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Large negative magnetoresistance effects in $Co_2Cr_{0.6}Fe_{0.4}Al$

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Abstract

Materials, which display large changes in resistivity in response to an applied magnetic field (magnetoresistance) are currently of great interest due to their potential for applications in magnetic sensors, magnetic random access memories, and spintronics. Guided by striking features in the electronic structure of several magnetic compounds, we prepared the Heusler compound $Co_2Cr_{0.6}Fe_{0.4}Al$. Based on our band structure calculations, we have chosen this composition in order to obtain a half-metallic ferromagnet with a van Hove singularity in the vicinity of the Fermi energy in the majority spin channel and a gap in the minority spin channel. We find a magnetoresistive effect of 30% in a small magnetic field of 0.1 T at room temperature. This demonstrates the feasibility of a cheap and simple magnetic sensor based on polycrystalline, intermetallic material.

Keywords: Half-metallic ferromagnet; Heusler compound; Magnetoresistance

1. Introduction

Multilayer systems consisting of interleaved magnetic and nonmagnetic layers presently show the best performance in magnetic sensors, and are in use in hard disk read heads [1–2]. Even larger magnetoresistivities (MR) are observed in the "colossal" magnetoresistive manganites [3] and GdI_2 [4], but the high magnetic fields required to induce the metal–insulator phase transition and the restricted temperature range present limitations for application. The manganites are considered to be half-metallic ferromagnets below their Curie temperature, i.e., only one spin direction is occupied at the conduction band edge. Half-metals are distinguished materials for spin electronics. Due to spin polarized tunneling between different magnetic domains, it is possible to achieve high magnetic field sensitivity of the resistance in polycrystalline bulk materials, polycrystalline films or pressed powder compacts of manganites [5–7], Fe_3O_4 [8] and CrO_2 [7–10]. This interface effect is usually observed at temperatures far below the Curie temperature (T_C). Therefore only relatively small effects are observed in manganites and CrO_2 near room temperature, due to their low T_Cs (<300 K).

This motivated our search for alternative materials with a high Curie temperature, and we considered the magnetic Heusler and half-Heusler compound in detail. The half-Heusler compound NiMnSb was proposed as potential half-metallic ferromagnetic material by band structure calculation in 1983 [11], but spin polarized tunneling has not been shown for NiMnSb to date [12]. However, large negative magnetoresistance effects due to a magnetic field induced phase transition have been found at low temperatures in doped Fe_2VAl [13] and Fe_2VGa [14] (of about 40% at 4.2 K in a field of $B = 13.9$ T) and in $CoV_{0.6}Mn_{0.4}Sb$ [15] (of about 15% at 200 K in a field of $B = 8$ T). A high degree of spin polarization at the Fermi energy is clearly favorable for both colossal magnetoresistivity and spin polarized tunneling magnetoresistivity.

Electronic structure calculations can help to understand the relation between structure and properties of complex systems such as extended inorganic solids. Necessary conditions for large MR effect are well-separated localized/magnetic bands and a strongly

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spin-differentiated conduction band [16]. An additional condition is a half-metallic ferromagnetism with a high density of states (van Hove Singularity, a saddle point in the band structure [4]) at the Fermi energy. Therefore these properties in our band structure calculations within the local spin density approximation served us as fingerprints for the identification of useful materials. A successful application of our recipe was the prediction and realization of large negative magnetoresistance effect near room temperature (70% at 7 T) in GdI_2 [4]. In GdI_2, the metallic Gd *d* states are polarized by the underlying *f* states. Such a band structure is realized for many Heusler and half-Heusler compounds including doped Fe_2VAl [13], Fe_2VGa [14] and $CoV_{0.6}Mn_{0.4}Sb$ [15]. Half-metallic Heusler and half-Heusler compounds show a Slater Pauling behavior and the total spin magnetic moment per unit cell scales with the total number of valence electrons following a simple electron counting scheme [17–20]. Nonmagnetic semi conducting or semi metallic Heusler (half-Heusler) compounds are formed for electron counts of 24 (18) valence electrons per formula unit. Compounds with less or more electrons are candidates for half-metallic ferromagnets, depending on the magnetic scope of the involved atoms. Co_2CrAl, with a valence electron count of $27 = 24 + 3$ (9 valence electrons from each Co, 3 from Al and 6 from Cr) has a saturation magnetization of 3.0 μ_B per formula unit according to this counting scheme [18].

