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Low-temperature magnetic properties of the Neuschwanstein EL6 meteorite

T. Kohout [a,b,c,*], A. Kosterov [d], M. Jackson [d], L.J. Pesonen [a], G. Kletetschka [c,e,g], M. Lehtinen [f]

[a] Division of Geophysics, University of Helsinki, Finland
[b] Department of Applied Geophysics, Charles University in Prague, Czech Republic
[c] Institute of Geology, Academy of Sciences of the Czech Republic, Prague, Czech Republic
[d] Institute for Rock Magnetism, University of Minnesota, Minneapolis, MN, USA
[e] Department of Physics, Catholic University of America, Washington D.C., USA
[f] Geological Museum, University of Helsinki, Finland
[g] GSFC/NASA, Code 691, Greenbelt, MD, USA

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Abstract

The low-temperature magnetic properties of the Neuschwanstein EL6 meteorite as well as of the daubreelite ($FeCr_2S_4$), troilite (FeS), and FeNi mineral phases were investigated. Low-temperature magnetic behavior of the Neuschwanstein meteorite appears to be controlled mostly by FeNi. However, two magnetic features at ~70 K (T_m) and 150 K (T_c), are due to a magnetic transition in and Curie temperature of ferrimagnetic daubreelite. The ~10 K variations in T_m and T_c among daubreelite in the Neuschwanstein meteorite, daubreelite from the Coahuila meteorite and synthetic daubreelite [Tsurkan, V., Baran, M., Szymczak, R., Szymczak, H., Tidecks, R., 2001a. Spin-glass like states in the ferrimagnet $FeCr_2S_4$. Physica B, 296, 301−305.] might be due to slightly different Fe/Cr stoichiometric ratios, the presence of impurities, or crystalline lattice defects.

In the antiferromagnetic troilite a magnetic transition at T_m ~60 K was identified. Its nature seems to be most likely due to a change in the orientation and attendant canting of the antiparallel spins. However, this feature was not identified in the Neuschwanstein meteorite measurements because of low concentration and weak magnetization of the troilite phase compared to those of FeNi and daubreelite.

Daubreelite with its T_c ~160 K might be a significant magnetic mineral in cold environment. Low-temperature magnetic data of daubreelite, troilite and FeNi presented here are useful for the interpretation of the low-temperature magnetic measurements of various extraterrestrial materials and for the identification of the presence of these phases.

Keywords: Neuschwanstein meteorite; daubreelite; troilite; kamacite; magnetism; magnetomineralogy; magnetic properties

1. Introduction

The Neuschwanstein meteorite fell on April 6, 2002 close to Neuschwanstein castle in Bavaria, Germany (Spurný et al., 2002; Oberst et al., 2004; ReVelle et al.,

* Corresponding author. Division of Geophysics, P. O. Box 64, 00014 Helsinki University, Finland. Tel.: +358 919151008; fax: +358 919151000.
E-mail address: tomas.kohout@helsinki.fi (T. Kohout).

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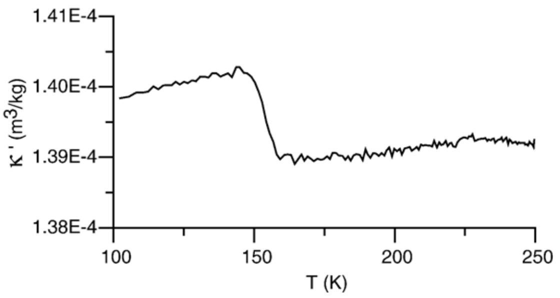

Fig. 1. An abrupt change in susceptibility at ~150 K was observed during the initial magnetic studies of Neuschwanstein meteorite. This feature was later linked to the Curie temperature of mineral daubreelite.

2004). Based on its chemical composition the Neuschwanstein meteorite is classified as an enstatite chondrite EL6 (Zipfel and Dreibus, 2003). In total three meteorite bodies were discovered. Two fragments coming from a 1750 g Neuschwanstein I. body found on July 14, 2002 were examined at the Division of Geophysics, University of Helsinki (HU). The relatively short time between the fall and recovery of the meteorite body (3 months) gives us an opportunity to study fresh unweathered material.

An initial magnetic study of the Neuschwanstein meteorite (Kohout et al., 2005) was carried out at HU. During the measurements an abrupt change in susceptibility at ~150 K was observed (Fig. 1). This feature was repeatable but, its nature was not well understood. The iron bearing sulfides (troilite FeS, daubreelite $FeCr_2S_4$, and alabandite (Mn,Fe)S) identified in the meteorite through mineralogical (optical and electron microscopy study of the Neuschwanstein thin sections — Bischoff and Zipfel, 2003) and Mössbauer analysis (Hochleitner et al., 2004) were considered as the candidate phases responsible for this magnetic susceptibility anomaly. The change in susceptibility at ~150 K is very close to the Curie temperature T_c ~170 K of the synthetic daubreelite ($FeCr_2S_4$) as reported by Tsurkan et al., 2001a. Thus the question is raised whether the ~150 K feature can be related to the daubreelite within Neuschwanstein meteorite.

