A high-field Mössbauer investigation on FeSb$_2$

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Abstract. In high-field Mössbauer measurements on FeSb$_2$ complex spectra were recorded, which could only be fitted with a higher number of subspectra, though crystallographically only one iron site exists. Due to their field dependence, these subspectra can be divided in two groups. The first, which covers 50-60% of the spectral area exhibits no field dependence of the internal fields on the applied field. The second shows internal fields increasing with the applied field.

1. Introduction

Although investigated since several decades [1] the electronic and magnetic structure of FeSb$_2$ is still under discussion. Increasing interest in this compound arose in recent years, because a colossal Seebeck coefficient [2], a rather high charge carrier mobility [3], and in Co-doped FeSb$_2$ colossal magnetoresistance [4] was found, which makes FeSb$_2$ an interesting candidate for applications, like thermoelectrica and high speed electronics. Most probably FeSb$_2$ is a nearly ferromagnetic small gap semiconductor [5] with a semiconductor-metal transition above 80 K [6, 7]. It crystallizes in the marcasite structure, where Fe has only one crystallographic site, surrounded by distorted Sb-octahedra [8]. The octahedra are corner shared in the ab-plane and edge sharing along the c-axis. The distortion of the octahedra increases with decreasing temperature, reaching a maximum around 100 K [9]. In a simple ionic picture [10] iron has a low spin Fe$^{4+}$ ($t_{2g}^4e_g^0$) ground state, because in this model the $t_{2g}$ levels split in a higher lying $d_{xy}$ and two lower lying $d_{xz}$ and $d_{yz}$ levels. In contrast to this a high spin ferric ground state was suggested from Mössbauer investigations [11]. In this work we report on $^{57}$Fe Mössbauer measurements in high-fields on polycrystalline FeSb$_2$.

2. Experimental

Polycrystalline samples enriched with $^{57}$Fe were prepared and checked for phase purity by X-ray investigations. For magnetic measurements in fields up to 9 T and temperatures between 2 and 400 K a Quantum Design PPMS-VSM was used. $^{57}$Fe Mössbauer measurements were performed between 4.2 K and room temperature and in fields up to 13.5 T. The zero-field $^{57}$Fe Mössbauer spectra were recorded in standard transmission geometry using a $^{57}$CoRh source (always at room temperature), relative to which all center shift data, CS, are given. The in-field measurements were performed in a cryostat with a superconducting solenoid (max. field 15 T) with the field direction parallel to the γ-ray direction. The source (also $^{57}$CoRh) is situated in a field compensated area ($B < 0.1$ T) at temperatures

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between 5 and 10 K. The spectra were analyzed by solving the full Hamiltonian in the fast relaxation limit, taking into account both electrical and magnetic interactions, as well as the sample thickness. The temperature stability during measurement was ±0.5 K.

3. Results

Magnetization curves indicate a magnetically ordered component, which saturates even at 300 K, superposed by a susceptibility term (figure 1). Calculation of the temperature dependence of the susceptibility from the high field slope of the curves gives similar behaviour as reported in [6, 7]. At low temperatures the susceptibility is constant, followed by an increase above 100 K. Up to now no secondary phases could be detected by X-ray investigations, however, traces of impurities (presumably on grain boundaries) cannot be excluded.

Zero field Mössbauer measurements show spectra which can be fitted with only one subspectrum (figure 2). The quadrupole splitting, increases with decreasing temperature and saturates around 50 K in good agreement with [12]. This corresponds to the fact that the distortion of the Sb-octahedra is lar-

**Figure 1.** Field dependence of magnetization of FeSb$_2$ at selected temperatures. **Inset:** High field susceptibility derived after correction for a magnetically ordered contribution versus temperature.

