A new diluted magnetic semiconductor:
The half-metallic ferromagnet CoTi$_{1-x}$Fe$_x$Sb.

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Abstract

Half-Heusler compounds with 18 valence electrons are semi-conducting. It will be shown that doping with electrons results in half-metallic ferromagnets, similar to the case of diluted semiconductors. CoTiSb is known to be a semi-conducting Half-Heusler compound. Doping by Fe is expected to result in ferromagnetic order. It was found that Ti can be replaced by up to about 10% Fe while its crystal structure still remains $C1_b$, which was proved by X-ray powder diffraction. SQUID magnetometry revealed a magnetic moment of 0.32$\mu_B$ per unit cell at 5K.

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I. INTRODUCTION

Within the last decade a new idea has revolutionised electronic devices: To use the spin of electrons in addition to its charge. This field of application is called spintronics. Half-metallic ferromagnets (HMF) seem to be a suitable class of materials which meet all requirements of spintronics. One reason is their exceptional electronic structure: They are metals in one spin direction and semiconductors in the other. The Half-Heusler compound NiMnSb was the first material being predicted by electronic structure calculations to be a HMF.

Many attempts have been made to prepare semi-conducting compounds which also have ferromagnetic properties. Mn-doped GaAs was considered to be a suitable compound, but its Curie temperature is only about 150 K and thus still far away from being suitable for application in electronic devices (see [4] for a recent review). Heusler compounds exhibit a large variety of different electronic and magnetic properties ranging from semi-conducting to ferromagnetic. This work focuses on the search for suitable compounds that bridge both semi-conducting and ferromagnetic properties. In particular, the research concentrates on finding half-metallic ferromagnetic Half-Heusler alloys with transition temperatures well above room temperature.

II. RESULTS AND DISCUSSION

CoTi\textsubscript{1-x}Fe\textsubscript{x}Sb samples were prepared by arc melting of stoichiometric amounts of the constituents in an argon atmosphere at 10\textsuperscript{-4} mbar. The polycrystalline ingots were then annealed in an evacuated quartz tube at 1000 K for 7 days.

A. Electronic properties

The electronic structure was calculated for pure and Fe doped CoTiSb in order to examine their electronic and magnetic structure. Self consistent calculations were performed by means of the full-relativistic, spin polarised Korringa-Kohn-Rostocker (KKR) method in combination with coherent potential approximation (CPA). As predicted by Tobola et al., CoTiSb turned out to be a semiconductor with a gap at the Fermi energy for both spin directions. Partial replacement of titanium by iron (10\%) (assuming that Fe is statistically
FIG. 1: X-ray diffraction pattern of CoTiSb and CoTi$_{0.9}$Fe$_{0.1}$Sb. The spectra were excited by Cu K$_\alpha$ radiation distributed on the Ti positions), has the result that the semiconductor is converted into a HMF: The DOS at the Fermi energy is clearly different from zero for only one spin direction, while remaining zero for the other. Measurements of the conductivity revealed the metallic character of the Fe-doped samples in contrast to the semi-conducting behaviour of the pure sample.

B. Structural properties

It was carefully proved that Fe occupies Ti positions and not an other vacant site. For that purpose, the X-ray powder diffraction pattern of the iron-substituted compounds were compared to that from pure CoTiSb. It was observed that no additional diffraction reflexes appear up to 10% Fe-doping, thus confirming that the structure remains the same as of pure CoTiSb, that is C1$_b$. The diffraction pattern of the pure and a 10% Fe doped sample are compared in Fig. The lattice parameter $a = 0.5883(4)$nm for CoTiSb changes slightly (0.1%) if 10% of Ti is replaced by Fe. The R values for the best fit in the Rietveld refinement are $R_i = 6\%$ and $R_p = 11\%$ confirming the high degree of site order of the sample.
C. Magnetic properties

The magnetic properties were investigated by means of magnetometry (SQUID). To determine the saturation magnetisation hysteresis loops of the CoTi$_{1-x}$Fe$_x$Sb samples for $x = 0.01, 0.02, 0.05$ and $0.1$ were measured. Already the sample with only 1% Fe exhibit ferromagnetism at room temperature. The total spin magnetic moment of the samples can be predicted from the generalised Slater-Pauling rule to be: $m = N_V - 18$, where $N_V$ is the number of valence electrons per unit cell.

CoTiSb carries no magnetic moment according to the Slater-Pauling rule because it has overall 18 valence electrons. Doping Fe on the Ti positions should lead to a magnetic moment. In the case of CoTi$_{0.9}$Fe$_{0.1}$Sb one can predict from the Slater-Pauling rule a saturation magnetisation of 0.4 $\mu_B$ per formula unit due to the 18.4 valence electrons of the compound. In Fig. 2 the hysteresis loops of CoTi$_{0.9}$Fe$_{0.1}$Sb at 5K, 300K and 768K are shown. Ferromagnetic behaviour is still observed at 768K which points to a very high Curie temperature. The saturation magnetisation at 768K has still half of the value at 5K. The calculated magnetic moments for the Fe-doped samples fit as well as the experimental values to the values one expected from the Slater-Pauling rule (see inset Fig. 2).

For more details and other properties of the series of CoTi$_{1-x}$Fe$_x$Sb with the Fe concentration ranging from $x = 0$ to 0.1 see Ref. [8].

III. SUMMARY

In summary, it was shown that Fe substituted CoTi$_{1-x}$Fe$_x$Sb is a new diluted semiconductor with a high Curie temperature of above 770K. Self consistent band structure calculations predict the alloy to exhibit half-metallic ferromagnetism. The future idea is to design devices which consist of alternating semi-conducting CoTiSb and half-metallic ferromagnetic CoTi$_{1-x}$Fe$_x$Sb layers. In that case, one may be able to design a device with the semi-conducting and ferromagnetic parts being of almost the same material.

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FIG. 2: Magnetic properties of CoTi$_{0.9}$Fe$_{0.1}$Sb.

The magnetisation as a function of the applied magnetic field at 5K, 300K and 768K is shown. Inset: The saturation magnetisation as a function of the Fe content is shown. Compared are the experimental results with the calculated values.

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