In order to answer this question detailed low-temperature magnetic measurements of the Neuschwanstein meteorite were carried out at the Institute for Rock Magnetism, University of Minnesota (IRM) and at the Institute of Geology, Academy of Sciences of the Czech Republic (GLI). Various magnetic parameters of Neuschwanstein meteorite were measured in the temperature range of 10–300 K. For purposes of comparison, similar measurements were made on natural daubreelite ($FeCr_2S_4$), troilite (FeS), and synthetic iron nickel alloy specimens. The samples are described in more detail below, together with their low-temperature magnetic characteristics.

2. Instruments and methods

The temperature dependence of magnetic susceptibility was measured on a KLY-3S kappa-bridge (operating at 875 Hz frequency and 300 A/m RMS field intensity) at HU, on a KLY-4S kappa-bridge (operating at 875 Hz frequency and 2–450 A/m RMS field intensity) at GLI, both equipped with CS-3 and CS-L units, and on

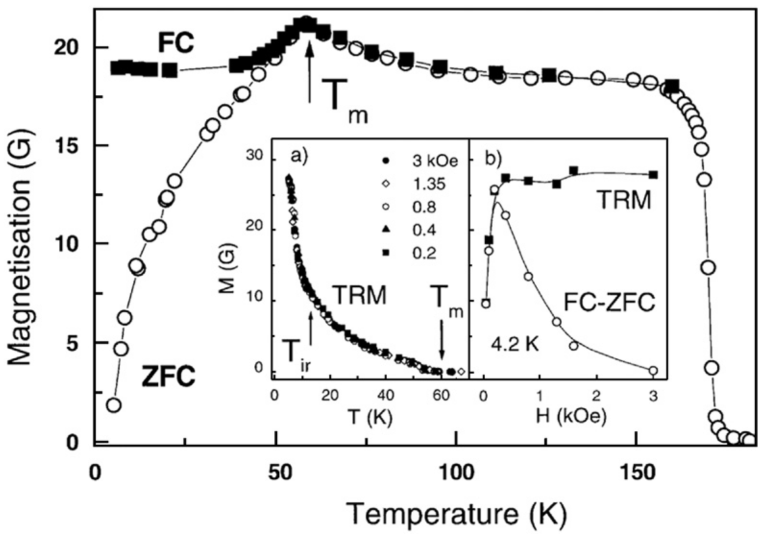

Fig. 2. Temperature dependences of the ZFC, FC and TRM magnetizations of a $FeCr_2S_4$ single crystal in a magnetic field of 10 mT applied in the direction of easy magnetization ⟨100⟩. Insets: (a) Temperature dependences of the TRM magnetization for different values of the cooling field. (b) Field dependences of the TRM magnetization and of the FC-ZFC difference at 4,2 K. The figure is adopted from Tsurkan et al., 2001a. Unit conversions: 1 Oe = 100 μT; 1 G = $10^3/4\pi$ A/m.

