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Highly ordered, half-metallic Co_2FeSi single crystals

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A wide variety of properties such as half-metallicity is found among Heusler compounds. In order to separate intrinsic and extrinsic properties, high quality single crystals are required. Here, we report on differently grown crystals of the half-metallic ferromagnet Co_2FeSi . All crystals show excellent ordering, resulting in outstanding electrical behavior with low residual resistivity and high residual-resistivity-ratio. All Co_2FeSi crystals show a plateau in the resistivity below 50 K, which might point to half-metallic ferromagnetism. The cross-over from this unusual to more conventional transport (T^2 dependence) around 50 K indicates the onset of spin flip scattering and thus is indispensable for understanding the strong temperature dependence of Co_2FeSi tunneling magnetoresistance-devices. © 2009 American Institute of Physics. [doi:10.1063/1.3242370]

Heusler compounds are ternary X_2YZ intermetallics where X and Y are transition metals and Z is a main group element. The electrical and magnetic properties of Heusler compounds range widely from metals to semiconductors (Fe_2VAl ,¹) and ferrimagnets to half-metallic ferromagnets (Co_2FeSi ,^{2,3}). The Cobalt based Heusler compounds, crystallizing in the $L2_1$ structure, show some of the highest Curie temperatures (1100 K), high magnetic moments ($5\text{--}6\mu_B/\text{f.u.}$), and complete spin polarization at the Fermi level, leading to their description as half-metallic ferromagnets (HMFs). The designation “half-metallic” indicates the existence of a gap in the density of states for the minority-spin electrons and a nonzero occupation at the Fermi level for the majority-spin electrons, thus giving 100% spin polarized electric conduction.⁴ Those unique properties render HMFs and in particular Co based Heusler HMFs good candidates for the integration in spintronic and spin logic devices.⁵ Recently, a magnetic tunnel junction (MTJ) showing 832% tunneling magnetoresistance (TMR) at 2 K and 386% at room temperature has been realized using the quaternary Heusler compound $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ (Ref. 6) and the half-metallicity at room temperature has been confirmed by Shan *et al.*⁷ Several MTJs of Co_2FeSi have successfully been fabricated, yielding a large TMR. However, in many cases the TMR is strongly temperature dependent, e.g., in Co_2FeSi and Co_2MnSi based MTJs.^{8–11} According to Chioncel *et al.*,¹² the strong temperature dependence arises from non-quasiparticle states and their crucial contribution to the finite-temperature spin polarization. In order to separate such extrinsic effects from possible intrinsic contributions to the temperature dependence of the TMR, the investigation of high quality single crystals is indispensable.

Highly ordered polycrystals of Co_2FeSi with $T_C = 1100$ K and saturation magnetization of $6\mu_B$ have already been synthesized and studied.^{2,3,13,14} However, no systematic

study of the influence of the (single) crystal quality, including grain boundaries, on the moment and transport properties has been undertaken yet. Here, we report on the growth of excellent crystals of the $L2_1$ ordered half-metallic Heusler compound Co_2FeSi using different growth methods and a systematic investigation of the corresponding resistivity behavior at different temperatures.

Polycrystalline bulk samples were prepared by arc melting as described elsewhere.^{2,3} The polycrystalline bulk samples exhibit the expected $L2_1$ structure and the magnetic moment of $6\mu_B$.^{2,3}

Two different single crystals were prepared. One was grown by the Czochralski method using a Centor Vacuum Industries Series Crystal Puller. Metallographic investigations of polished pieces of the Czochralski grown single crystal revealed single crystalline areas of 2–3 mm width and 5–7 mm length.

The other single crystal was grown by the optical floating zone technique. Zone melting was carried out in a GERO SPO optical floating zone furnace with two 1000 W halogen lamps with the radiation focused by ellipsoidal, gold coated mirrors. To avoid oxidation the furnace was flushed with 5.0 purity argon for several hours, and during growth a gas flow rate of 300 mL/min of argon with 2% hydrogen was maintained. The seed and feed rods were counter rotated at 45 and 15 rpm, respectively, the growth speed was set at 20 mm/h. Metallographic investigations revealed the single crystal to be about 1–3 cm long and to have nearly the width of the whole rod, except a thin layer at the surface of the freshly grown crystal, which contains some small additional grains.

