 amounts to  $\sim 7.3$  Am<sup>2</sup>/kg at 5 K (Table 2) and it is consistent with a presence of  $\sim 19$  wt.% of  
192 hausmannite (assuming the bulk value of  $M_S$  for pure  $Mn_3O_4$  to be 38 Am<sup>2</sup>/kg [Tebble and  
193 Craik, 1969; Vázquez-Olmos et al., 2005]). According to Rietveld refinement, the amount of  
194 hausmannite in this oxidized sample equals to 23 wt.%. A difference between the values  
195 determined from Rietveld refinement and magnetic measurements may reflect the fact that  
196 hausmannite forms thin surface layer on alabandite particles. The small size of oxide particles

197 could result in a reduced saturation magnetization of hausmannite with respect to the bulk  
198 value due to finite size effect [Batlle and Labarta, 2002]. Moreover, the presence of thin  
199 surface layer of manganese oxides was also confirmed through broad diffraction peaks of  
200 hausmannite in the XRD pattern (Figure 1d). The limited periodicity of the phases forming  
201 the surface oxide shell could also negatively influence the result of Rietveld refinement.  
202 From the  $M_S$  values, we can also determine the hausmannite content in other samples.  
203 Approximately 2.3 wt.%, 0.1 wt.%, and 5 wt.% of hausmannite are required to produce the  
204 low-temperature magnetic response observed in SA1 (before oxidation), SA2, and natural  
205 alabandite (NA) samples, respectively. These values are close to, or below, the detection limit  
206 of XRD measurements and thus not observed in the XRD pattern of these samples except NA  
207 sample (~7 wt.% of  $Mn_3O_4$  calculated from Rietveld refinement).  
208 Furthermore, the profile of the temperature-dependent induced FC magnetization curve of  
209 samples NA, SA1 and especially SA1\_OX displays a tendency to follow the Curie-Weiss law  
210 above 40 K. The hysteresis loops below 40 K show also shift along field (horizontal) axis  
211 towards negative values (compare  $B_{c+}$  and  $B_{c-}$  in Table 2) which seems to be manifestation  
212 of exchange interactions between antiferromagnetic (alabandite) and ferrimagnetic  
213 (hausmannite) phases.  
214 In the sample SA2 with extremely low (~0.1%) hausmannite content, the magnetic signal  
215 above 40 K does not have tendency to follow the Curie-Weiss law and the low-temperature  
216 behavior is dominated by stronger alabandite antiferromagnetic response. This confirms our  
217 hypothesis that the anomaly at 40 K does not correspond to a magnetic transition in alabandite  
218 and is consistent with ferri- to paramagnetic transition of  $Mn_3O_4$  present in oxidized surface  
219 layer of alabandite grains.  
220 Upon heating in the temperature range between  $T_C$  of hausmannite and  $T_N$  of alabandite, the  
221 decreasing paramagnetic response of hausmannite overlaps with the slightly increasing

222 antiferromagnetic response of alabandite. A local minimum in the induced FC curve can be  
223 observed in this temperature range and it is shifted to the higher temperatures with increasing  
224 magnitude of hausmannite content (insets in Figure 2). In this case, it appears that there is a  
225 **direct correlation between the amount of hausmannite present in the sample and temperature**  
226 **at which the minimum occurs.** The estimated temperatures are 44 K, 89 K and 146 K for SA2,  
227 SA1, and NA samples, respectively, and follow positive trend with increasing hausmannite  
228 content. For sample SA1\_OX, we do not observe the minimum in temperature range from 40  
229 to 155 K because the paramagnetic response of hausmannite (and perhaps also of bixbyite)  
230 dominates over the antiferromagnetic response of alpha-MnS.