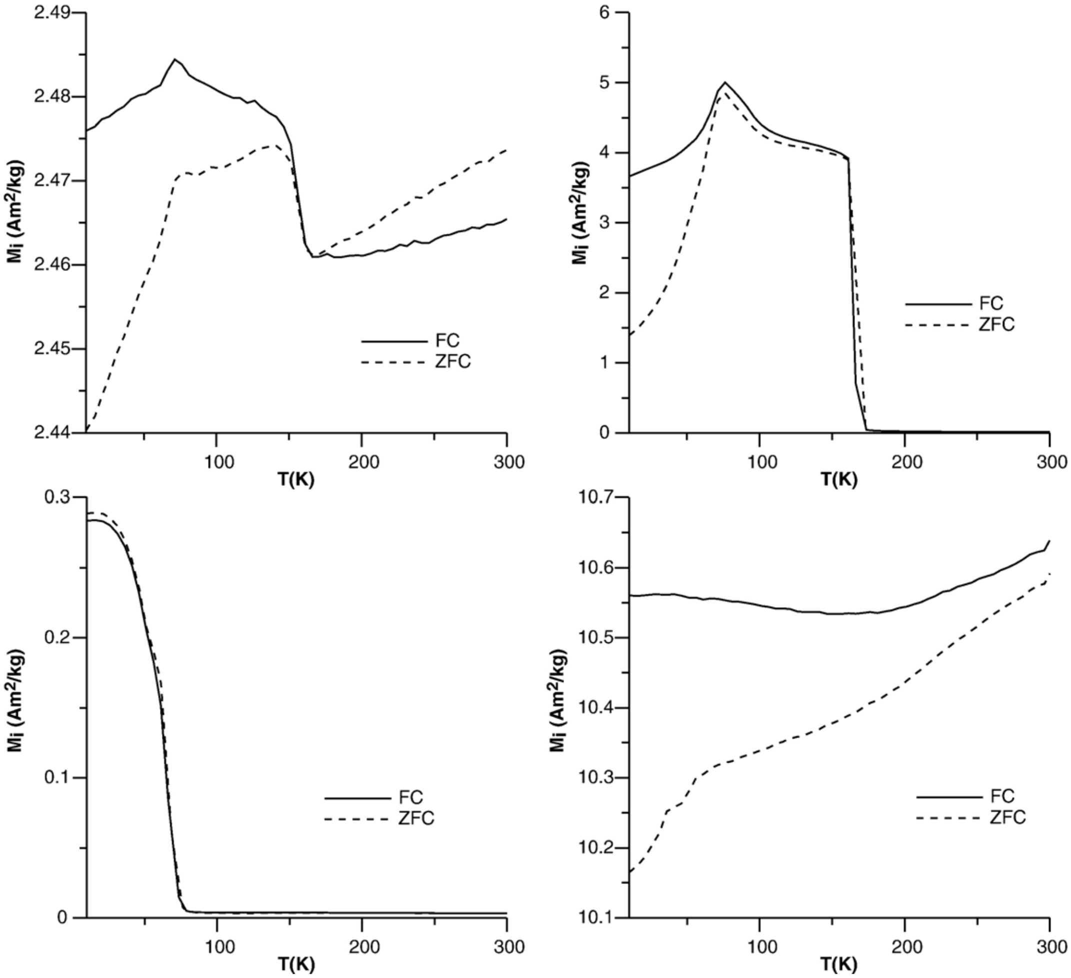

Fig. 3. FC and ZFC induced magnetization of the Neuschwanstein meteorite (upper left), daubreelite (upper right), troilite (lower left), and FeNi20 (lower right).

a LakeShore 7000 Series AF susceptometer (operating at 40–4000 Hz frequency and 30–2000 A/m RMS field intensity) at IRM.

The low-temperature hysteresis loops (max. field 1 T) were measured on a Princeton Measurements Corporation Model 3900 VSM (Vibrating Sample Magnetometer) and additional measurements were done on a Quantum Designs MPMS-5S cryogenic susceptometer (AC/DC, max. field 5 T), both at IRM.

The MPMS-5S was used also for the FC (Field Cooled) and ZFC (Zero Field Cooled) curves of remanent (imprinted by 2.5 T field) and induced (10 mT field) magnetization.

3. Synthetic and natural daubreelite ($FeCr_2S_4$)

Daubreelite is the naturally occurring mineral that crystallizes in the cubic spinel lattice, Fe^{2+} occupying tetrahedral and Cr^{3+} octahedral sites. Below the Curie temperature T_c ~170 K Fe^{2+} and Cr^{3+} spins are antiparallel, their inequality producing an overall ferrimagnetic order. Much recent interest in $FeCr_2S_4$ has been stimulated by the discovery of its colossal magnetoresistance (CMR) effect (Ramirez et al., 1997; Kim et al., 2002). Magnetic properties of the synthetic $FeCr_2S_4$ are summarized in Tsurkan et al. (2001a,b,c). From the Fig. 2 published in Tsurkan et al. (2001a) the FC and ZFC curves of the weak-field induced magnetization indicate the Curie temperature T_c ~170 K and a magnetic transition at T_m ~60 K. Further cooling through magnetic transition at T_m is accompanied by spin-glass-like features and cubic-to-triclinic symmetry reduction within crystallographic domains (Tsurkan et al., 2001a, b,c; Maurer et al., 2003; Müller et al., 2006).

The natural daubreelite crystals extracted from the Coahuila IIAB hexaedrite iron meteorite (obtained at HU

