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Magnetic anisotropy in FeSb studied by ^{57}Fe Mössbauer spectroscopy

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ABSTRACT

The $Fe_{1+x}Sb$ compound has been synthesized close to stoichiometry with $x=0.023(8)$. The compound was investigated by ^{57}Fe Mössbauer spectroscopy in the temperature range 4.2–300 K. The antiferromagnetic ordering temperature was found as 232 K i.e. much higher than for the less stoichiometric material. Regular iron was found to occupy two different positions in proportion 2:1. They differ by the electric quadrupole coupling constants and both of them exhibit extremely anisotropic electric field gradient tensor (EFG) with the asymmetry parameter $\eta \approx 1$. The negative component of both EFGs is aligned with the *c*-axis of the hexagonal unit cell, while the positive component is aligned with the $\langle 120 \rangle$ direction. Hence, a model describing deviation from the NiAs $P6_3/mmc$ symmetry group within Fe-planes has been proposed. Spectra in the magnetically ordered state could be explained by introduction of the incommensurate spin spirals propagating through the iron atoms in the direction of the *c*-axis with a complex pattern of the hyperfine magnetic fields distributed within *a*–*b* plane. Hyperfine magnetic field pattern of spirals due to major regular iron is smoothed by the spin polarized itinerant electrons, while the minor regular iron exhibits hyperfine field pattern characteristic of the highly covalent bonds to the adjacent antimony atoms. The excess interstitial iron orders magnetically at the same temperature as the regular iron, and magnetic moments of these atoms are likely to form two-dimensional spin glass with moments lying in the *a*–*b* plane. The upturn of the hyperfine field for minor regular iron and interstitial iron is observed below 80 K. Magneto-elastic effects are smaller than for FeAs, however the recoilless fraction increases significantly upon transition to the magnetically ordered state.

1. Introduction

Iron antimony binary system is characterized at low pressure and temperature by some substitutional solubility of the antimony in α-Fe, presence of the non-stoichiometric FeSb metallic compound with the excess iron, highly stoichiometric $FeSb_2$ intermetallic compound and α-Sb with virtually none iron dissolved in [1,2]. The iron mono antimonide crystallizes in the hexagonal structure within $P6_3/mmc$ group in similarity to NiAs [1,3]. Antimony forms almost perfect hexagonal lattice with two layers along the *c*-axis of the chemical unit cell. These layers are mutually shifted once versus another in the *a*–*b* plane to conform to the close packing conditions. They are interlaced with the fully occupied hexagonal sheets of iron, the latter having all sites equivalent one to another from the chemical point of view – regular iron. There are two interstitial positions per chemical cell (one per chemical formula) called double tetrahedral interstitials DTI_1 and DTI_2, respectively. They are accessible to the excess iron atoms with equal probabilities for each of them [4]. The compound is unstable very close to stoichiometry and hence, some interstitial iron is always present within relatively large range of concentration. Hence, the real chemical formula takes on the form $Fe_{1+x}Sb$. The range of the parameter x is reported as $0.08<x<0.38$ [2]. It seems that excess iron is distributed randomly over interstitials at least for small departures from stoichiometry. It was found that iron diffusivity is much higher than antimony diffusivity and that iron diffuses via interstitials DTI_1 and DTI_2 following the chain regular–interstitial–regular [4].

There is a small net magnetic moment per iron atom leading to the magnetic ordering at low temperatures. The ordering temperature strongly depends on stoichiometry and drops with the increase of the excess iron concentration [5–7]. The highest reported ordering temperature amounts to 211 K for $x=0.13$ [8,7]. Magnetic moments of iron order in the *a*–*b* plane in an antiferromagnetic triangular fashion [6]. Neither magnetic moment nor the hyperfine magnetic field is associated with the antimony. However some transferred magnetic hyperfine field was observed on tin substituting antimony [9]. The excess iron is characterized by larger magnetic moment and it orders magnetically as well with moments being perpendicular to the *c*-axis. Mictomagnetic

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clusters are formed for higher concentration of the interstitial iron, while for the low concentration one observes spin glass [10,11]. There are controversies concerned with the ordering temperature of the excess iron. Some reports show that this temperature is lower than the ordering temperature of the regular iron [10,11].

The compound $Fe_{1+x}Sb$ has been investigated previously by the Mössbauer spectroscopy [4,5,7–12]. Iron Mössbauer spectra exhibit at least two iron sites even above the magnetic ordering temperature. Such feature has been interpreted in terms of the distinctly different environment for regular and interstitial iron. One has to note as well, that regular iron is octahedrally co-ordinated by antimony, and one can expect competing contributions from the direction dependent covalent bonds and more isotropic metallic bonds in some similarity to the FeAs despite different crystal structure [13].

Hence, it is important to look more carefully at this system, in particular for the single-phase samples being as close to stoichiometry as possible. Additionally iron pnictides seem interesting compounds as iron-based superconductivity [14] is generated within iron–pnictogen [15,16] or iron–chalcogen [17,18] sheets.

2. Experimental

Ceramic pellets of iron antimonide material were prepared by solid state reaction technique. To this end the stoichiometric amounts of high purity (at least 99.99%, Alfa Aesar) powders of iron and antimony were homogenized together under argon atmosphere, pressed into pellets and sealed in evacuated quartz ampoules. Next the ampoules were heated to 1060 °C and annealed over 5 h, afterwards the furnace was slowly (5 °C/h) cooled down to 600 °C and finally to room temperature over next two hours. The pre-synthesized material was then powdered in an inert atmosphere, pressed again into pellets, sealed in evacuated quartz ampoules and re-annealed at 800 °C over 60 h followed by further thermal treatment at 400 °C for another 48 h.

