Magnetostuctural transition in Fe₅SiB₂ observed with neutron diffraction

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The crystal and magnetic structure of Fe₅SiB₂ has been studied by a combination of X-ray and neutron diffraction. Also, the magnetocrystalline anisotropy energy constant has been estimated from magnetisation measurements. High quality samples have been prepared using high temperature synthesis and subsequent heat treatment protocols. The crystal structure is tetragonal within the space group I₄/mcm and the compound behaves ferromagnetically with a Curie temperature of 760 K. At 172 K a spin reorientation occurs in the compound and the magnetic moments go from aligning along the c-axis (high T) down to the ab-plane (low T). The magnetocrystalline anisotropy energy constant has been estimated to 0.3 MJ/m³ at 300 K.

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1. Introduction

Magnetic materials, and especially permanent magnets, are of great importance for energy conversion, whether the application comprises energy production or vehicles [1]. The best permanent magnet material known today is the rare earth containing Nd₂Fe₁₄B, which was discovered in 1979 [2] with a saturation magnetisation (Msat) of 1.28 MA m⁻¹. Optimisation of the microstructure gave this compound the world record for the energy density (BHmax) with a value of 0.474 MJ/m³. However, due to high and unstable prices of rare earth elements [3] motivation for research in rare earth free magnetic materials has risen. To manufacture rare earth free permanent magnets, compounds with high amount of 3d-elements should be used. Magnetism comes from the spin angular momentum of unpaired electrons in the outer shell of transition metals (3d, 4d, 5d) or rare earth elements (4f) [4]. In a rare earth magnet the magnetism comes from the interplay of two different sublattices, one with transition metals and one with rare earths. The 3d elements in a rare earth magnet is what gives the magnet a high Curie temperature (Tc) and high Msat. However, the spin–orbit coupling between the 4f and 3d electrons will give the compound a high magnetocrystalline anisotropy, which potentially gives a high coercivity. In transition metal based magnets the anisotropy comes from the interplay between the crystal field and spin–orbit interactions. The crystal field is given by the 3d electron clouds orientation relative to the crystalline unit cell axis. The spin orbit coupling is dependent on the electrons circular motion.

To find an optimal material for rare earth free permanent magnets one (or several) of the magnetic 3d-elements (Cr, Mn, Fe, Co and Ni) should be present in the material in high concentrations. The 3d-elements will contribute with large and stable magnetic moments and high Tc. However, usually the magnetocrystalline anisotropy energy (MAE) is low in such compounds, resulting in low coercivity in the manufactured magnet giving a soft magnetic material. To overcome the low coercivity, compounds with a uniaxial crystal structure should be used to gain a higher MAE [2]. Examples of this approach are the compounds MnAl and FeNi both crystallising in the L1₀ structure, an ordered body centred tetragonal (bct) structure, where the separate atoms are alternating in layers along the c-axis [4]. This ordered L1₀ phase results in high magnetocrystalline anisotropy, but these structures are often metastable (MnAl) or need extremely slow
2. Experimental

2.1. Sample preparation

Samples were synthesised by arc melting stoichiometric amounts of iron (Leico Industries, purity 99.995%), surface oxides were reduced in H₂-gas, silicon (Highways International, purity 99.99%) and boron (Wacher-Chemie, purity 99.995%) under argon atmosphere. Neutron diffraction samples with isotope ¹¹B (Los Alamos National Laboratories, pure ¹¹B) were also synthesised with arc melting under argon. The synthesis was performed in two steps, first FeB was prepared and second Fe₅SiB₂ was produced from FeB, iron and silicon. The arc melted samples were remelted five times to ensure homogeneity. All samples were crushed, pressed into pellets and heat treated in evacuated silica tubes at 1273 K for 14 days (30 days for the ¹¹B-sample) and subsequently quenched in cold water.

2.2. X-ray powder diffraction

Phase analysis and crystal structure determinations were performed using high resolution X-ray powder diffraction (XRD) obtained at the I711 beamline [12] at the Max II synchrotron (Lund, Sweden). Samples were measured at the temperature 298 K, in transmission mode in 0.3 mm spinning capillaries, using a NewPp diffractometer equipped with a Pilatus 100 K area detector mounted 76.5 cm from the sample (λ= 0.9940 Å). The detector was scanned continuously, from 5° to 125° in approx. 6–10 min, recording 62.5 images/deg (step size 0.016°) for each measurement. The true 2θ position of each pixel was recalculated, yielding an average number of 100,000 pixels contributing to each 2θ value. Integration, applying no corrections for the tilt of the detector, provided FWHM values of 0.03–0.08° from 5 to 125°. Diffraction patterns were also recorded as a function of temperature with a Bruker D8 diffractometer equipped with a Lynx-eye position sensitive detector (PSD, 4° opening) using CuKα₁ radiation (λ = 1.540598 Å), in a 2θ range of 20–90°.