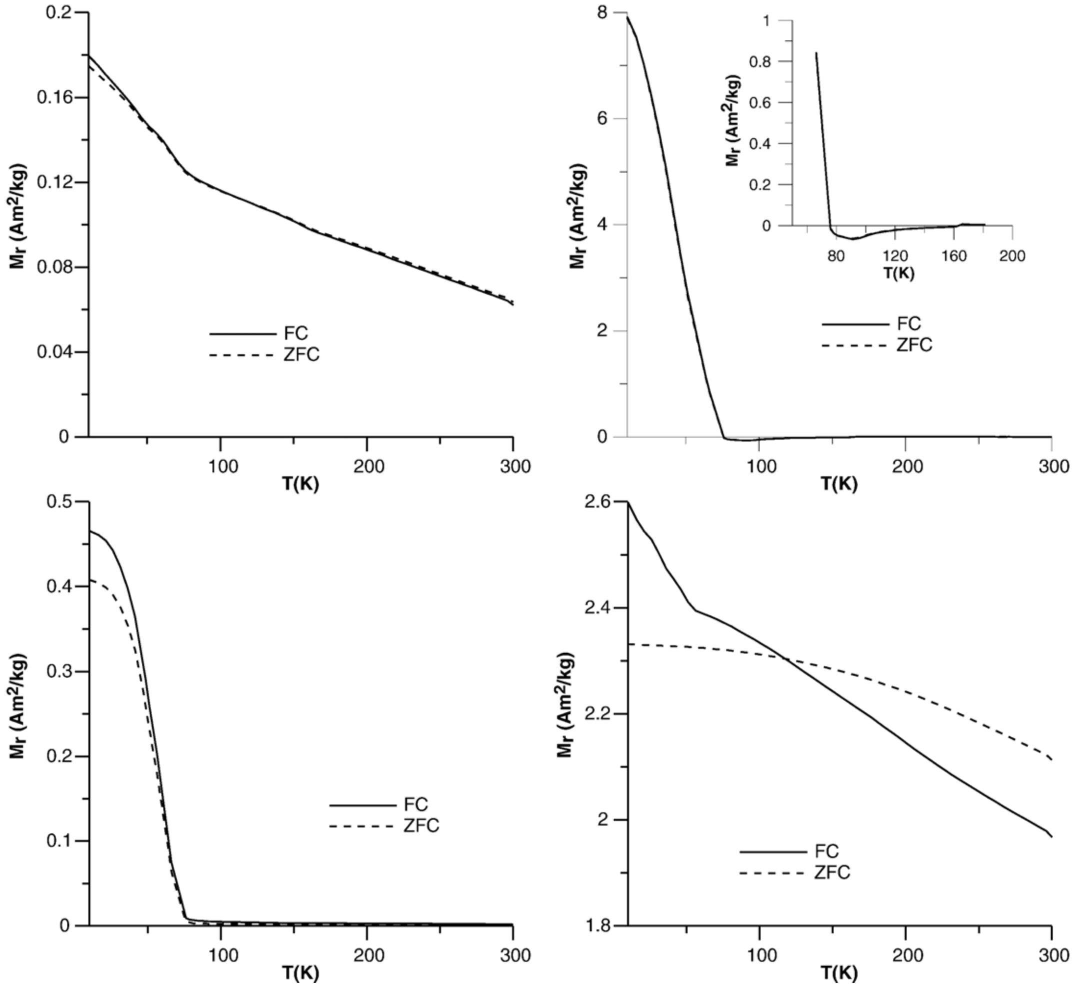

Fig. 4. FC and ZFC remanent magnetization of the Neuschwanstein meteorite (upper left), daubreelite (upper right), troilite (lower left), and FeNi20 (lower right). Note the reversal of remanence in daubreelite while heating above T_m.

Geological Museum) were used in this study for the low-temperature magnetic properties measurements. The low-temperature magnetic properties of the natural daubreelite (this work) are similar to those of synthetic $FeCr_2S_4$ (published in Tsurkan et al., 2001a, Fig. 2). From the FC and ZFC curves of the induced magnetization the Curie temperature $T_c \sim 160$ K and magnetic transition $T_m \sim 74$ K can be identified (Fig. 3). The FC and ZFC curves of the remanent magnetization show the presence of significant remanence at temperatures below T_m (Fig. 4). However, warming above T_m almost completely erases the low-temperature remanence: the moment for $T > T_m$ is only ~1% of the initial value, and moreover it is of opposite sign.

The low-temperature magnetic susceptibility curves (Figs. 5 and 6, and Figs. 9 and 10 in the Appendix) reveal both T_m and T_c and show a slight field dependence (probably due to the multi-domain (MD) character of our samples) which is significantly biased at temperatures around T_m.

The low-temperature hysteresis properties of daubreelite (Fig. 7) are characterized by a steep increase in saturation magnetization M_s and an appearance of coercivity B_c at temperatures below T_c. The M_s reaches maximum (~30 Am^2/kg) around T_m. Below T_m, M_s starts slightly to drop and B_c significantly increases up to 23 mT at 10 K.

4. Troilite (FeS)

Troilite is an iron sulfide with ideal composition FeS. It crystallizes into a peculiar lattice (space group $P\bar{6}2c$), which can be thought of as being derived from the NiAs structure. The troilite supercell axes are given as