Guided by these features in the electronic structure, we prepared the Heusler compound $Co_2Cr_{0.6}Fe_{0.4}Al$. We find a magnetoresistive effect of 30% in a small magnetic field of 0.1 T at room temperature. Following our suggestion very recently Inomata et al. have prepared a spin valve type tunneling junction with a $Co_2Cr_{0.6}Fe_{0.4}Al$ Heusler compound film which shows a tunneling magneto resistance of 16% at room temperature [21].

2. Experimental section

Starting from the elements (Co 99.8%, Cr 99.9%, Fe 99.9% and Al 99.95%, Chempur) we synthesized polycrystalline samples by arc melting. Regrinding and remelting were performed to ensure homogeneity. Finally the samples were pressed to pellets. Annealed samples were prepared at 1100 K for 1 day in a sealed evacuated silica tube. All the samples were quenched to room temperature. Slowly cooled samples showed additional lines in neutron diffraction. This counter-intuitive temperature treatment is based on a variety of experimental observations and is in agreement with the results of Nishino et al. [22]. Annealed pellets and pressed powder compacts (typical dimension: diameter 8 mm, thickness 1 mm) were used for resistance measurements. Polycrystalline samples were characterized by magnetic measurements, using a SQUID magnetometer (Quantum Design MPMS-XL5). Powder neutron diffraction pattern at room temperature of $Co_2Cr_{0.6}Fe_{0.4}Al$ were taken with neutrons of wavelength 2.3433 Å (Ge (1–10) monochromator) at the ORPHEE reactor of Laboratoire Leon Brillouin (LLB) in Saclay, France. The neutron scattering lengths employed in the structure refinement were 0.3635, 0.9450, 0.3449 and

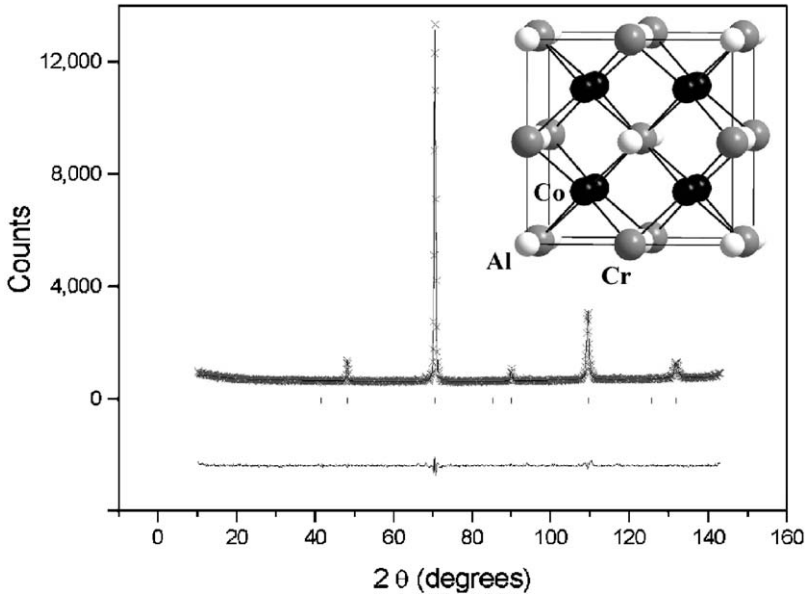

Fig. 1. Powder neutron diffraction pattern at room temperature of $Co_2Cr_{0.6}Fe_{0.4}Al$ and the crystal structure of a Heusler compound Co_2CrAl (inset). Data shown as crosses, and the difference plot between model and data shown below. The vertical lines (bottom) show the Bragg peak positions for $Co_2Cr_{0.6}Fe_{0.4}Al$. The Refinement agreement, weighted profile agreement, and χ^2 values were $R = 3.22\%$, $R_W = 4.39$ and $\chi^2 = 1.98$.

