Transport properties of the ferromagnetic Heusler alloy Co_2TiSn

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We report the results of magnetization, zero-field resistivity, and magnetoresistance measurements in the ferromagnetic Heusler alloy Co_2TiSn. There is a striking change in the character of electron transport as the system undergoes the paramagnetic to ferromagnetic transition. In the paramagnetic state, the nature of the electron transport is like that of a semiconductor. This changes abruptly to metallic behavior at the onset of ferromagnetic ordering. Application of external magnetic field tends to suppress this semiconducting-like transport leading to a negative magnetoresistance that reaches a peak in the vicinity of the Curie temperature. Comparison is made with the similar unusual behavior observed in other systems, including UNiSn and manganites.

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In recent years, recognition of the half-Heusler compound NiMnSb as a potential spin-injector material for spintronics applications[1] and the discovery of a large magnetic shape memory effect in the full Heusler compound Ni_2MnGa (Ref. 2) have stimulated much research activity on Heusler alloys in general. The full Heusler alloys have composition X_2YZ forming in $L2_1$ structures while the half-Heusler alloys with composition XYZ forms in $C1_b$ structures. Here X and Y are transition elements and Z is an sp element. Traditionally, compounds with Mn occupying the Y site have been drawing the most attention as they form ideal systems for studying localized three-dimensional (3D) metallic magnetism, and such studies of course revealed various interesting functionalities in these materials. Non-manganese Heusler alloys are interesting too. For example Fe_2VAl (Ref. 3) and Fe_2TiSn (Ref. 4) have been the subject of much attention since the 1990s due to their possible heavy fermion behavior. On the other hand, Co-based Heusler alloys Co_2YZ, where Y=Ti, Zr, Hf, etc., and Z=Sn or Al, are considered to be good candidates for studying itinerant electron ferromagnetism.[5] Of these, Co_2TiSn is particularly interesting because of its similarity with the prototype half-metallic system NiMnSb.[6] The shape of the spin-polarized total density of states and the dispersion curves for Co_2TiSn resembles the electronic spectra of half-metallic ferromagnets.[7] Also, the magnetic moment per formula unit is close to an integer number ($1\mu_B$), which should be the case for half-metallic systems. Here we present the results of a magnetization, resistivity, and magnetoresistance studies in a polycrystalline sample of Co_2TiSn. The resistivity shows metallic behavior below the paramagnetic (PM)-ferromagnetic (FM) transition temperature ($T_{Curie} \approx 355$ K). This is consistent with earlier resistivity studies on Co_2TiSn between 4 and 300 K.[8] The nature of the resistivity behavior, however, changes from metallic to semiconductorlike at T_{Curie}. We show that the resistivity around T_{Curie} is quite sensitive to the applied magnetic field. The anomalous negative coefficient of resistivity above the magnetic ordering temperature has earlier been observed in various $(Fe_{1-x}M_x)_3Ga$ (M=V and Ti) and $(Fe_{1-x}N_x)_3Si$ (N=V, Mn, Ti, and Cr) pseudobinary alloys[9,10] and UNiSn.[11] We shall compare our results with these earlier experimental findings. Further, we discuss our results in the light of a fairly recent theory on the resistivity due to the spin-dependent scattering of carriers in ferromagnetic metals with localized spins.[12]

Polycrystalline samples of Co_2TiSn are prepared by argon-arc melting from starting materials of 4N purity. The sample has been annealed *in vacuo* at 800 °C for 7 days. The sample is characterized with a standard x-ray diffraction study and it consists of a single phase with a cubic $L2_1$ Heusler structure. Magnetization measurements are performed with a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5). Resistivity of the sample is measured with the standard four-probe technique. A homemade cryocooler is used for zero-field resistivity measurements in the temperature regime 30 K$\leqslant T \leqslant$385 K. A separate oven system is employed to extend the temperature range to 450 K. A superconducting magnet with a field up to 80 kOe is used for magnetoresistance study.

Figure 1 presents the magnetization (M) versus temperature (T) plot for the polycrystalline Co_2TiSn sample in fields of 100 Oe, 10 kOe, and 50 kOe. The T_{Curie} is estimated from the inflection point in the M vs T curve (or even better from the peak of dM/dT vs T curve). The estimated T_{Curie} from the 100 Oe M vs T data is $\approx$350 K. This is slightly lower than the reported value of 359 K.[13] However, it is clear from Fig. 1 that with the increase in the applied field the ferromagnetism continues to persist in the higher T regime. Consequently the estimated values of T_{Curie} are higher. These results clearly show that the magnetic properties of Co_2TiSn around the PM-FM transition are quite sensitive to the applied field.