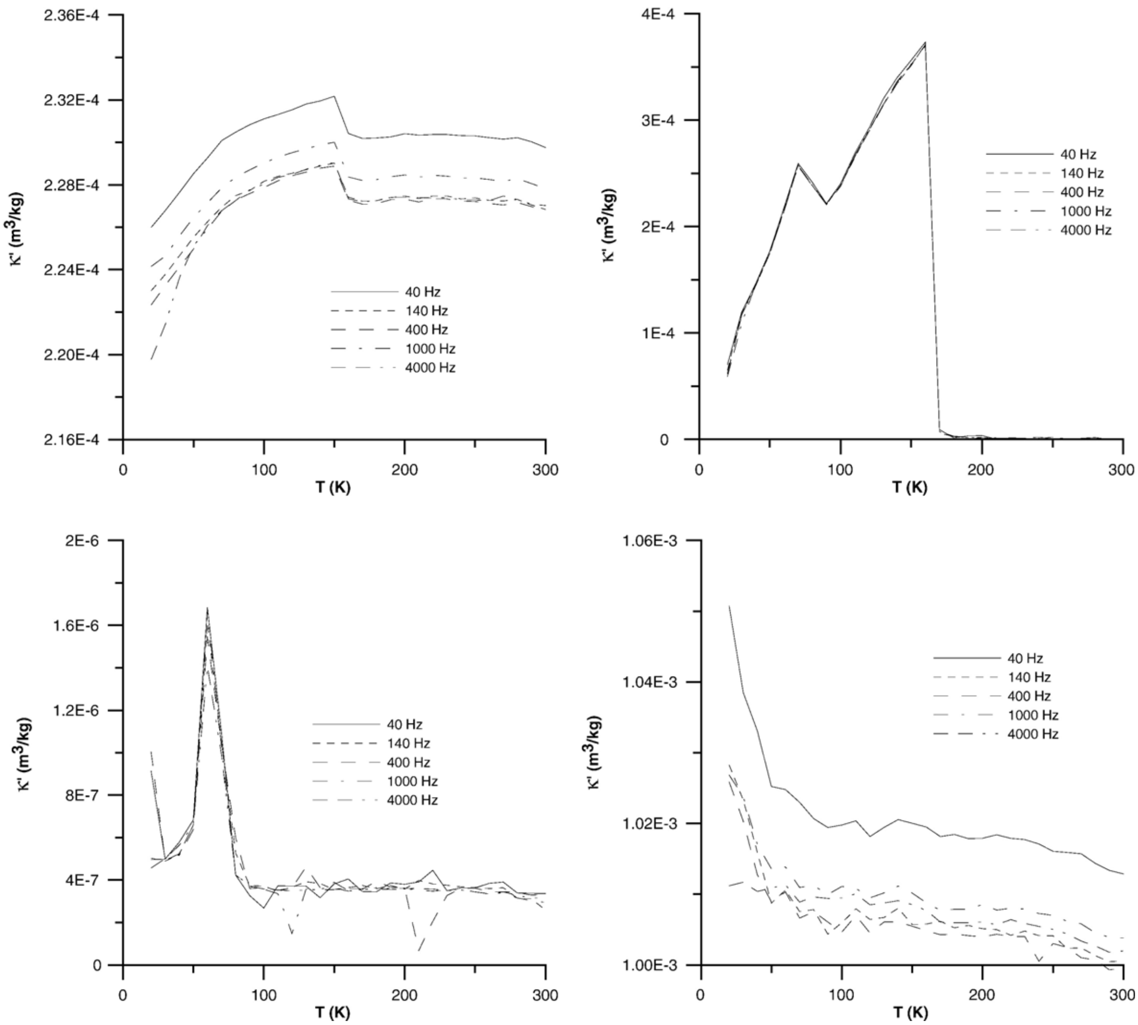

Fig. 5. Real component of the magnetic susceptibility (measured at 200 A/m and various frequencies) of the Neuschwanstein meteorite (upper left), daubreelite (upper right), troilite (lower left), and FeNi20 (lower right).

$a=\sqrt{3}A$ and $c=2C$, where A and C are NiAs subcell axes (Hägg and Sucksdorff, 1933). Magnetic properties of troilite above room temperature have been studied extensively (Haraldsen, 1937, 1941; Murakami and Hirahara, 1958; Hirahara and Murakami, 1958; Murakami, 1959; Schwarz and Vaughan, 1972; Horwood et al., 1976; Li and Franzen, 1996). Between room temperature and Neél temperature of 588 K (315 °C) troilite is antiferromagnetic, with spins parallel to the C-axis of the NiAs subcell below ca. 445 K (Horwood et al., 1976) and orthogonal to it at higher temperatures up to the Neél point. However, we were unable to find in the literature any data on the magnetic properties of troilite between 4.2 K and 300 K.

To fill this gap, we have measured low-temperature magnetic properties of the troilite powderized fraction extracted from the Bruderheim L6 chondrite (this sample was obtained from Dr. Peter Wasilewski, NASA Goddard Space Flight Center). From the FC and ZFC curves of the induced (by a 10 mT field) and remanent (imprinted by a 2.5 T field) magnetizations a magnetic transition at T_m ~60 K is inferred (Figs. 3 and 4). In susceptibility curves this transition is characterized with peaks in real and imaginary component showing both frequency and field dependence (Figs. 5 and 6, and Figs. 9 and 10 in the Appendix). Below T_m both M_s and B_c rapidly increase (Fig. 7). Hysteresis loops measured at low (5 K and 10 K) temperatures (Fig. 8) indicate that below T_m the material becomes extremely magnetically hard with coercivity over 200 mT and saturation not fully reached even in a 5 T field. The above data suggest that this transition should involve a change in the orientation of the antiparallel