2.3. Neutron powder diffraction

Atomic and magnetic structures were determined using neutron powder diffraction at the D1B beamline at ILL (Grenoble, France). A pyrolytic graphite monochromator (reflection 002) was used, giving a wavelength of 2.52 Å. Diffraction patterns were recorded at the discrete temperatures 16, 150, 200, 300 and 500 K and upon ramping between each step with a 2θ range of 5–128°. The sample was kept as an annulus located between the inner and outer walls in a double-walled V container to minimise absorption by the sample.

2.4. Refinement of the crystal and magnetic structures

The X-ray and neutron powder diffraction patterns were analysed using the FullProf software [13] utilizing the Rietveld method [14]. For the X-ray case, the pseudo-Voigt profile function was used to describe the profile function and the background was described by linear interpolation between chosen points. In the refinement the following 18 parameters were varied: zero point, background, scale factor, peak shape, half width parameters (3), unit cell parameters (2), atomic occupations (4), isotropic temperature parameter and atomic coordinates (5). To precisely determine the unit cell parameters refinements were performed in the software UnitCell [15]. The magnetic structure was described in the Shubnikov groups I4/mcm’ and Ima’m’ for 300 and 16 K respectively found from simulated annealing and representational analysis (SARAh) [16]. All Fe atoms were described using the Fe²⁺ form factors.

2.5. Magnetisation

Magnetisation, M, measurements were performed using a Quantum Design PPMS 6000 Vibrating Sample Magnetometer (VSM). The low field M vs temperature, T, dependence was recorded between T = -950 K and T = 10 K at a constant applied field, H, of 40 kA/m. For the range between T = -950 K and 305 K, the sample was mounted in the PPMS furnace option, added to the VSM. M vs H at constant T = 300 K and at T = 10 K were measured in the range -7.2 MA/m to +7.2 MA/m.

3. Results and discussion

3.1. Phase analysis

The XRD investigation confirms that Fe₅SiB₂ crystallises in the tetragonal space group I4/mcm with the refined unit cell parameters a = 5.5541(1), c = 10.3324(5) Å and 10.3324(5) Å for a and c respectively. Fe₅SiB₂ crystallises at the Cr₅B₃-type structure [6,7], and is isostructural with Fe₅PB₂ within the space group I4/mcm [8]. For Fe₅SiB₂ (as well as for Fe₅PB₂) iron occupies the 16l and 4c sites whereas silicon (phosphorus) and boron occupy the 4a and 8h sites respectively [9]. Fe₅SiB₂ is ferromagnetic at room temperature with a critical temperature at 784(1) K reported from Mössbauer spectroscopy and a suggested magnetisation along the c-axis [10]. Mössbauer spectroscopy at low temperatures reveals a change in the easy magnetisation axis at ∼-140 K [11] where a transition from the c-axis to the ab-plane for the magnetisation direction is proposed to take place. This can be seen by a non-linear shift in both the electric quadrupole splitting and the hyperfine field, especially for the iron at the 4c position. It has however never been experimentally verified using other methods.

In this study we present direct measurements of the magnetic structures for Fe₅SiB₂ using neutron powder diffraction at high and low temperatures as well as the magnetocrystalline anisotropy energy constant from magnetic measurements; structural parameters were obtained using simultaneous refinement of X-ray and neutron diffraction data.

One compound that is rich in 3d-elements with a uniaxial crystal structure is the tetragonal compound Fe₅SiB₂ [6] (discovered in 1959), with unit cell parameters 5.5498(2) Å and 10.3224(5) Å for a and c respectively. Fe₅SiB₂ crystallises at the Cr₅B₃-type structure [6,7], and is isostructural with Fe₅PB₂ within the space group I4/mcm [8]. For Fe₅SiB₂ (as well as for Fe₅PB₂) iron occupies the 16l and 4c sites whereas silicon (phosphorus) and boron occupy the 4a and 8h sites respectively [9]. Fe₅SiB₂ is ferromagnetic at room temperature with a critical temperature at 784(1) K reported from Mössbauer spectroscopy and a suggested magnetisation along the c-axis [10]. Mössbauer spectroscopy at low temperatures reveals a change in the easy magnetisation axis at ∼-140 K [11] where a transition from the c-axis to the ab-plane for the magnetisation direction is proposed to take place. This can be seen by a non-linear shift in both the electric quadrupole splitting and the hyperfine field, especially for the iron at the 4c position. It has however never been experimentally verified using other methods.
3.2. Magnetic measurements

