Magnetic properties, Mössbauer effect and first principle calculations study of laves phase HfFe$_2$

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Abstract. The magnetic properties and hyperfine interaction parameters for Laves phase HfFe$_2$ with C14 type structure are studied using SQUID magnetometer and Mössbauer measurement. The saturation magnetization, remanent magnetization, coercive field, magnetic moment per unit formula and the hyperfine magnetic field at Fe site are reported. In addition, a detailed theoretical study of the electronic structure and hyperfine magnetic fields of the two possible HfFe$_2$ structures, C15 and C14, is presented. Using the full-potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN 97 package, the equilibrium volume, bulk moduli, magnetic moments and hyperfine magnetic fields for the two structures are calculated. The obtained results are compared with the measured data.


1 Introduction

The magnetic properties of Laves phase compounds of AB$_2$-type, where A is a transition metal and B is iron, have been extensively investigated in the past [1–6]. It is known since a long time that Laves phase intermetallic compounds with Fe-base, like TMFe$_2$ (TM = Zr, Hf, Ti, Sc) show more or less strong magnetovolume effects (Invar-like behaviour) in their thermal expansion, besides a rich spectrum of other magnetic anomalies [7].

HfFe$_2$ is a representative of this group of compounds that provides the possibility of observing hyperfine interactions at both sites: at Hf by TDPAC on the $^{181}$Hf cascade and at Fe by Mössbauer spectroscopy in the $^{57}$Fe nuclei. HfFe$_2$ has a C15 cubic structure of MgCu$_2$ type which exists in a narrow composition range around the stoichiometry. Additionally, it crystallizes in MgZn$_2$ (C14) hexagonal structure type.

The hyperfine interactions and magnetic properties of HfFe$_2$, in both of its crystallographic modifications, have been extensively investigated in the past. Ikeda [1] has shown that HfFe$_2$ is ferromagnetic in the hexagonal as well as in the cubic phase and measured two slightly different values for their saturation magnetization. Livi et al. [3] revealed that many of the difficulties encountered in the study of this compound can be understood as originating in an instability of the cubic phase, with formation of segregations of an hexagonal phase C14 structure, the amount and size of which depend on the preparation procedure of the sample [8]. Their study of the HfFe$_2$ predominantly cubic phase has revealed a population ratio of 3:1 for the magnetically inequivalent Fe sites, indicating that the easy direction of magnetization is along the (111) direction. Investigating the pseudo-binary system Zr$_x$Hf$_{1-x}$Fe, Akselrod et al. [9] have come to the conclusion that for $x < 0.2$, the hexagonal phase appears in addition to the predominant cubic phase, whereas in the samples of pure HfFe$_2$ the C14 phase seems to prevail. Xia et al. [10] have recorded room temperature Mossbauer spectrum of the C14 MgZn$_2$ Laves structure, which displays two magnetic sub-spectra attributed to the two crystallographically inequivalent Fe atoms.

Despite the obvious interest in the magnetic properties and hyperfine interactions of this compound there are still some open questions, mainly regarding the electronic origin of the measured hyperfine fields.

Here we present Mossbauer and magnetization measurements of HfFe$_2$ with hexagonal C14 structure. In order to interpret the obtained results we have performed ab-initio calculations of the electronic structure and hyperfine magnetic fields (HMF). Since experimental data for the other structural modification of HfFe$_2$ exist in literature, we also present results of our theoretical calculations for the cubic C15 structure. In addition, we have determined a number of structural and electronic ground state properties for both structures.
2 Experimental details

The HfFe₂ sample was obtained in a radio-frequency induction furnace under pure argon atmosphere. The component materials were of high purity, 99.99% iron and 99.97% hafnium. All the peaks of the X-ray diffraction pattern can be indexed with the hexagonal C14 structure, but the presence of a small percent of C15 phase can not be ruled out. The magnetic properties of the sample have been investigated by Mössbauer spectroscopy and magnetization measurements using a superconducting quantum interference device (SQUID) magnetometer.

The magnetization measurements as a function of applied field were performed using a Quantum Design MPMS 5 XL 5 SQUID magnetometer, equipped with a superconducting magnet producing fields up to 50 kOe and calibrated using a Pd standard; the sensitivity for the superconducting magnet producing fields up to 50 kOe is 10⁻⁸ emu. The first magnetization curves and hysteresis loops have been recorded at 5 K and 298 K; the mass of the sample was 12 mg. The Mössbauer absorption spectrum was obtained in a radio-frequency induction furnace under pure argon atmosphere, using rhodium (37 MBq). A calibration was performed using a 10 mg/cm² thick natural α-iron foil; the isomer shift values are reported. Uncertainties on the measured values are given in parentheses as errors on the last digit.

Table 1. Magnetization data obtained from the magnetization measurements for HfFe₂ sample. The saturation magnetization (Ms), the remanent magnetization (Mr), the coercive field (Hc) and the magnetic moment per unit formula (μB) are reported. Uncertainties on the measured values are given in parentheses under the last digit.

<table>
<thead>
<tr>
<th>T[K]</th>
<th>Ms[emu/g]</th>
<th>Mr[emu/g]</th>
<th>Hc[Oe]</th>
<th>μB/μB</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>60(1)</td>
<td>0.6(1)</td>
<td>7(1)</td>
<td>3.12(4)</td>
</tr>
<tr>
<td>298</td>
<td>55(1)</td>
<td>0.7(1)</td>
<td>8(1)</td>
<td>2.86(4)</td>
</tr>
</tbody>
</table>

in the inset, where the details of the loop in the region –20 Oe < H < 20 Oe are shown.

The saturation magnetization (Ms) was evaluated by extrapolation of the magnetization versus 1/H for H → ∞. The saturation magnetization value, obtained in this way, is 60 emu/g. The magnetization exceeds 90% of the saturation value in a field of 1000 Oe. The magnetic moment per formula unit for this sample was deduced from the saturation magnetization value at low temperature, and was found to be 3.12 μB. All the measured data are given in Table 1. As can be seen, HfFe₂ exhibits low values of remanent magnetization and coercive field, which is typical for soft magnetic materials.

Figure 4 shows the Mössbauer absorption spectrum for the same sample at room temperature. The spectrum consists of two superimposed magnetic spectra, each of six

3 Experimental results

Figure 1 presents the initial magnetization curve of HfFe₂, recorded at 5 K and 298 K. The hysteresis loop, recorded at 5 K is shown in Figure 2. The hysteresis loop is very narrow, with small values of the remanent magnetization and coercive field, as can be observed in more detail in the inset. The room temperature hysteresis loop is shown in Figure 3. There are only faint differences with respect to the low temperature loop, as it can be better observed in the inset, where the details of the loop in the region –20 Oe < H < 20 Oe are shown.