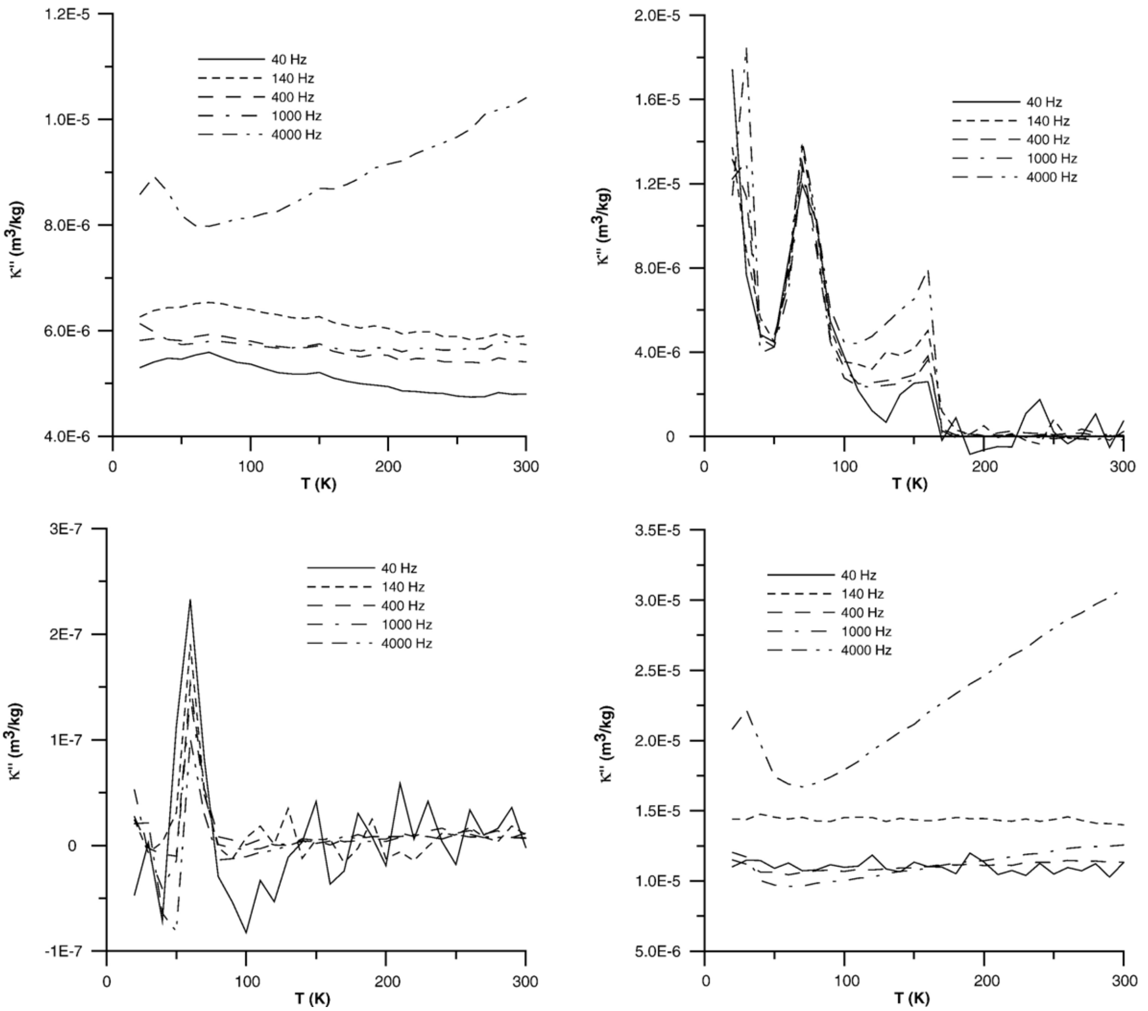

Fig. 6. Imaginary component magnetic susceptibility (measured at 200 A/m and various frequencies) of the Neuschwanstein meteorite (upper left), daubreelite (upper right), troilite (lower left), and FeNi20 (lower right).

magnetic spins. A most likely candidate is canting of antiparallel spins below T_m which would result in an increase of magnetic susceptibility as well as of the induced and remanent magnetization, similar to that observed in hematite when passing through the Morin transition from below. The extreme magnetic hardness of the low-temperature phase is then explained by random orientation of canted antiparallel spins in a powdery sample. However, it must be stressed that the nature of this transition is not yet fully understood and need further study.

5. Iron nickel alloys

The synthetic FeNi20 (20% of Ni) and FeNi24 (24% of Ni) alloys (obtained from Dr. Peter Wasilewski, NASA Goddard Space Flight Center) were used for comparison with the Neuschwanstein meteorite sample behavior. Prior to the experiments the alloys were hand-filed to ~0.5 mm grain size. Both samples show similar magnetic behavior. The difference between the FC and ZFC curves of the induced magnetization (Fig. 3 and Fig. 11 in the Appendix) points to the presence of a significant remanence. The FC curves of the remanent magnetization (Fig. 4 and Fig. 11 in the Appendix) shows a multiple sudden changes in slope at temperatures below ~60 K. These features are also visible as a sudden increase of M_s in the same temperature range (Fig. 7 and Fig. 11 in the Appendix). The origin of this behavior is not clear.