0.2490 for Cr, Fe, Al and Co (cm^{-12}), respectively. Mössbauer spectra were collected at room temperature with a constant-acceleration type Mössbauer spectrometer equipped with a 1024 channel analyzer operating in the time scale mode and a 25 mCi $^{57}Co/Rh$ source was employed. The spectra were analyzed using a computer program (ENFINO) [23].

Heusler compounds crystallize with $L2_1$ structure (Fig. 1, inset). In $Co_2Cr_{0.6}Fe_{0.4}Al$ the Al atoms form a FCC lattice with Co atoms on the tetrahedral sites and Cr and Fe atoms on the octahedral sites. Self-consistent first principle calculations within the local density approximation of the electronic structure of $Co_2Cr_{0.6}Fe_{0.4}Al$ were preformed using the LMTO method in the atomic sphere approximation (ASA). The sphere radii were chosen by the program automatically. A detailed description of the LMTO-ASA method and its application on electronic structure calculation is given elsewhere [24]. Super structure calculations were performed assuming an ordered arrangement of Fe and Cr on the octahedral site.

3. Results and discussion

Co_2CrAl has a half-metallic ferromagnetic electronic structure. The calculated spin polarized density of states shows a gap for minority spin electrons and exhibits conducting electrons at the Fermi level for the majority spin direction only. But we do not observe a significant magnetoresistive effect. However, our fingerprint, a van Hove singularity, is situated 0.015 eV (corresponding to 0.8 electrons per formula unit within a rigid band model) above the Fermi energy. In order to tailor the properties within the framework of our model, adjustment of the electron count is necessary to increase the Fermi energy to the density of states (DOS) peak of the majority bands, which coincides with the density of states peak of the van Hove Singularity. This special feature in the band structure is found at an electron count of about $27.8 = 24.0 + 3.8$ valence electrons. To do so, we have chosen Fe as a dopant, because it is expected that this substitution will also increase the T_C of the material. The calculated spin polarized density of states of $Co_2Cr_{0.6}Fe_{0.4}Al$ is shown in Fig. 2. Different models for the superstructure on Cr/Fe positions have always given a half-metallic band structure. The Fermi energy for this doping indeed coincides with a DOS peak of the majority spin direction due to a van Hove singularity and a gap in the minority spin direction. The local magnetic moments are 0.96 μ_B on Co, 2.77 μ_B on Fe and 1.52 μ_B on Cr. Chromium and iron states are completely polarized, with exchange splittings of 1.2 and 1.7 eV, respectively. The splitting between the Co-majority and minority bands is smaller (1.0 eV). The Co–Cr- and the Co–Fe-interactions, as the strongest bonding interactions, lead to a gap in the minority band and determine the position of the Fermi energy. The interaction between all transition metals is ferromagnetic, leading to a total calculated moment of 3.8 μ_B. The Al-states are only slightly polarized, due to a weak bonding between Cr and Al.