231 Last but not least, the temperature dependence of induced ZFC measurements of NA, SA1,  
232 SA2 and SA1\_OX samples exhibits a sharp peak below the Curie temperature ascribed to  
233 hausmannite, and then on subsequent heating drops down to very low values (Figures 2 and  
234 5a). The observed peak can be interpreted as a Hopkinson peak observed just prior to a  
235 transition from magnetically ordered state to paramagnetic one [Dunlop and Özdemir, 1997]  
236 rather than as an effect accompanying a magnetic transition from ferromagnetic to  
237 antiferromagnetic state as suggested by *Petrakovski et al.* [2001].

238 The positive correlation between Mn enrichment and magnitude of the 40 K feature observed  
239 in synthetic alabandite by *Petrakovski et al.* [2001] can be explained as the extra Mn added  
240 did not enter alabandite structure and rather reacted with oxygen to produce manganese  
241 oxides including hausmannite. Thus higher addition of Mn resulted in higher production of  
242 hausmannite causing higher amplitude of the 40 K feature.

243

### 244 **3.3. Comparison to other low-temperature magnetic minerals**

245 Similar low-temperature magnetic transition, as described above in alabandite – hausmannite  
246 system, is observed at ~70 K in other sulfur monosulfide - troilite FeS [Kohout *et al.*, 1997;

247 *Cuda et al.*, 2011]. *Gattacceca et al.* [2011] recently reported that chromite with Curie  
248 temperature in 40–80 K range exists in certain meteorites and further suggest that chromite  
249 contamination within troilite samples may be responsible for the observed ~70 K feature in  
250 troilite. In this respect alabandite with hausmanite contamination is analogue to troilite with  
251 proposed chromite contamination. Thus, in following paragraph we briefly compare  
252 alabandite – hausmannite system to the troilite and chromite.

253 At the first look both systems show very similar behavior with sharp increase in both induced  
254 and remanent magnetization and onset of ferromagnetic-like hysteresis below the transition  
255 temperature. The difference between these two systems is in nature of the contaminant.  
256 Hausmannite is of similar composition to alabandite (both manganese bearing phases) and is  
257 localized to surface coatings of alabandite grains. Thus it can be easily overlooked in EMPA  
258 analysis of polished grains. In contrast, chromite contamination is supposed to be present  
259 within interior of troilite grains and thus should be more easily observable. The thorough  
260 analytical data (EMPA and SEM-BSE (BackScattered Electrons) observation of polished  
261 grain sections, AAS (Atomic Absorption Spectroscopy), XRD and Mössbauer spectroscopy  
262 of bulk troilite samples in *Cuda et al.* [2011]) reveal chromium content one to three orders of  
263 magnitude lower than predicted for chromite amount explaining the low-temperature  
264 magnetic observations. Another difference can be observed on induced ZFC magnetization  
265 curves. While in alabandite – hausmannite case the ZFC induced magnetization stays well  
266 below FC showing pronounced Hopkinson peak just below  $T_C$  of hausmannite (Figure 2), the  
267 ZFC curve of troilite do not show obvious presence of Hopkinson peak (Figure 3 in *Kohout et*  
268 *al.* [1997]). Thus, the nature of the contaminant or mechanism of the low-temperature  
269 transition in troilite is likely to be different than proposed chromite (or similar to alabandite –  
270 hausmannite case).

271

272 **4. Conclusions**

273 Based on our detailed investigation, the low-temperature phenomenon at ~40 K, previously  
274 observed in some synthetic alabandite samples and ascribed to nonstoichiometry of the latter,  
275 is not the intrinsic property of alabandite. It appears to be a result of ferri- to paramagnetic  
276 transition of hausmannite ( $Mn_3O_4$ ) present in oxidized surface layer on crystals/grains of  
277 alabandite. Presence of hausmannite even in amounts below 1 wt.% can have a detectable  
278 effect on magnetic response of alabandite, which is otherwise a purely antiferromagnetic  
279 material below its Néel temperature of ~153 K without any other low-temperature magnetic  
280 transitions. This conclusion rules out pristine alabandite to significantly contribute to  
281 remanent or induced magnetism of minor Solar System bodies. In contrary, no prove of  
282 similar contamination has been found in troilite showing similar transition ~70 K.

