

Thermal and transport properties of the Heusler-type compounds $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$

C. S. Lue

Department of Physics, National Cheng Kung University, Tainan 70101, Taiwan

Y.-K. Kuo^{a)}

Department of Physics, National Dong Hwa University, Hualien 97401, Taiwan

(Received 12 April 2004; accepted 3 June 2004)

We have studied the thermoelectric properties of the stoichiometric and off-stoichiometric Heusler compounds $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$ between 10 K and 400 K. It is found that the electrical resistivity and Seebeck coefficient are very sensitive to the off-stoichiometry. Seebeck coefficient (S) measurements indicate that all studied materials are p -type materials with moderate S values of about 20–30 $\mu\text{V}/\text{K}$ at room temperature. Broad maximums at around 330 K are observed in S for Fe_2TiSn and $\text{Fe}_{2.05}\text{Ti}_{0.95}\text{Sn}$, and this maximum shifts to higher temperatures with replacing more Ti for Fe. These features are consistent with other experimental results and are related to issues raised by band-structure calculations. © 2004 American Institute of Physics. [DOI: 10.1063/1.1776639]

I. INTRODUCTION

The cubic $L2_1$ Heusler alloys (Cu_2MnAl -type) with general formula X_2YZ , where X and Y are transition metals, and Z often is an element with sp -type valence electrons from columns III through VI in the periodic table, have been of considerable interest due to their unusual magnetic and transport properties. Semiconductors, semimetals, normal Pauli metals, weak ferromagnets, antiferromagnets, as well as half-metallic ferromagnets exist in this class of materials. The variety of physical behavior observed in these Heusler compounds seems to be related to strong modifications of the electronic structure near the Fermi level, as the number of valence electrons per formula unit (Z_t) changes.^{1–3} A recent theoretical study using the full-potential screened Korringa-Kohn-Rotoker method on several Fe-based Heusler alloys indicated that the total spin moment per unit cell (M_t) scales with Z_t , following the simple Slater-Pauling rule $M_t = (Z_t - 24)$.⁴ Accordingly, the net moment disappears with $Z_t = 24$, which corresponds to Fe_2VAl , Fe_2VGa , etc. The Heusler alloys with $Z_t = 24$ are of particular interest, as semiconducting or semimetallic behavior are commonly observed in this family.^{5–10} Most intriguingly, the reported physical properties of Fe_2VAl are reminiscent of heavy fermions in many aspects.⁵

Fe_2TiSn , which also belongs to the group of Heusler alloys with $Z_t = 24$, is found to be nonmagnetic, in agreement with the aforementioned Slater-Pauling relation.^{11,12} The temperature dependence of the electrical resistivity displays typical semimetallic behavior, and an optical conductivity measurement on Fe_2TiSn further confirmed a low carrier density at the Fermi level,¹³ consistent with band-structure calculations.^{11–14} Anomalous low-temperature specific heat was also found for Fe_2TiSn , yielding a huge effective mass enhancement as compared to the value predicted by band-structure calculations.¹¹ These features are quite similar to

the most-studied isostructural compound Fe_2VAl .^{5,15} In order to learn more about the electronic structures of Fe_2TiSn , we have performed a systematic study of the thermoelectric properties including electrical resistivity ρ , Seebeck coefficient S , as well as thermal conductivity κ on $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$ with $-0.05 \leq x \leq 0.10$. These measurements allow us to examine the evolution of the pseudogap and other band features with respect to composition change in these alloys.

II. EXPERIMENTAL DETAILS AND RESULTS

Polycrystalline $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$ samples were fabricated by mixing appropriate amounts of elemental metals. A mixture of high-purity elements was placed on a water-cooled copper crucible and then melted several times in an Ar arc-melting furnace. Due to the volatility of Sn at high temperatures, we started with excess Sn for each sample and determined the x values in $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$ after preparing the ingots, assuming that the weight loss during melting arose entirely from the Sn element. To promote homogeneity, these ingots were annealed in a vacuum-sealed quartz tube at 800 °C for three days and then followed by furnace cooling. Subsequent x-ray analysis of powdered specimens verified the single-phase $L2_1$ cubic Heusler structure, with no other phases evident in the diffraction patterns.