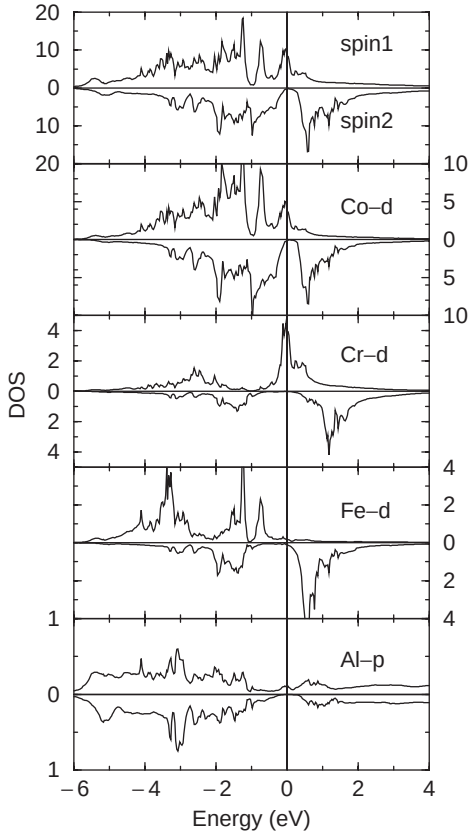

Fig. 2. Spin polarized density of states SDOS and the partial densities of states of the 'ordered' Heusler compound $Co_2Cr_{0.6}Fe_{0.4}Al$. We have used the tight binding linearized muffin tin orbital method within the atomic sphere approximation (TB-LMTO-ASA) of the Andersen group [24].

The measured ambient temperature neutron powder diffraction diagram of $Co_2Cr_{0.6}Fe_{0.4}Al$ (Fig. 1) reveals the well-ordered structure of a Heusler phase with a cubic lattice (Fm-$3m$) and a lattice constant of $a = 5.737$ Å. The data set can be refined with Al atoms on a FCC lattice with a distribution of Co atoms on the tetrahedral sites and Cr and Fe atoms statistically distributed on the octahedral sites. Slowly cooled samples show additional lines indicating a phase separation. The data shown below therefore are from quenched samples only. For the undoped Co_2CrAl we find a lattice constant of $a = 5.727$ Å. Data are shown as crosses, and the difference plot between model and data shown below. The vertical lines (bottom) show the Bragg peak positions for $Co_2Cr_{0.6}Fe_{0.4}Al$. The Refinement agreement, weighted profile agreement, and χ^2 values were $R = 3.22\%$, $R_W = 4.39$ and $\chi^2 = 1.98$. Due

to the similar scattering lengths of Al and Cr we cannot exclude disorder on this position, however, our band structure calculations have shown that this kind of disorder ($B2$ structure) does not destroy the half-metallic gap [25].

The Curie temperature of $Co_2Cr_{0.6}Fe_{0.4}Al$ (27.8 valence electrons) was determined by high temperature SQUID measurements to be around 750 K (Fig. 3 inset). A T_C of 693 K is reported for the 28 electrons compound Co_2MnAl [23]. Using a SQUID magnetometer, we detected a saturation magnetic moment of 93 emu/g at $T = 6.5$ K and $B = 1$ T. The remnance of 2 emu/g and coercitive field of 1 mT indicate that $Co_2Cr_{0.6}Fe_{0.4}Al$ is a soft magnet. This high magnetic moment corresponds to 3.4 μ_B per formula unit (Fig. 3) and is slightly reduced compared with the magnetic moment predicted by the LDA-band-structure calculation. The reduction may be explained by the presence of paramagnetic clusters in the solid solution alloy not visible via neutron diffraction but observable in the Mössbauer spectra. It is evident in Fig. 4 that for $Co_2Cr_{0.6}Fe_{0.4}Al$ most of the Fe-atoms (93%) couple ferromagnetically (sextet) and a small fraction (7%, doublet) is in a paramagnetic state. The magnetic moment of slowly cooled samples is reduced to ca. 70% again in agreement with the Mössbauer spectra. The ferromagnetic contribution of around 70% is significantly smaller compared to the quenched samples.