$M$ vs $H$ for both samples were recorded using VSM technique. The result is shown in Fig. 4 where the different curves correspond to $T = 10$ K (solid black line) and $T = 300$ K (solid red line); $Fe_5Si_{11}B_2$, $T = 10$ K (dashed black line) and $T = 300$ K (dashed red line). For all samples, the density 6900 kg/m$^3$ was used for the transformation to SI units. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this paper.)

### Table 1

Atomic positions and occupancies for $Fe_5SiB_2$ at room temperature. Derived from high resolution XRD patterns.$^a$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1</td>
<td>4c</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.976(8)</td>
</tr>
<tr>
<td>Fe2</td>
<td>16l</td>
<td>0.1683(1)</td>
<td>0.6683(1)</td>
<td>0.1384(1)</td>
<td>1</td>
</tr>
<tr>
<td>Si</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0.25</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>8h</td>
<td>0.6162(9)</td>
<td>0.1162(9)</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$ Space group: $I4/mcm$; unit cell parameters: $a = 5.5541(1)$ Å, $c = 10.3429(2)$ Å; Agreement factors: $R_{Bragg} = 9.31$, $R_{wp} = 20.7$; Overall displacement parameter: $B_{iso} = 1.0085$ Å.$^2$

### Table 2

Magnetic moments and the anisotropy energy constants for the samples from $M$ vs $H$ measurements at 10 and 300 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$ (K)</th>
<th>$M_{sat}$ (MA/m)</th>
<th>Total magnetic moment ($\mu_B$)</th>
<th>$K_1$ (MJ/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_5$SiB$_2$</td>
<td>10</td>
<td>1.10</td>
<td>1.87</td>
<td>0.33</td>
</tr>
<tr>
<td>Fe$_5$SiB$_2$</td>
<td>300</td>
<td>1.02</td>
<td>1.75</td>
<td>0.30</td>
</tr>
<tr>
<td>Fe$<em>5$Si$</em>{11}$B$_2$</td>
<td>10</td>
<td>1.01</td>
<td>1.72</td>
<td>0.55</td>
</tr>
<tr>
<td>Fe$<em>5$Si$</em>{11}$B$_2$</td>
<td>300</td>
<td>0.92</td>
<td>1.58</td>
<td>0.20</td>
</tr>
</tbody>
</table>

$Fe_5$SiB$_2$ (solid line) and $Fe_5$Si$_{11}$B$_2$ (dashed line) at $T = 300$ K (red) and $T = 10$ K (black). From Fig. 4, the saturation magnetisation, $M_{sat}$ (defined as $M$ at $H = 7.2$ MA/m) is estimated (see Table 2). The magnetic moment per Fe-atom, due to the $Fe_5$Si$_{11}$B$_2$ sample in particular, is smaller compared to the results predicted from neutron powder
diffraction. However, according to the XRD results, the Fe₅Si₂B₂ sample is nearly single phase while Fe₅Si₁₁B₂ has higher amounts of a secondary phase. Assuming this phase to be nonmagnetic (or anti-ferromagnetic), it explains, at least to the major extent, the difference in magnetic moment.

Assuming the samples to consist of grains of uniaxial anisotropy, the magnetocrystalline anisotropic energy can be expressed as

\[ E_{\text{anis}} = K_1 \cos^2 \theta + K_2 \cos^4 \theta \]  

where \( \theta \) is the angle between the magnetisation and the easy axis of magnetisation and \( K_1 \) and \( K_2 \) are anisotropic constants. Information relating to the magnetocrystalline anisotropy can be extracted using the so-called law of approach to saturation [17],

\[ M - M_{\text{sat}} = \left( 1 - b \frac{H^2}{K_1} \right) \]

where

\[ b = \frac{4}{15} \left( \frac{K_{\text{eff}}}{\mu_0 M_{\text{sat}}} \right)^2 \]

and defining

\[ K_{\text{eff}}^2 = K_1^2 + \frac{16}{3} \left( K_1 + \frac{2}{3} K_2 \right) K_2 \]