A. Electrical resistivity

The electrical resistivity data were obtained by a standard dc four-terminal method. In Fig. 1 we display the temperature variation of normalized electrical resistivity $\rho(T)/\rho(300\text{ K})$ for $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$ measured during the warming process. On the whole, the character of the normalized electrical resistivity is sensitive to the composition change. We found that an increase of titanium substitution for iron causes a substantial growth of the electrical resistivity of $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$, as the system exhibits metallic behavior with $x \leq 0.05$ but shows semiconducting characteristics with $x > 0.05$. The room-temperature electrical resistivities are on

^{a)}Electronic mail: ykkuo@mail.ndhu.edu.tw

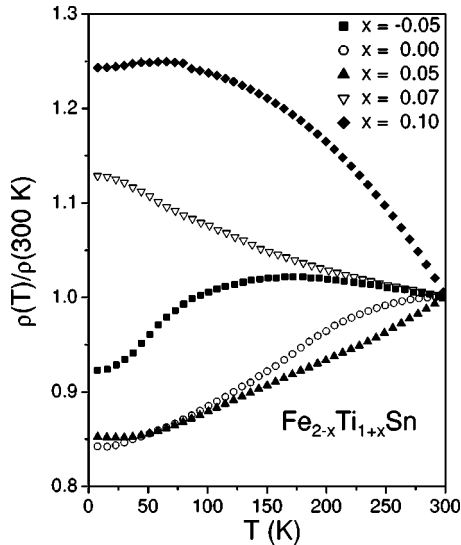


FIG. 1. Normalized electrical resistivity $\rho(T)/\rho(300\text{ K})$ vs temperature for $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$.

the order of $1\text{ m}\Omega\text{ cm}$ for Fe_2TiSn and $3\text{ m}\Omega\text{ cm}$ for $\text{Fe}_{1.90}\text{Ti}_{1.10}\text{Sn}$, respectively, indicative of a semimetallic nature of these alloys. We notice that such a character is quite similar to those observed in the $\text{Fe}_{2-x}\text{V}_{1+x}$ and $\text{Fe}_{2-x}\text{V}_{1+x}$ systems, where these materials become more semiconducting-like with increasing x value.^{5,8,9,16}

B. Seebeck coefficient

Seebeck coefficients for the $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$ series were measured with a dc pulse technique. Seebeck voltages were detected using a pair of thin Cu wires electrically connected to the sample with silver paint at the same positions as the junction of a differential thermocouple. The stray thermal emfs were eliminated by applying long current pulses ($\sim 100\text{ s}$) to a chip resistor which serves as a heater, where the pulses appear in an off-on-off sequence.

In Fig. 2, we show the observed Seebeck coefficient as a

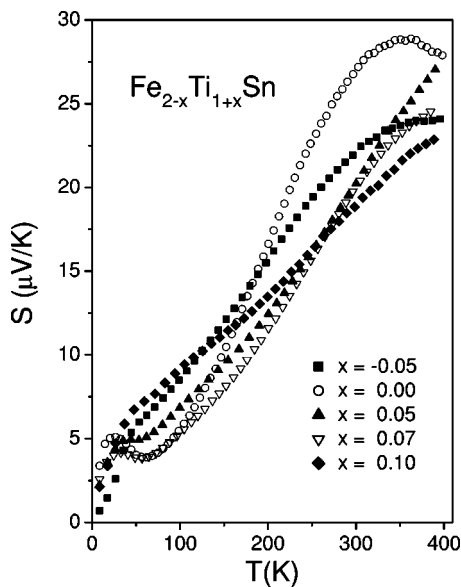


FIG. 2. Seebeck coefficient vs temperature for $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$.

function of temperature. For all studied compositions, the values of S are positive suggesting that the thermal transport is governed by hole-type carriers for these materials. At around $30\text{--}40\text{ K}$, clear peaks in S develop. The coincidence of the maxima in the Seebeck coefficient and thermal conductivity indicates that the low-temperature variation in S is due to the phonon-drag effect. In addition, broad maximums in S were found at around 340 K for both $x=0$ and $x=-0.05$ samples. However, the S maximum has not yet reached up to 400 K with $x>0$, but the trend of flattening out at higher temperatures is clearly seen. We attribute this feature to the thermally excited negative carriers across the band edges near the Fermi surface, and the band splitting within these alloys becomes wider with increasing x in $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$.