Magnetoresistance measurements were performed on the pressed powder compacts. In the simplest case, polycrystalline material is expected to form a network of spin polarized 'tunneling' devices [7]. In this case electron transport from grain to grain will depend on the spin directions of the neighboring grains and grain connectivity. In powder samples this can give rise to large magnetoresistive effects below the Curie temperature. Indeed we find a negative magnetoresistivity of more than 30% at room temperature in a magnetic field of only $\mu_0 H = 0.1$ T as is shown in Fig. 5. This is far higher than that observed in other metallic bulk materials. The effect is saturated in a field of only 0.2 T and even high fields up to 8 T will not induce

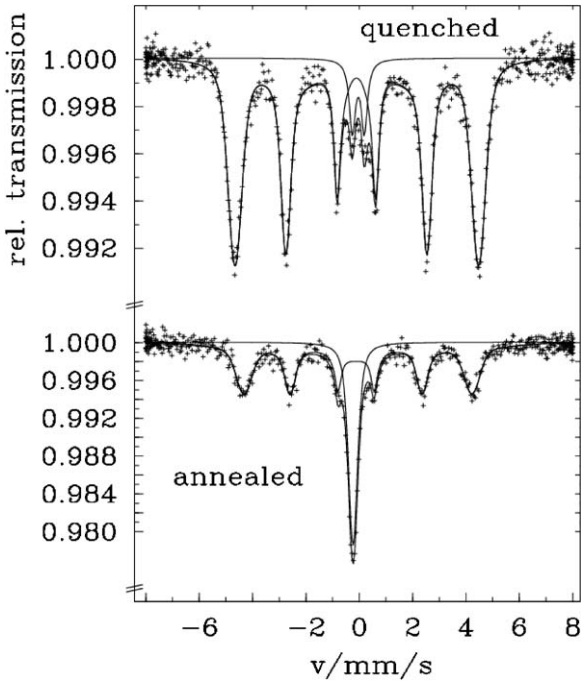

Fig. 4. Room temperature Mössbauer Spectra of $Co_2Cr_{0.6}Fe_{0.4}Al$. Quenched sample upper panel, annealed and slowly cooled lower panel.

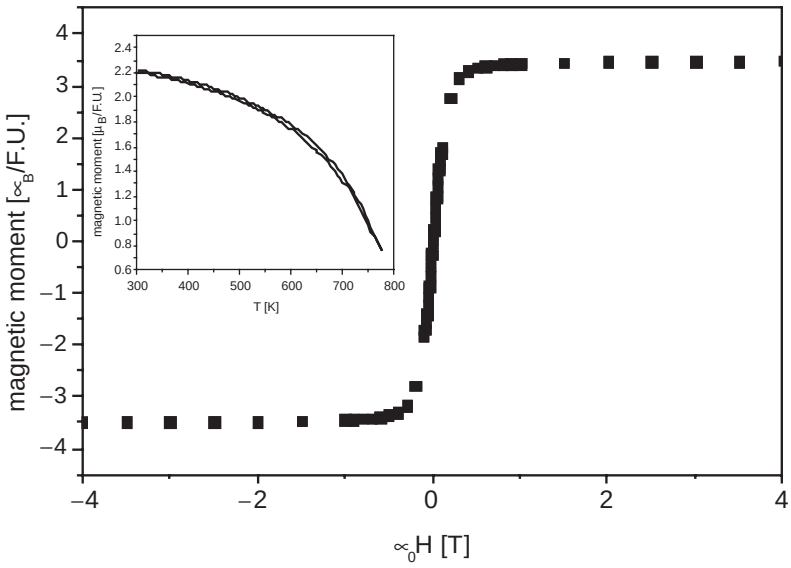

Fig. 3. Magnetization of $Co_2Cr_{0.6}Fe_{0.4}Al$ measured at 5 K with a SQUID magnetometer. The coercive field $\mu_0 H$ is of the order of 1 mT and therefore the magnetic hysteresis is not visible on this scale. Inset: Temperature dependence of the saturation moment measured in an external field of $\mu_0 H = 0.1$ T (sample not in saturation).