The susceptibility behavior of the FeNi20 and FeNi24 samples is similar. The real component (Fig. 5 and Fig. 12 in the Appendix) show slight decrease with increasing temperature. The ~60 K feature can be observed at lower frequencies as a change in slope of the susceptibility vs. temperature curve.

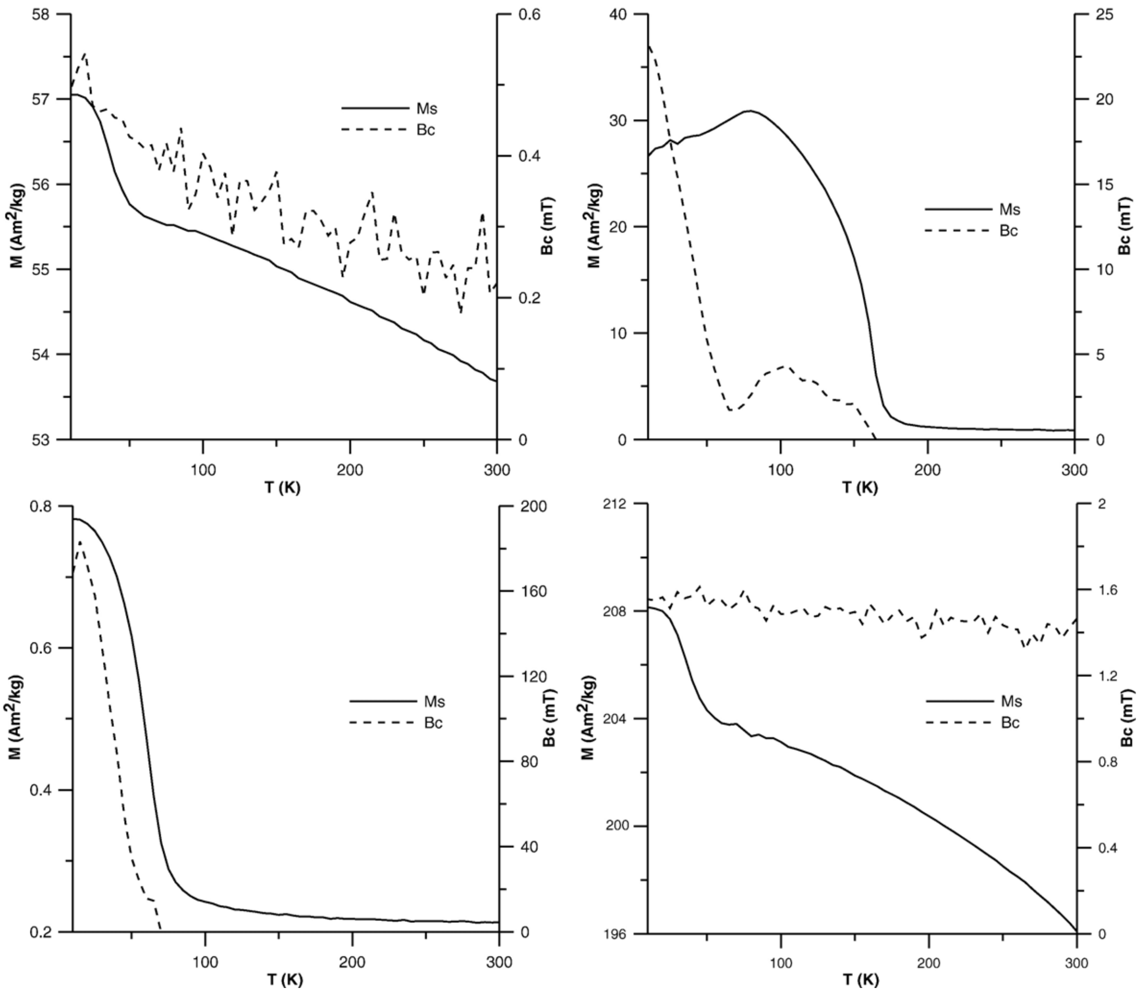

Fig. 7. Low temperature saturation magnetization (measured at 1 T field) and coercivity of the Neuschwanstein (upper left), daubreelite (upper right), troilite (lower left), and FeNi20 (lower right).

In contrast, the imaginary component of the magnetic susceptibility (Fig. 6 and Fig. 12 in the Appendix) slightly oscillates at temperatures below 60 K, but then show an increase with increasing temperature at higher frequencies and temperatures above 60 K. The slope of the susceptibility curve sharply increases with increasing frequency.