Phase purity of the FeSb sample was characterized by powder X-ray diffraction method. Measurements were performed at room temperature with D8 Advance Bruker AXS diffractometer with Cu – $K\alpha_{1,2}$ (1.5406 Å) radiation. For the measurements a piece of the ceramic pellet was ground into powder under inert atmosphere and loaded into the low background airtight sample holder to protect the material from oxidation. The X-ray pattern, shown in Fig. 1, is consistent with the $P6_3/mmc$ group and the lattice constants were found as $a=0.406(6)$ nm and $c=0.513(3)$ nm. The refinements of the crystal structure parameters were performed with FULLPROF program [19] with the use of its internal tables. It is known that lattice constants increase with the departure from stoichiometry, and lattice constants for our sample are equal (c) or smaller (a) than the smallest constants reported [7].

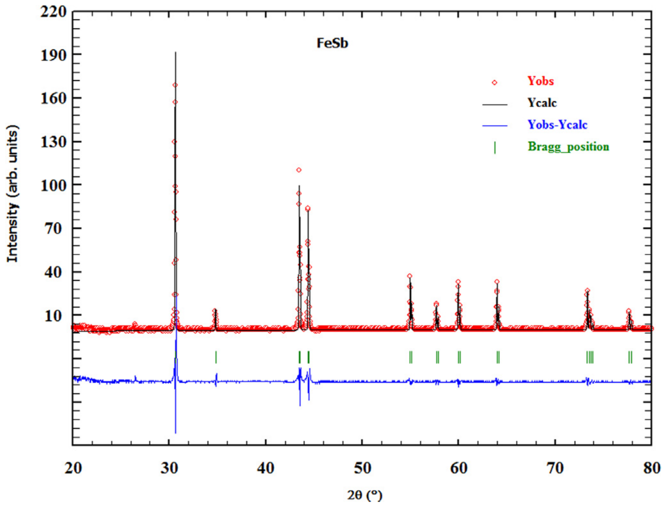

Fig. 1. Powder X-ray diffraction pattern obtained at room temperature using Cu – $K\alpha_{1,2}$ (1.5406 Å) radiation. The symbol 2Θ stands for the scattering angle.

Elemental composition of the prepared sample was studied using μXRF (micro X-ray fluorescence) spectroscopy (Orbis Micro-XRF Analyzer, EDAX). Measurements were carried out in vacuum, applying white X-ray radiation produced by Rh-tube (35 kV and 500 μA). The X-ray primary beam was focused to a spot of 30 μm diameter. Prior to the measurements an elemental calibration of the instrument has been done using as a standard carefully weighted, homogenized and pressed into pellet mixture of high purity powders of Sb and Fe. The stoichiometry of the prepared material was found to be $Fe_{1.023(8)}Sb_{1.000(2)}$. Hence, highly stoichiometric sample with $x=0.023(8)$ was obtained.

Mössbauer spectra for 14.41-keV transition in ^{57}Fe have been collected in standard transmission geometry applying commercial $^{57}Co(Rh)$ source kept under ambient pressure and at room temperature. Absorber was made in the powder form mixing 43 mg of FeSb with the B_4C carrier. Absorber thickness amounted to 21.4 mg/cm^2 of FeSb with a natural isotopic composition. A Janis Research Co. SVT-400 cryostat was used to maintain the absorber temperature, with the long time accuracy better than 0.01 K (except at 4.2 K, where the accuracy was better than 0.1 K). A RENON MsAa-3 Mössbauer spectrometer equipped with a Kr-filled proportional counter was used to collect spectra in the photo-peak window. Velocity scale of the Mössbauer spectrometer was calibrated by using Michelson–Morley interferometer equipped with the He–Ne laser. Spectral shifts are reported versus ambient pressure and room temperature natural α-Fe. Spectra were fitted within transmission integral approximation by means of the GMFeAs application of Mosgraf-2009 [20].

3. Results and discussion

Mössbauer spectra are shown in Fig. 2. One can see that magnetic order starts at about 232 K, i.e., much higher than for less stoichiometric samples [7]. Fully developed magnetic spectra at lowest temperatures could be fitted assuming two distinct regular iron sites contributing to the resonant cross-section in proportion 2:1 (called major and minor regular iron) and some additional site with larger hyperfine field contributing 2.1(5)% to the cross-section due to excess interstitial iron. Hence, the chemical formula established by means of the Mössbauer spectroscopy reads as $Fe_{1.021(5)}Sb$ in perfect accordance with the μXRF result. Regular iron sites are best described by spirals of the hyperfine fields propagating along the c-axis and probably incommensurate with the respective lattice period. The excess iron is characterized by single hyperfine field larger than the average field of the proposed spirals.

Average magnetic hyperfine fields for all three iron sites and versus temperature are shown in Fig. 3, while the total spectral shifts and quadrupole coupling constants for regular iron sites and versus temperature are shown in Fig. 4.

Even high temperature (paramagnetic) Mössbauer spectra exhibit two different sites in a rough proportion 2:1. It is assumed that the recoilless fraction is isotropic and practically the same for all iron sites (at all temperatures investigated) and sample has random orientation. These two sites differ by the electric quadrupole splitting, while the total shift is practically the same for both of them at high temperature. The site with smaller quadrupole splitting shows two times larger absorption cross-section in comparison with the second site. One can learn more about the