Figure 2 presents the resistivity (ρ) vs T plot in zero applied field. There is a distinct change in the resistivity from metallic to semiconductor-like taking place at 355 K. This temperature matches well with the T_{Curie} determined from the magnetization measurements; hence, we comment that this change in the character of electronic transport is associated with the FM-PM transition. Although the resistivity in the FM regime shows metallic character, the magnitude of the resistivity remains fairly high (above 300 $\mu\Omega$ cm) even

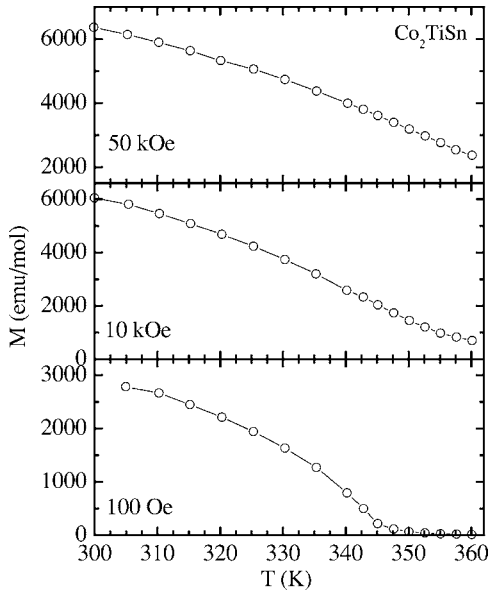

FIG. 1. Magnetization vs temperature data of Co_2TiSn for different applied fields. Data exist down to 5 K but are not shown here for the sake of clarity.

in the low temperature regime. However, it was possible to fit this metallic resistivity with a standard Bloch-Gruniessen law plus a T^2 term. The Debye temperature estimated from this fitting is 411 K, which is comparable to that of the isostructural Heusler compound Fe_2TiSn.[4] The T^2 term can arise due to the spin-flip scattering of charge carriers by magnons in a ferromagnet, and also due to strong interactions in the Fermi liquid. A careful study of resistivity, at least down to the helium temperature, is needed to discern among the various possible origins. Such a study is in progress now. On the other hand, the resistivity above 355 K can be fitted into an expression $e^{Eg/2k_BT}$ representing activated behavior in a semiconductor. Figure 3 presents logarithm of resistivity vs $1/T$

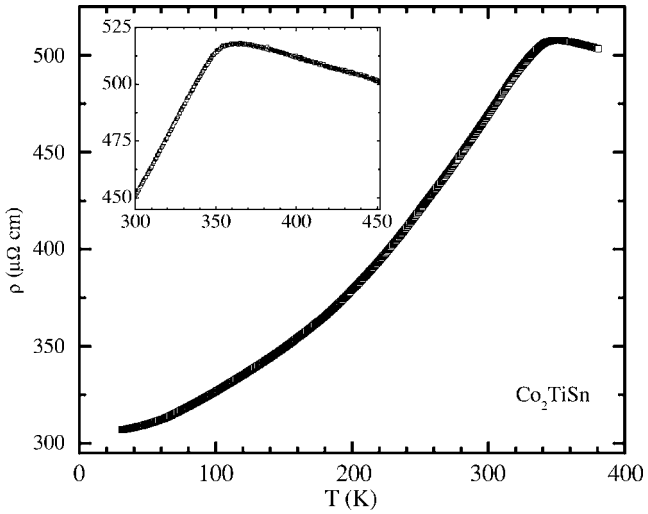

FIG. 2. Resistivity behavior of Co_2TiSn as a function of temperature. The inset shows an enlarged view of the high temperature data (300–450 K) measured in an oven.

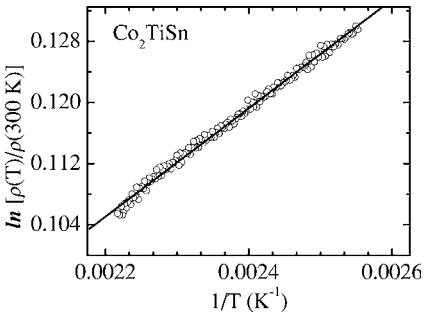

FIG. 3. Natural logarithm of the normalized resistivity as a function of inverse temperature. The solid line is a linear fit to the data. The temperature range covered is 380–450 K.

plot and a band gap of 12.3 ± 1 meV is estimated from the slope of this plot.