Strong field dependence of susceptibility (Figs. 9, 10 and 12 in the Appendix) is most likely due to self-demagnetization and weak-field hysteresis as expected for these MD samples.

6. Neuschwanstein Meteorite

The low-temperature magnetic properties of Neuschwanstein meteorite are dominated by the ~70 K and 150 K anomalies. The FC and ZFC induced magnetization curves reveal both anomalies while the remanent magnetization curves reveal the ~70 K anomaly only (Figs. 3 and 4). Comparing the Neuschwanstein FC and ZFC induced and remanent magnetization curves to those of daubreelite, troilite, and FeNi, we find that contributions from both daubreelite and FeNi can be seen in the Neuschwanstein curves. The ~70 K and 150 K anomalies have signatures similar to the T_m and T_c of natural and synthetic daubreelite and thus are most likely caused by the presence of daubreelite in the Neuschwanstein meteorite. The ~ 10 K variations in T_m and T_c among daubreelite in the Neuschwanstein meteorite, daubreelite from the Coahuila meteorite and synthetic daubreelite (Tsurkan et al., 2001a) might be due to slightly different Fe/Cr stoichiometric ratios, the presence of impurities, or crystalline lattice defects.

No signature of troilite is found in Neuschwanstein curves. This is readily explained bearing in mind that M_s of troilite is a factor of 40 smaller than that of daubreelite

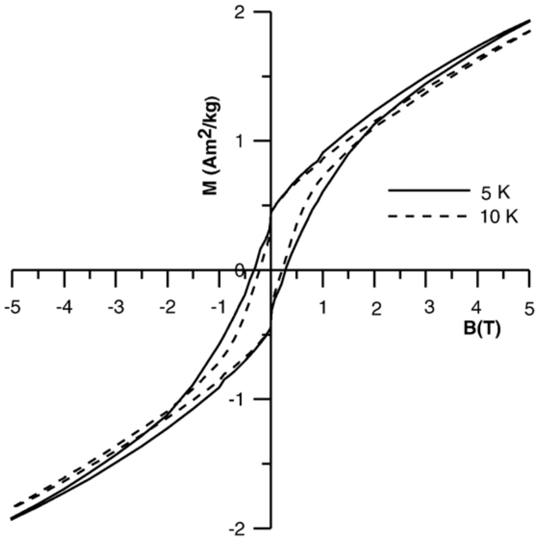

Fig. 8. 5 K and 10 K hysteresis loops of troilite powderized fraction from Bruderheim L6 chondrite.

and 100–200 times smaller than that of FeNi alloys. Even if troilite was present in the same concentration as two above phases it would not be detectable with magnetic measurements.

On the Neuschwanstein's real component (Fig. 5) magnetic susceptibility curve the T_c of daubreelite can be identified at 150 K. There is also slight field dependence (Fig. 9 in the Appendix probably due to the presence of the MD FeNi grains. The imaginary component (Fig. 6 and Figs. 10 and 12 in the Appendix) is similar to that of FeNi20 and FeNi24 samples.

In the low-temperature hysteresis data the overall low coercivity (<10 mT) and the increase in the saturation magnetization M_s at temperatures below 50 K can be identified (Fig. 7). This is similar to the low-temperature behavior of both FeNi20 and FeNi24 samples (Fig. 7 and Fig. 11 in the Appendix). Thus the FeNi phase controls hysteresis properties of the Neuschwanstein sample. There is no distinct signature of daubreelite visible in the hysteresis data.

7. Conclusions

The low-temperature magnetic properties of the Neuschwanstein meteorite are dominated by both FeNi and daubreelite. The ~150 K magnetic feature in the Neuschwanstein meteorite has been correlated to the T_c of daubreelite. The more detailed low-temperature magnetic measurements revealed the presence of the daubreelite magnetic transition at T_m ~70 K as well. Overall shape of the AC susceptibility and hysteresis curves for Neuschwanstein most strongly resemble those of FeNi, whereas remanent and induced magnetization curves more clearly show the daubreelite characteristics. The magnetic signal of troilite in Neuschwanstein meteorite was not detected due to its relatively low magnetic susceptibility and saturation magnetization.

Daubreelite with its T_c ~150 K may be a significant magnetic mineral in cold environment. However, warming above T_m almost completely erases the low-temperature remanence and results in the loss of the low-temperature magnetic information. Further heating through T_c results in magnetic unblocking and loss of the magnetic information. Based on empirical observations as well as on theoretical models (Spencer et al., 1989; Lim et al., 2005) the present surface temperatures of the NEAs (Near Earth Asteroids) and asteroids within the main asteroid belt are above T_c where daubreelite has paramagnetic properties.

The presented low-temperature magnetic data of daubreelite, troilite and FeNi can be useful for the interpretation of the low-temperature magnetic measurements of various extraterrestrial materials and can serve as a mineralogical tool for qualitative detection of daubreelite and troilite in the samples.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2007.06.022.

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