**Figure 2.** $^{57}$Fe Mössbauer spectra of FeSb$_2$ obtained at different temperatures in zero field.

**Figure 3.** $^{57}$Fe Mössbauer spectra of FeSb$_2$ obtained at 13.5 T for 4.2 and 50 K, analysed within model M 1 and M 2.
Figure 4. Temperature dependence of center shift in zero external fields (triangle down) and mean center shift obtained with models M 1 (full symbols) and M 2 (open symbols) in different external fields. Full line fit according to the Debye model. Black dotted line is a guide for the eye. No corrections for different source temperatures were performed.

gest around 100 K [9]. However, no anomaly in the center shift is present near the proposed semiconductor-metal transition close to 70 K [6]. Assuming that the temperature dependence of the center shift is only due to the second order Doppler shift, the analysis in terms of a Debye model gives a Debye temperature of 372 ± 20 K (figure 4). This fits well to the value of 380 K reported by [12].

In-field Mössbauer measurements show complex spectra (figure 3), which cannot be fitted by only one subspectrum. Two models (M 1 and M 2) were used to analyze the data. In M 1 five subspectra (neglecting randomization of orientation of field gradient direction with respect to $\gamma$-ray direction) were used to fit the measured spectra for all fields and temperatures, although the rather large half width (up to 0.45 mm/s) indicates, that this is only a minimum number. The mean value of the quadrupole splitting shows the same temperature dependence as for the zero-field measurements. Within measuring accuracy no field dependence is present. The same holds for the temperature and field dependence of the mean value of the center shift (figure 4). The shift between the values of the zero-field and in-field measurements is due to the difference in the source temperature. The subspectra measured at 9 and 13.5 T are fully polarized, indicated by the vanishing of the second and fifth line. At 4.5 T angles $\theta$ up to 11° between hyperfine field and external field $B_a$ are found for some subspectra.

As the measured hyperfine field $B_{hf}$ is the vector sum of the internal field $B_{int}$, and the applied field $B_a$, $B_{int}$ can be determined according to $B_{int}^2 = B_{hf}^2 + B_a^2 - 2B_{hf}B_a\cos(\theta)$. Figure 5 shows the internal fields in dependence of the applied field for typical temperatures. $B_{int}$ for the two subspectra - indicated by large symbols - representing ~60% of the area of the measured spectra, are within experimental accuracy zero for all applied fields, whereas $B_{int}$ for the subspectra representing the remaining ~40% of the spectral area increase with $B_a$. Although the fits with M 1 are satisfying, this result could only be reached by fitting the polycrystalline sample like a single crystal. Similar problems are reported also for other compounds [e.g. 13 and references herein]. In contrast to M 1, in M 2 the polycrystalline nature of the sample (by randomization of the field gradient direction with respect to $\gamma$-ray direction) and the asymmetry parameter $\eta$ were taken into account. But with this model up to now only fits of the spectra at 4.2 and 50 K were satisfying (figure 3). Six subspectra were used with half widths between 0.18 and 0.30 mm/s. The results for higher temperatures are presently not finished. Within the errors the mean values for QS and CS obtained with M 2 are the same as those obtained from M 1 (figures 4). The same holds for the internal field. There is one subspectrum, which represents ~50% of the measured spectral area, with a field independent $B_{int} \sim 0$. For $\eta$ large values between 0.98 and 0.8 inde-
Figure 5. Internal fields over applied field for FeSb$_2$ for typical temperatures obtained using model M 1 (full symbols) and M 2 (open symbols). Large symbols indicate the majority spectra.

In summary, the zero-field results of the investigated FeSb$_2$ sample agree well with the ones reported in literature. The spectra can be fitted with only one subspectrum. Although crystallographically only one iron site is present, the in-field spectra are very complex. Common to the two fitting models discussed is that the mean values for quadrupole splitting and center shift fit well to the zero-field results. In both cases two types of internal fields are found. 50 to 60% of the sample has zero $B_{\text{int}}$, whereas the rest show an increase with $B_a$.

If valence contributions to $B_{\text{int}}$ are not negligible so that $B_{\text{int}}$ is not only determined by the core contribution, the spectra exhibiting the field dependence of the internal hyperfine field may be allocated to Fe in the impurity phase contributing to the increase of the magnetization at low fields. This allocation, however, would be in complete discrepancy to the present X-ray investigations, in which no foreign phases could be detected. The spectral area of this contribution amounts about 40% and secondary phases of such order must be clearly visible in X-ray diffraction measurements.

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