Figure 4 presents the effect of the applied magnetic field on the resistivity in and around the PM-FM transition region. The zero-field semiconductinglike behavior tends to get suppressed with the increase of the magnetic field. For the sake of clarity, we present in Fig. 4 only the results with the extreme fields of 0 and 80 kOe. Our preliminary study indicates that the semiconducting gap is reduced by 10% with the application of a 10-kOe field. However, we need to extend the present temperature range of the field-dependent resistivity measurement to make a firm comment on the field dependence of the semiconducting gap. In Fig. 5 we plot the magnetoresistance obtained from the results presented in Fig. 4. Magnetoresistance shows a distinct extremum around T_{Curie}, which suggests a correlation between the spin orientation and the electron scattering. This conjecture is further supported by the observed change in the temperature dependence of magnetization with H in the same T regime (see Fig. 1). We have also measured magnetoresistance as a function of the field at various fixed temperatures between 50 and 380 K. Magnetoresistance becomes negligibly small below 200 K and above 370 K.

A negative coefficient of resistance has earlier been reported above the Curie temperatures for Ni-doped Co_2TiSn alloys.[8] In that work the resistivity measurement for pure Co_2TiSn, however, was up to 300 K only; hence only metallic behavior was reported for this parent compound. It is well

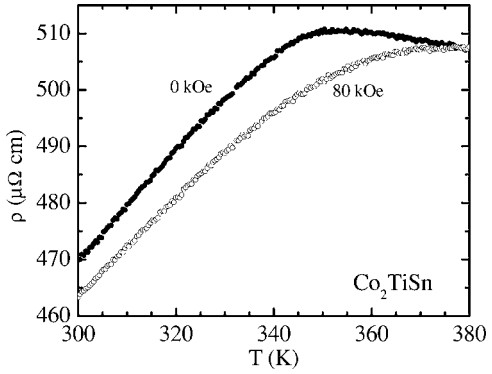

FIG. 4. Resistivity vs temperature plot measured at 0 and 80 kOe magnetic fields.

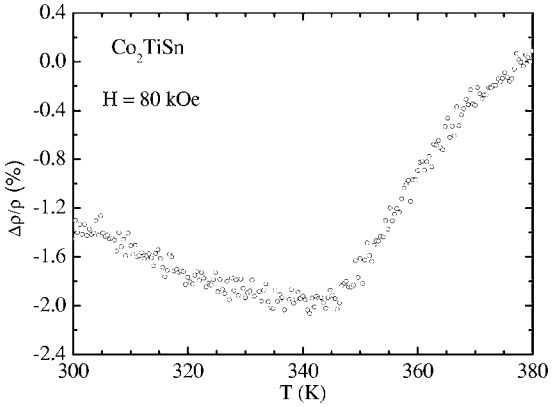

FIG. 5. Magnetoresistance ($\Delta\rho/\rho$) as a function of temperature at 80 kOe of applied magnetic fields. Here $\Delta\rho$ is defined as $[\rho(80\ \text{kOe})-\rho(0\ \text{Oe})]$ and ρ is $\rho(0\ \text{Oe})$.

known from the band-structure calculation that the spin-down density of states function of Co_2TiSn varies strongly with energy at the Fermi level (E_F). As a consequence a slight change in the position of the Fermi level can cause significant variations in the transport properties and this aspect was investigated in detail with doping studies.[8] However, no definite explanation was provided for the observed negative coefficient of resistance in the Ni-doped Co_2TiSn.

Such unusual correlation between the semiconductor-metal transition and the magnetic transition was observed earlier in UNiSn and this has been a subject of considerable experimental[11] and theoretical[14,15] attention. UNiSn, like its isostructural compound NiMnSb, is considered to be a half-metallic ferromagnet.[14–16] From the resistivity measurements, an energy gap of 120 meV has been estimated for the semiconducting state of UNiSn. It is conjectured that at the onset of the magnetic transition, the energy gap of at least one of the spin bands disappears leading to the metallic behavior in resistivity. This picture is consistent with the half-metallic character of the magnetic state. These results can prompt us to think of a one-to-one correspondence between UNiSn and Co_2TiSn. However, some notes of caution here: first the half-metallic nature of Co_2TiSn is yet to be established firmly, and second, there remains some controversy on the magnetic ground state of UNiSn: whether it is ferromagnetic[11] or antiferromagnetic.[15,16]