283

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296



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387

388 **Figure captions**

389 **Figure 1** XRD patterns of the samples: (a) NA, (b) SA1, (c) SA2, and (d) SA1\_OX. Result of  
390 the Rietveld refinement of SA1\_OX sample is: 24 wt.% of MnS, 23 wt.% of Mn<sub>3</sub>O<sub>4</sub>, 23 wt.%  
391 of Mn<sub>2</sub>O<sub>3</sub>, and 30 wt.% of sulfur. The respective PDF cards are: 1 - 01-088-2223 (MnS); 2 -  
392 01-075-1560 (Mn<sub>3</sub>O<sub>4</sub>); 3 - 01-089-4836 (Mn<sub>2</sub>O<sub>3</sub>); 4 - 01-078-1888 (S).

393

394 **Figure 2** Induced-ZFC and FC magnetization curves in the external magnetic field of 10 mT  
395 for samples: (a) NA, (b) SA1 and (c) SA2.

396

397 **Figure 3** ZFC-FC curves of remanent magnetization imprinted by a field of 2.5 T for  
398 samples: (a) NA and (b) SA1.

399

400 **Figure 4** Hysteresis loops of samples: (a) NA, (b) SA1 and (c) SA2, measured at 5 K (the  
401 high-field slope has been subtracted).

402

403 **Figure 5** (a) Induced-ZFC and FC magnetization curves in the external magnetic field of  
404 10 mT for SA1\_OX sample. Induced-FC curves of the SA1 sample before and after oxidation  
405 are displayed for comparison in the inset. (b) ZFC-FC curves of remanent magnetization  
406 imprinted by a field of 2.5 T for the SA1\_OX sample. Remanent-FC curves of the SA1 before  
407 and after oxidation are displayed for comparison in the inset. (d) Hysteresis loops of the SA1  
408 sample before and after oxidation at 5 K after slope correction.

**Table 1** Alabandite samples.

Sample	Description of sample preparation	Stoichiometry of alabandite	Stoichiometry by means of
NA	natural alabandite	$\text{Mn}_{1.007}\text{S}$	EMPA on polished specimen
SA1	solvothermal process	n.d.	
SA2	direct thermal synthesis from S and Mn powders	$\text{MnS}_{0.998}\text{S}$	SEM/ WDS on polished specimen
SA1_OX	oxidation product of sample SA1	n.d.	

n.d. stands for not determined values.

**Table 2** Parameters of the hysteresis loops of (i) the NA, (ii) SA1, (iii) SA2 and (iv) SA1\_OX at 5 K after the high-field slope has been subtracted.

Sample	$T$ (K)	$M_{S+}$ (Am <sup>2</sup> /kg)	$M_{S-}$ (Am <sup>2</sup> /kg)	$B_{C+}$ (mT)	$B_{C-}$ (mT)	$M_{R+}$ (Am <sup>2</sup> /kg)	$M_{R-}$ (Am <sup>2</sup> /kg)
NA	5	1.910 ± 0.001	1.905 ± 0.001	424 ± 1	-608 ± 1	1.315 ± 0.001	-1.326 ± 0.001
SA1	5	0.882 ± 0.001	-0.874 ± 0.001	29 ± 1	-59 ± 1	0.344 ± 0.001	-0.225 ± 0.001
SA2	5	0.039 ± 0.001	-0.035 ± 0.001	4 ± 1	-24 ± 1	0.008 ± 0.001	-0.002 ± 0.001
SA1_OX	5	7.277 ± 0.001	7.235 ± 0.001	395 ± 1	-426 ± 1	4.564 ± 0.001	-4.376 ± 0.001

$M_{S+}$  is the positive saturation magnetization,  $M_{S-}$  is the negative saturation magnetization,  $B_{C+}$  is the positive coercivity,  $B_{C-}$  is the negative coercivity,  $M_{R+}$  is the positive remanent magnetization and  $M_{R-}$  is the negative remanent magnetization.

Diffraction intensity (a. u.)