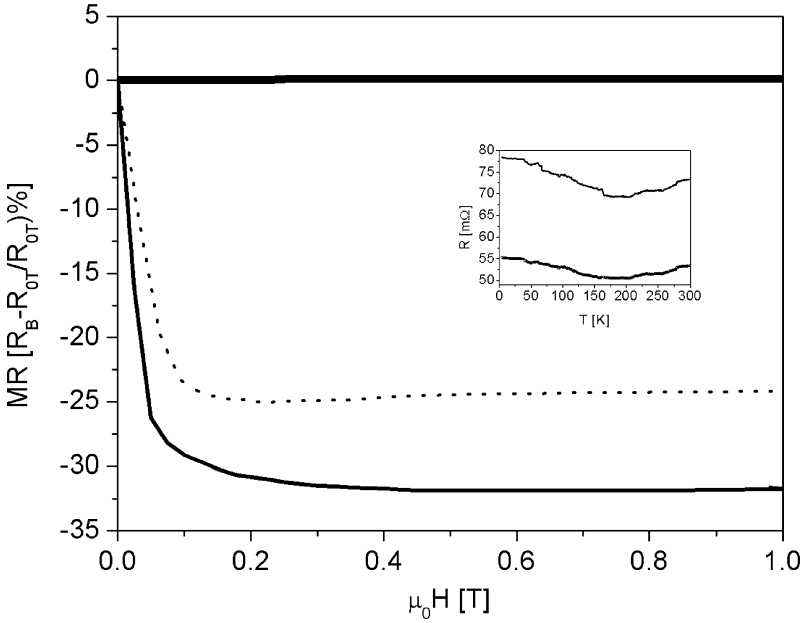

Fig. 5. Magnetoresistance of $Co_2Cr_{0.6}Fe_{0.4}Al$ and Co_2CrAl at room temperature as a function of an external field. Polycrystalline powder compacts of Co_2CrAl show no remarkable effect (thick line). Polycrystalline powder compacts of $Co_2Cr_{0.6}Fe_{0.4}Al$ show a large effect (solid line). Annealing the pressed pellets reduces the magnetoresistive effect slightly (dashed lines). The Inset shows the resistivity versus temperature curve of $Co_2Cr_{0.6}Fe_{0.4}Al$ at a zero field (solid line) and within an external field of 8 T (circles).

additional magnetoresistive effects. The effect is nearly temperature independent over the whole investigated temperature range (see Fig. 5, inset). Therefore magnetic-field induced suppression of thermal spin disorder cannot be responsible for the high magnetoresistance-effect. Additionally it should be noted that in polycrystalline bulk material the 'tunneling' magnetoresistivity is expected to be much smaller than in thin-film devices with the same degree of spin polarization in the material itself. This is due to the fact that in the latter case the spins can switch from parallel to antiparallel alignment, while for powders the spins are randomly aligned in a zero field. In this experiment the current contacts were aligned in the direction of the magnetic field. Astonishingly for current contacts aligned perpendicular to the magnetic field a positive magnetoresistivity of the same order of magnitude is observed. This anisotropy is not expected for spin polarized tunneling and requires strong spin–orbit coupling effects, magnetostriction changing grain coupling, grain movement or other effects. An anisotropic effect is also found in manganites, double perovskites and Fe_3O_4, the effect is attributed to an orbital moment on the surface layer [8]. Though we cannot give a decisive answer for the origin of the magnetoresistive effect in our powder samples, a tunneling magnetoresistive effect has been shown to exist in thin film TMR devices recently [21], following our suggestions. For comparison we have measured also the magnetoresistance effect of the ferromagnetic half-metal Co_2CrAl. In spite of very similar magnetization data and analogous preparation of the pellets no significant magnetoresistivity can be found over the whole investigated temperature range in agreement with the absence of the fingerprint in band structure calculations.

Our observation of a large magnetoresistance effect at room temperature in moderate fields establishes the ferromagnetic Heusler compound $Co_2Cr_{0.6}Fe_{0.4}Al$ as a new material suitable for magnetoresistive sensors based on cheap powder technology. In contrast to the half-metallic oxides, the absence of oxygen will allow also easier integration of these intermetallic compounds into semiconductor technology. The high Curie temperature also allows for the possibility of applications above room temperature, as will be necessary for instance in automotive applications.

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