It is interesting to note here that the electronic structure calculations in the sister compound Fe_2TiSn predicted a nonmagnetic ground state and the existence of a pseudogap at the Fermi level.[4] In real systems, lattice disorder complicated the possibility of a metal-semiconductor transition; a weak ferromagnetic ground state was observed below 240 K followed by semimetal to semiconductorlike transition around 50 K.[4] In addition, there is evidence of heavy fermion behavior in Fe_2TiSn in the low T regime.[4] The effect of Co-doping in Fe_2TiSn has been studied in detail and a negative coefficient of resistivity has been reported for FeCoTiSn for a substantial temperature regime starting from room temperature.[17] However, no definite explanation is available for such behavior. It is also interesting to note that the Heusler alloy Fe_2VAl, which is also on the verge of a magnetic ordering, shows semiconducting behavior down to 2 K.[3] While initial specific heat measurements[3] indicated the possibility of electronic mass enhancement in this compound, later studies suggested that a sample-dependent Schottky anomaly originating from magnetic clusters associated with the Fe defects might be at the origin of the anomalous specific heat behavior.[18]

A negative coefficient of resistivity above the Curie temperature has earlier been reported for ferromagnetic systems such as V- and Ti-doped Fe_3Ga,[9] V-, Ti-, Mn-, and Cr-doped Fe_3Si pseudobinary alloys.[10] A combination of a small conduction electron number per atom and a very large spin-disorder scattering was proposed to be the cause of such anomalous resistivity behavior above the Curie temperature. It was experimentally observed that only those alloys with the resistivity in the paramagnetic state above 150 $\mu\Omega$ cm showed the unusual resistivity behavior.[10] We note here that the resistivity value of $\approx$500 $\mu\Omega$ cm in the paramagnetic state of Co_2TiSn fulfills this criterion. A more recent experiment on the transition metal compound MnRhP has revealed all these interesting features.[19]

The changing sign of the coefficient of resistivity at the PM-FM transition is one of the remarkable features of many manganite compounds showing colossal magnetoresistance (CMR). The magnitude of the resistivity change and its sensitivity to applied H around T_{Curie} is very high in CMR manganites, hence leading to the drastic CMR effects.[20] While we note that the magnetoresistance in Co_2TiSn is definitely not comparable with the CMR observed in various manganites, qualitatively the observed peak in magnetotransport around T_{Curie} in Co_2TiSn is very similar in nature. Magnetic interactions and the underlying microscopic origin of the magnetic phase transition in Heusler alloys are expected to be quite different from those in manganites. The underlying connections between these two different classes of materials are not very obvious. However, there is a fairly recent theoretical effort to understand such behavior in terms of the spin-dependent scattering of carriers in ferromagnetic materials with localized spins.[12] In this theoretical framework, carrier concentration is a key factor and so is the spin fluctuation, especially when a ferromagnetic state is almost unstable against another magnetic state. This theory suggests that in the systems with a small Fermi surface, critical spin fluctuations with long wavelengths can contribute to the resistivity to give rise to a peak at T_{Curie}. This peak becomes sharper in a metal whose ferromagnetic state is on the verge of an instability. External magnetic fields can easily suppress critical spin fluctuations with long wavelengths, resulting in a negative magnetoresistance. A ferromagnetic metal with a small Fermi surface can often become half metallic because of the splitting of the up and down spin bands due to magnetization. While Co_2TiSn has a low carrier concentration and it is supposedly a half-metallic ferromagnet, it is not very clear to the present authors whether the detail characteristics of the Fermi surface of Co_2TiSn would really fit within such theoretical picture.

In conclusion, combining the results of magnetic and transport measurements we show that Co_2TiSn undergoes a semiconductor-metal transition around 350 K and this is associated with a PM-FM transition. In the light of the existing

results on UNiSn and recent theoretical studies on spin-dependent scattering of carriers in ferromagnetic materials, the metallic behavior in the ferromagnetic state of Co_2TiSn is consistent with the conjectured half-metallic character of this compound. It seems that Co_2TiSn belongs to a growing class of ferromagnets with low carrier concentration that shows such unusual correlation between magnetic ordering and metal-semiconductor transition.

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