It is known that the Seebeck coefficient measurement is a sensitive probe of the energy relative to the Fermi surface, and the results could reveal information about the Fermi-level band structure. From the band calculations, Fe_2TiSn , characterized as a semimetal, has a slightly indirect overlap between electron and hole pockets which yields a small density of states at the Fermi surface.^{11,14} The observed positive Seebeck coefficient for all studied compositions of $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$ suggests the hole pockets are larger than the electron ones or a higher hole mobility, leading to the p -type carriers dominating their transport properties.

As temperature increases, intrinsic electrons and holes are excited across the pseudogap. If the electrons have a slightly higher mobility than the holes at high temperatures, the thermal transport is increasingly dominated by n -type carriers. As a result, the positive Seebeck coefficient would decrease after passing through a broad peak, as we found in these materials. Such an interpretation is consistent with optical conductivity measurements, where a peak at 7000 cm^{-1} was observed and attributed to excitation of quasiparticles across the pseudogap in the optical spectrum of Fe_2TiSn .¹³ In addition, the peak positions in S appear to shift to higher temperatures with increasing x , indicative of a wider pseudogap for higher Ti content in $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$. Accordingly, substituting Ti on Fe sites has an effect on band edge modification which leads to an enhancement of band splitting for these compounds.

It is worthwhile comparing the present S results in $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$ with those of the $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ and $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ compounds.¹⁶ The observed S maximum appears at around 340 K for Fe_2TiSn —higher than for Fe_2VGa ($\sim 130\text{ K}$) and compatible with Fe_2VAl ($\sim 300\text{ K}$). It thus indicates that the size of the pseudogap in Fe_2TiSn is close to that of Fe_2VAl , which has been determined to be $0.2\text{--}0.3\text{ eV}$ by nuclear magnetic resonance and optical conductivity measurements.^{6,7,17} Notice that the value of the pseudogap deduced from the Seebeck coefficient measurement is a bit smaller than those predicted from band-structure calculations for Fe_2TiSn .^{11,14} We believe that atomic disorder is responsible for this discrepancy, as suggested by Jeziarski and Slebarski.¹⁴

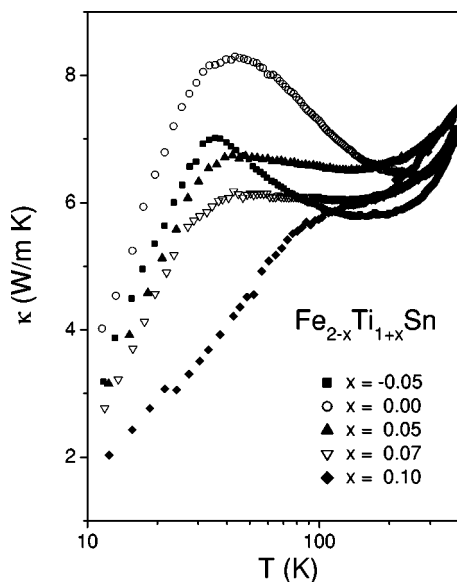


FIG. 3. Temperature dependence of the observed thermal conductivity in $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$.

C. Thermal conductivity

Thermal conductivity measurements were carried out in a close-cycle refrigerator, using a direct heat-pulse technique. Samples were cut to a rectangular parallelepiped shape of typical size of $1.5 \times 1.5 \times 5.0 \text{ mm}^3$ with one end glued (with thermal epoxy) to a copper block that served as a heat sink, while a calibrated chip resistor as a heat source was glued to the other end. The temperature difference was measured by using an *E*-type differential thermocouple with junctions thermally attached to two well-separated positions along the sample. The temperature difference was controlled to be less than 1 K to minimize the heat loss through radiation, and the sample space is maintained in a good vacuum (better than 10^{-4} torr) during measurements. All experiments were performed on warming with a rate slower than 20 K/h. The absolute accuracy of our thermal conductivity measurements is approximately 20%, mainly due to the error in the determination of sample dimensions.