Measurements of the electrical resistivity were performed in the temperature range of 2–300 K on a PPMS (Quantum Design) and in a home made apparatus with a standard 4-point technique using an alternating dc-current.

The nuclear magnetic resonance (NMR) experiments were performed at 4.2 K in an automated, home-built, coherent, phase sensitive and frequency-tuned spin echo

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FIG. 1. (Color online) Laue diffraction pattern of the zone molten single crystal. In addition, the simulated diffraction pattern assuming $Fm\bar{3}m$ symmetry and a lattice constant of 5.66 Å is represented by bright dots on the bottom of Fig. 1. The perfect matching between the measured diffraction pattern and the simulation demonstrates single crystalline nature and a high degree of order of the zone melted single crystal.

spectrometer.^{15–17} A pulse length of 0.1–0.5 μs was used, depending on the sample and coil geometry. The NMR spectra were recorded in the frequency range of 120–240 MHz in steps of 0.25 MHz; no external field was applied. All NMR spectra shown here were corrected for the enhancement factor as well as the ω^2 dependence, resulting in a relative spin echo intensity which is proportional to the number of nuclei with a given NMR resonance frequency.

Laue diffraction with a spot size of $2 \times 2 \text{ mm}^2$ was performed on the floating zone crystal with 25 kV incident copper radiation at 20 mA in reflection geometry. The resulting diffraction patterns (Fig. 1) were compared with simulations (bright dots on bottom of Fig. 1).¹⁸ The good match verifies the single crystalline nature of the sample. High quality $L2_1$ ordering in space group $Fm\bar{3}m$ with a fitted unit cell parameter of 5.66 Å is confirmed, which is in good agreement with previous results.^{2,3} The simulation also confirms the crystal growth along the [110] axis without twinning.

Spin echo NMR probes the local hyperfine fields of the active atoms, which strongly depend on the local environment. NMR is able to reveal the next neighboring shells of the ^{59}Co nuclei in the different Co_2FeSi crystals^{15–17,19} and thus, giving insight also into the local ordering. In the case of complete $L2_1$ type ordering, there is only one possible way to distribute the atoms on the crystal lattice, leading to one hyperfine field for the ^{59}Co nuclei and therefore to one narrow resonance line.^{17,20} As expected, NMR shows a very sharp line at 139 MHz in both the floating zone single crystal

FIG. 2. (Color online) ^{59}Co NMR measurements of (a) the Czochralski grown single crystal (triangles) (b) the polycrystal (squares), (c) the floating zone single crystal (dots). The inset shows the additional resonance lines with a spacing of 30 MHz, indicating B2 type contributions in the Czochralski grown single crystal.

(dots in Fig. 2) and the polycrystal (squares), in line with the results of Inomata *et al.* measured for polycrystals²⁰ and in contrast to previously reported broader NMR lines of, e.g., Co_2FeSi thin films.¹⁷ Thus, the NMR spectra further confirm the high degree of order in the polycrystal and the floating zone molten single crystal, also on a local scale. In contrast, the resonance line of the Czochralski grown single crystal (triangles in Fig. 2) is shifted about 3 MHz toward higher frequencies and by a factor 2 broader with additional shoulders on both sides of the main line with a spacing of about 25 MHz due to exchange of iron and silicon atoms (B2 type structure), reflecting a lower degree of order.