as the effective value of the anisotropic constants [17]. In uniaxial systems, \( K_1 > 0 \) and \( K_2 < - K_0 \) and often \( K_2 < K_0 \), e.g. BaFe₁₂O₁₉ [18] and Nd₂Fe₁₄B [19]. In these cases, \( K_{\text{eff}} = K_1 \) which then can be estimated from a plot of \( M - M_{\text{sat}} \) vs \( 1/H^2 \) according to the equations above. In case of easy plane anisotropy, either \( K_1 \) or \( K_2 \), or both, will be negative. Using the law of approach to saturation only, the sign of \( K_{\text{eff}} \) cannot be extracted. In our case, however, judging from the low temperature neutron data, we can conclude \( K_{\text{eff}} < 0 \) at \( T = 10 \) K. The magnitude of \( K_{\text{eff}} \) estimated using the above method is given in Table 2.

In Fig. 5, the Fe₅Si₁₁B₂ low field susceptibility \( \chi = M/H \) is plotted vs \( T \). The Curie temperature \( T_C = 800 \) K is estimated from the plot \( 1/\chi \) vs \( T \) (cf. inset in Fig. 5). At the lower part of the temperature range, there is a pronounced maximum in \( \chi \), peaking at \( T_t = 169 \) K. The \( \chi \) vs \( T \) plot on the Fe₅Si₂B₂ sample (not shown) yields \( T_C = 760 \) K and \( T_t = 172 \) K. The maximum in Fe₅Si₁₁B₂ is indicative of the spin reorientation revealed by the results from neutron powder diffraction. With decreasing temperature, going from the uniaxial to the easy plane state, \( K_1 \) (and \( K_2 \)) will decrease in magnitude, change sign and then increase in magnitude. The zero-crossing in the anisotropic constants is mirrored by the maximum in \( \chi \) at \( T_t \) since the material will be in a
magnetically more soft state. Tentatively speaking, in the easy plane state, the number of easy directions “available” will be larger compared to a uniaxial case and thus the response of the magnetisation to an applied field, i.e. $\chi$, will be larger.

3.3. Magnetic structure

The neutron diffraction patterns show differences above and below the magnetic spin reorientation. Intensities from magnetic scattering at the 004, 211 and 114 peaks are changing with temperature, shown in Fig. 6, indicating a rearrangement in the magnetic structure. All peaks with magnetic contributions to the intensities are at crystallographic peak positions, therefore the magnetic and crystallographic unit cells are the same. This indicates ferromagnetism which is in agreement with the magnetic measurements. The refined neutron powder diffraction patterns can be found in Fig. 7. From the peaks with additional magnetic intensities the direction of the magnetisation is found to be along the $c$-axis at high temperatures and in the $ab$-plane at low temperatures. These proposed magnetic structures (from neutron diffraction) are also in agreement with the magnetic structure model proposed from Mössbauer measurements [11].

The magnetic moment for the high temperature phase has been refined to $2.06(7) \mu_B$ and $1.72(5) \mu_B$ for Fe1 and Fe2 respectively. This gives a mean value for the magnetic moment of $1.79 \mu_B$ which is in good agreement with the value calculated from $M_{sat}$ from the $M$ vs $H$ measurement for the Fe5SiB2 sample. For the low temperature phase the moments are $2.31(6) \mu_B$ and $2.10(4) \mu_B$, see Table 3, giving a mean value of $2.14 \mu_B$, which is a little higher, but still in agreement with, the corresponding value from $M_{sat}$ for Fe5SiB2. The structural models used to refine the neutron powder diffraction patterns for different temperatures are shown in Fig. 8.

4. Conclusions

The magnetic structure of Fe5SiB2 has been studied using a combination of X-ray and neutron powder diffraction, and the model proposed from Mössbauer spectroscopy has been verified. The neutron diffraction patterns in combination with magnetic measurements reveal a magnetic structure transition at 172 K where the direction of the magnetisation changes from aligning along the $c$-axis to fall down towards the $ab$-plane upon cooling. Furthermore, the magnetic properties for permanent magnet applications have been studied. The saturation magnetisation is high, comparable to that of Nd$_2$Fe$_{14}$B, 1.1 MA/m. However, the magnetocrystalline anisotropy energy is too low for the material to get hard magnetic properties. Therefore, the usefulness as a permanent magnet material is low, although the magnetocrystalline anisotropy could possibly be increased by e.g. substitutions on the iron sites.

Acknowledgements

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References