The temperature-dependent thermal conductivity of $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$ is plotted in Fig. 3. For all samples we investigated, the room-temperature κ values are around 7 W/m K, relatively little affected with respect to the composition change. At low temperatures, κ increases with temperature and a maximum appears between 40 K and 50 K, similar to those observed in the isostructural Heusler compounds.¹⁶ This is a typical feature for the reduction of thermal scattering in metals at low temperatures. A clear trend found in κ is that the height of the low-temperature peak gradually decreases with increasing substitution level, and finally disappears with $x=0.10$. This observation indicates a strong enhancement in the phonon scattering by substitution. In general, the total thermal conductivity for ordinary metals

and semimetals is expressed as a sum of electronic and lattice terms. The electronic thermal conductivity (κ_e) can be evaluated using the Wiedemann-Franz law $\kappa_e = L_o T / \rho$. Here the Lorentz number $L_o = 2.45 \times 10^{-8} \text{ W } \Omega / \text{K}^2$ and ρ is the measured resistivity data. This estimate gives a very small contribution of κ_e , suggesting that the thermal conductivity shown in Fig. 3 is essentially due to the lattice thermal conductivity (κ_L). It is noted that the κ_L features in $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ and $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ behave in a similar manner.¹⁶ We thus conclude that at least in this regard, the total thermal conductivity is dominated by κ_L for the semimetallic Heusler-type alloys.

III. CONCLUSIONS

In summary, transport and thermoelectric properties including electrical resistivity ρ , Seebeck coefficient S , as well as thermal conductivity κ in the Heusler-type compounds $\text{Fe}_{2-x}\text{Ti}_{1+x}\text{Sn}$ were studied in detail. We found that the electrical resistivity and Seebeck coefficient are very sensitive to the off-stoichiometry. The downturns in S at higher temperatures are presumably due to the contribution of thermally excited quasiparticles across their band edges. These features are consistent with the band signatures determined from the band-structure calculations.

ACKNOWLEDGMENTS

The authors thank Professor S. T. Lin of National Cheng Kung University in Taiwan for the help with sample preparation. This work was supported by National Science Council, Taiwan under Grant Nos. NSC-92-2112-M-006-012 (C.S.L.) and NSC-92-2112-M-259-011 (Y.K.K.).

¹M. Weinert and R. E. Watson, Phys. Rev. B **58**, 9732 (1998).

²A. Bansil, S. Kaprzyk, P. E. Mijnders, and J. Tobola, Phys. Rev. B **60**, 13396 (1999).

³A. Kellou, N. E. Fenineche, T. Grosdidier, H. Aourag, and C. Coddet, J. Appl. Phys. **94**, 3292 (2003).

⁴I. Galanakis, P. H. Dederichs, and N. Papanikolaou, Phys. Rev. B **66**, 174429 (2002).

⁵Y. Nishino, M. Kato, S. Asano, K. Soda, M. Hayasaki, and U. Mizutani, Phys. Rev. Lett. **79**, 1909 (1997).

⁶C. S. Lue and J. H. Ross, Jr., Phys. Rev. B **58**, 9763 (1998).

⁷C. S. Lue and J. H. Ross, Jr., Phys. Rev. B **61**, 9863 (2000).

⁸K. Endo, H. Matsuda, K. Ooiwa, M. Iijima, K. Ito, T. Goto, and A. Ono, J. Phys. Soc. Jpn. **66**, 1257 (1997).

⁹N. Kawamiya, Y. Nishino, M. Matsuo, and S. Asano, Phys. Rev. B **44**, 12406 (1991).

¹⁰C. S. Lue and J. H. Ross, Jr., Phys. Rev. B **63**, 054420 (2001).

¹¹A. Slebarski *et al.*, Phys. Rev. B **62**, 3296 (2000).

¹²A. Slebarski, M. B. Maple, A. Wrona, and A. Winiarska, Phys. Rev. B **63**, 214416 (2001).

¹³S. V. Dordevic, D. N. Basov, A. Slebarski, M. B. Maple, and L. Degiorgi, Phys. Rev. B **66**, 075122 (2002).

¹⁴A. Jezierski and A. Slebarski, J. Magn. Magn. Mater. **223**, 33 (2001).

¹⁵C. S. Lue, J. H. Ross, Jr., C. F. Chang, and H. D. Yang, Phys. Rev. B **60**, R13941 (1999).

¹⁶C. S. Lue and Y.-K. Kuo, Phys. Rev. B **66**, 085121 (2002).

¹⁷H. Okamura *et al.*, Phys. Rev. Lett. **84**, 3674 (2000).