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Iron sulfide (troilite) inclusion extracted from Sikhote-Alin iron meteorite: Composition, structure and magnetic properties

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HIGHLIGHTS

- The presence of daubréelite in iron sulfide inclusion in Sikhote-Alin iron meteorite.
- The presence of the ideal FeS and iron deficient $Fe_{1-x}S$ in iron sulfide inclusion.
- New way of the iron sulfide Mössbauer spectrum approximation.

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ABSTRACT

Iron sulfide (troilite) inclusion extracted from Sikhote-Alin IIAB iron meteorite was examined for its composition, structure and magnetic properties by means of several complementary analytical techniques such as: powder X-ray diffractometry, scanning electron microscopy combined with energy-dispersive X-ray spectroscopy, magnetization measurements, ferromagnetic resonance spectroscopy and ^{57}Fe Mössbauer spectroscopy with a high velocity resolution. The applied techniques consistently indicated the presence of daubréelite ($FeCr_2S_4$) as a minority phase beside troilite proper (FeS). As revealed by ^{57}Fe Mössbauer spectroscopy, the Fe atoms in troilite were in different microenvironments associated with either the ideal FeS structure or that of a slightly iron deficient $Fe_{1-x}S$. Phase transitions of troilite were detected above room temperature by ferromagnetic resonance spectroscopy. A novel analysis of 295 and 90 K ^{57}Fe Mössbauer spectra was carried out and the hyperfine parameters associated with the ideal structure of troilite were determined by considering the orientation of the hyperfine magnetic field in the eigensystem of the electric field gradient at the ^{57}Fe nucleus.

1. Introduction

Iron sulfide FeS (troilite) is very rare material found at the Earth [1] while often found in various extraterrestrial objects, from meteorites to cosmic dust particles, in particular, in iron meteorites [2–5]. Iron meteorites based on Fe–Ni–Co alloy contain elements such as: P, S and C. Their presence leads to the formation of

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precipitates of iron-nickel phosphides (Fe,Ni)$_3$P in the form of schreibersite and rhabdite and/or iron sulfide and iron-nickel carbides. These elements play an important role in the cooling rate of the metal melt (see [6]). Therefore, the study of the former precipitates in various iron meteorites is of interest for the analysis of the origin, composition and formation processes of iron meteorites as well as their thermal and impact history. As Goldstein et al. [6] mentioned, sulfur is virtually insoluble in solid metal and thus is found only in the form of inhomogeneously distributed troilite inclusions that likely represent melt trapped during the crystallization process. Troilite is a mineral which is the end-member of the pyrrhotite group with stoichiometric FeS or non-stoichiometric (Fe$_{1-x}$S) content. At ambient temperatures the crystal structure of troilite is hexagonal ($P\overline{6}2c$) – as demonstrated by investigations of troilite from various meteorites (iron, chondrites) and synthetic analogues (see, for instance [7–11], and references therein). On heating, troilite transforms into the orthorhombic MnP-type structure ($Pnma$) at around $T_\alpha \approx 413$ K, and successively to the hexagonal NiAs-type structure ($P6_3/mmc$) at ~483 K (see [8,10] and references therein).

In addition to the crystal structure, information on the atomic level structure of iron bearing mineral phases in meteorites can be gained using Mössbauer spectroscopy (see, e.g., [8–10]). However, the accurate decomposition of the ^{57}Fe Mössbauer spectra of bulk meteoritic samples is often made difficult by the presence of several iron bearing mineral phases and the overlap of their respective Mössbauer spectral components, e.g., in the case of ordinary chondrites [12–21]. Non-stoichiometry in troilite can lead to a multitude of different iron microenvironments, which results in further difficulties concerning the exact analysis of Mössbauer spectra. Even in the case of stoichiometric troilite, special attention has to be paid to the orientation of the hyperfine magnetic field with respect to the electric field gradient during spectral analysis. Namely, if we do not take into account the possible non-collinearity of the hyperfine magnetic field and the principal axis of electric field gradient, it is not possible to fit the Mössbauer spectrum of troilite correctly [7–9,13,16]. Accurate determination of the Mössbauer parameters of troilite in meteorite samples is important because they are supposed to reflect the conditions of crystallization of the parent body of the corresponding meteorites [16]. In the present work we also deal with the above mentioned problems of the troilite spectrum fit in a novel way for more reliable analysis of iron sulfide.