All crystals show metallic behavior in the resistivity measurements, see Fig. 3(a). As expected, the resistivity decreases with decreasing temperature in the temperature range between 300 and 50 K. Remarkably, the resistivity below 50 K is temperature independent, in agreement with the results of Ambrose *et al.*²¹ The residual resistivity at 2 K is 0.0155 $\mu\Omega \text{ m}$ for the floating zone single crystal, 0.0344 $\mu\Omega \text{ m}$ for the polycrystal, and 0.134 $\mu\Omega \text{ m}$ for the Czochralski grown single crystal, respectively. Note that all measurements of the electrical resistivity shown here are well below the Curie-temperature reported to be 1100 K for Co_2FeSi .³

The residual resistivity ratio (RRR) (here $\rho_{300 \text{ K}}/\rho_{2 \text{ K}}$) is a measure of the quality of a crystal.²² Good ordering is inferred in both the zone melted and the polycrystal by the RRR of 5.2 and 5.9, respectively. The RRR values reported

FIG. 3. (Color online) (a) Resistivity as a function of temperature for the Czochralski grown single crystal (triangles), the polycrystal (squares) and the zone molten single crystal. The inset shows the resistivity as a function of T^2 to demonstrate the linear dependence and, thus, the T^2 power law dependence of the resistivity as a function of temperature. (b) Resistivity as a function of temperature on a logarithmic scale to show the plateau at temperatures below 50 K.

here are on the same order of magnitude as found in a Co_2MnSi single crystal (6.5), which is the highest RRR reported for a Heusler compound.^{22,23} The RRR of the Czochralski grown crystal is lower by a factor of 2 and has relatively poor performance compared to the zone molten and polycrystal, indicating a lower degree of order, in line with our NMR results. However, all RRR presented here indicate excellent crystallinity and homogeneity compared to previously reported RRR for Heusler compounds or alloys in general (see, e.g., Refs. 21 and 24–26). The observation of a higher resistivity in the polycrystal compared to the floating zone single crystal might arise from microscopic cracks at the grain boundaries present in the polycrystal, leading to longer transport paths.

Figure 3(b) shows the resistivity as a function of temperature on a logarithmic scale to demonstrate the temperature independence of the resistivity below 50 K. Above 50 K, the resistivity curves of all crystals follow a T^N power law (fit not shown), where $N=1.9$ for the zone molten single crystal, $N=2.1$ for the polycrystal, and $N=1.6$ for the Czochralski grown single crystal, respectively. The resistivity for all three crystals is reasonably well described by an appropriate T^2 behavior in the high temperature regime, a transition regime, and the temperature independent regime below 50 K, while the range of the transition regime is slightly different for the different crystals. The resistivity curves of the zone molten single crystal and the polycrystal approximately scale with each other by a factor of 2.55. The validity of the T^2 behavior in the high temperature regime is further confirmed by a plot of the resistivity as a function of T^2 , demonstrating a linear dependence (see inset of Fig. 3). A T^2 behavior is expected for a conventional ferromagnet due to coherent one-magnon scattering processes.²⁷ Assuming one-magnon scattering of conduction electrons, there must be the possibility for spinflips, and thus, both the spin-up and the spin-down electrons are present at the Fermi level.²⁷ Consequently, one expects the absence of one-magnon scattering in HMFs, where only one spin channel contributes to the electrical transport. The absence of any T^2 contributions at temperatures below 50 K might suggest the absence of a one-magnon channel and thus half-metallic ferromagnetism in Co_2FeSi at temperatures below 50 K. The cross-over to more conventional ferromagnetic transport behavior above 50 K indicates the onset of spin scattering which needs to be taken into account (besides interface and impurity scattering) for understanding the temperature dependence of the tunneling magnetoresistance in Co_2FeSi devices.^{8,9,28–32}

Excellent crystals of the $L2_1$ ordered half-metallic Heusler compound Co_2FeSi confirmed by Laue diffraction, NMR, and the residual resistivity were obtained. The ratio between the residual resistivity at 300 and 2 K is on the same order of magnitude as the best RRR previously reported for a Heusler compound. The resistivity as a function of temperature roughly follows a T^2 behavior in the high temperature regime, as expected for ferromagnets. Remarkably, the resistivity is temperature independent at low T , which might indicate half-metallic ferromagnetism of Co_2FeSi in the low temperature regime. The synthesis of such high quality Heusler single crystals opens a promising route to exploit the rich physical properties that are realized in various Heusler compounds.

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