Sikhote-Alin IIAB iron meteorite contains some minor iron bearing inclusions in kamacite matrix such as iron-nickel phosphides (Fe,Ni)$_3$P in the forms of schreibersite and rhabdite, as well as iron-sulfur compounds in the forms of troilite FeS and daubréelite FeCr$_2$S$_4$. Previously, we have analyzed extracted (Fe,Ni)$_3$P in both forms using magnetization and Mössbauer spectroscopy [22–24]. In the present work we continue the analysis of iron containing inclusions extracted from the Sikhote-Alin kamacite matrix by focusing our attention on a sample with an extracted troilite inclusion. We present a detailed analysis carried out by using powder X-ray diffractometry (PXRD), scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS), magnetization measurements, ferromagnetic resonance spectroscopy and ^{57}Fe Mössbauer spectroscopy with a high velocity resolution (with a higher discretization order of the velocity scale). The last-named technique demonstrates significant advances in comparison with conventional Mössbauer spectroscopy in chemical analyses of iron-containing species in materials, cosmochemical and biomedical sciences [25–29].

2. Materials and methods

By cutting a fragment of Sikhote-Alin IIAB iron meteorite a massive iron sulfide inclusion was found (Fig. 1). This troilite inclusion was mechanically extracted from the kamacite matrix and powdered for further investigation. This powder (with an iron surface density of 10 mg Fe/cm^2) was glued on iron-free aluminum foil for Mössbauer measurements. SEM and EDS measurements were performed by ΣIGMA VP microscope (Carl Zeiss) with EDS device X-max (Oxford Instruments). PXRD study was carried out using PANalytical X'pert PRO diffractometer (The Netherlands) with Cu K$_\alpha$ radiation and Ni filter at the Ural Federal University (Ekaterinburg). Measurements were done in the 2Θ range of 17–90° with steps of 0.013° and a step time of 300 s. To minimize the effect of different crystal sizes as well as the texture effect the sample was rotated in horizontal plane with revolution time of 8 s. The observed X-ray diffractograms were fitted with the least squares procedure using the program Panalitical X'Pert High Score Plus (version 2.2c) employing the Rietveld full profile refinements and PDF-2 database. Magnetic measurements were made using commercial SQUID magnetometer MPMS-5S (Quantum Design) at the Hebrew University (Jerusalem).

Ferromagnetic resonance (FMR) spectroscopy measurements were carried out on 2.3 mg of the powdered sample, by a Bruker ElexSys E500 X-band spectrometer equipped with a variable-temperature flow-through type insert in conjunction with a digital temperature control unit, at the Institute of Materials and Environmental Chemistry (Budapest). Measurements were carried out first (series A) in the range of 320–140 K (by applying evaporated liquid nitrogen as coolant), and subsequently (series B) in the range of 300–550 K. The conditions of FMR measurements involved 2 scans, each with a sweep time of ~84 s, with modulation frequency of 100 kHz, modulation amplitude of 5 G, microwave power of ~2 mW (series A) and ~10 mW (series B), and microwave frequency in the range of 9.33–9.44 GHz. The spectra (being proportional to the first derivative of the power of microwave absorption with respect to the applied magnetic field) were recorded in 2048 channels in the magnetic field range of 200–10800 G. The magnetic field axes of the spectra have been scaled together to the common microwave frequency of 9.338 GHz before processing.

Mössbauer spectra with a high velocity resolution were measured at the Ural Federal University (Ekaterinburg) using an automated precision Mössbauer spectrometric system built on the

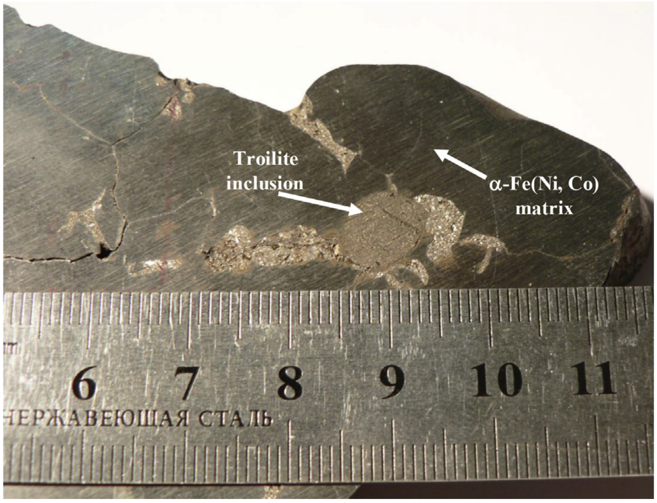

Fig. 1. Fragment of the Sikhote-Alin iron meteorite with troilite inclusion.