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Original Scientific Paper

Transport and Spectral Properties of Taylor-phase T-$Al_{73}Mn_{27}$ Complex Intermetallic*

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Abstract. We report the experimental results for the electrical conductivity and the thermoelectric power of the complex intermetallic polygrain compound T-$Al_{73}Mn_{27}$. The electrical conductivity shows the non-metallic behavior, but with finite value in the $T = 0$ limit, and with unusual $\sqrt{T}$ term appearing at the low temperature. This indicates the existence of an electronic pseudo-gap in the system, whereas more detailed theoretical analysis reveals a non-analytic behavior of the spectral conductivity function in the vicinity of the Fermi energy.

Keywords: metallic alloys, Taylor phases, electrical conductivity, spectral density

INTRODUCTION

Complex metallic alloys (CMA) denote intermetallic phases with a giant unit cell containing from tens up to thousands atoms. Typically, the atoms inside the giant unit cell are arranged in clusters with the local icosahedral symmetry. In this paper we study transport properties of the binary compound T-$Al_{73}Mn_{27}$, first discovered by Hofmann[1] and later studied by Taylor.[2,3] It is closely related to decagonal quasi-crystal phase and it is often referred as the Taylor (T) phase. There are a number related ternary compounds where a fraction of manganese atoms are substituted either with Pd or Fe.

The transport properties, as are the electrical conductivity, the thermopower, and the electronic part of the thermal conductivity *etc.*, can all be studied within a unified theoretical approach of the Kubo-Greenwood response theory.[4,5,6] The central quantity of this formalism is the spectral conductivity function $\sigma_S(E)$ that incorporates both, the band structure of the system through the density of states, $n(E)$, and the transport properties through the diffusivity, $D(E)$:

$$\sigma_S(E) = n(E) \cdot D(E)$$

The diffusivity $D(E)$ is the mean-square velocity of particles in the system multiplied by the scattering relaxation time $\tau(E)$. We would like to emphasize that in the Kubo-Greenwood response theory all temperature dependence of the transport coefficients appears in the Fermi-Dirac distribution function, while all peculiarities of the scattering processes are incorporated in the spectral conductivity function through its energy dependence. There are no temperate dependent terms in the spectral conductivity function, and neither there are temperature dependent terms in the diffusivity $D(E)$.[4,5,6] It is interesting that one can make such an energy-temperature dependence separation. In principle, the spectral conductivity function $\sigma_S(E)$ can be obtained from the calculations of the band structure and related scattering processes. Here we take an opposite approach and use the experimental data to infer the properties and the detailed shape of the spectral conductivity in vicinity of the Fermi level.

EXPERIMENTAL

Polygrain ingot sample was produced from constituent elements by levitation induction melting in a water-cooled copper crucible under an argon atmosphere. Parts of the sample was annealed in argon at 900 and 930 °C for up to 698 h and subsequently quenched into water. Further details on the preparation, characterization, and structural quality of the samples can be

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found in a recent publication.[7] The sample was single phase of a binary T-Al_3Mn of composition $Al_{73}Mn_{27}$. The structure of the Taylor phase is built of two atomic layers stacked along the *b* crystallographic axis, a flat layer F, and a puckered layer composed of two sublayers P1 and P2. The orthorhombic unit cell (space group *Pnma*) contains 156 atoms.[8] In order to perform transport measurements, three bar-shaped samples of dimensions $1 \times 1 \times 7$ mm^3 were cut from the ingot. Electrical resistivity $\rho(T)$ (conductivity $\sigma(T) = 1/\rho(T)$) was measured between 300 K and 2 K using the standard four-terminal technique.[9] The thermoelectric power (the Seebeck coefficient *S*) was measured between 300 K and 2 K by using a standard temperature-gradient technique.[10]

RESULTS AND DISCUSSION

The experimental data on electrical conductivity, $\sigma(T)$, are presented in Figure 1. It shows non-metallic behavior in the whole range of temperatures, but remains finite in the zero temperature limit. The unusual convex behavior is observed in the low temperature region.

This convex behavior is identified as a $\sqrt{T}$ dependence, whereas the formula

$$\sigma(T) = \sigma_0 + \sigma_1 \cdot \sqrt{T} + \sigma_2 \cdot T \qquad (1)$$

fits very well the electric conductivity data in the entire temperature region. The fit, also shown in Figure 1, uses the coefficients $\sigma_0 = 140\ \Omega^{-1}\ \mathrm{cm}^{-1}$ $\sigma_1 = 2.42\ \Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{K}^{-1/2}$ and $\sigma_2 = 0.0534\ \Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{K}^{-1}$. These data are also in agreement with another work[11] on a decagonal approximant of composition similar to ours.

Figure 2 shows the experimental data on thermoelectric power (Seebeck coefficient) for the same

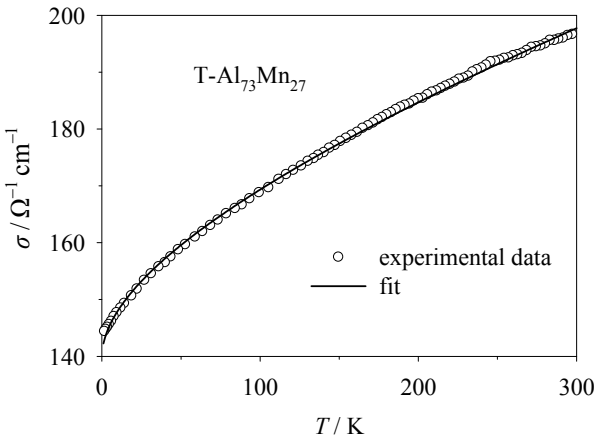

Figure 1. The electrical conductivity of T-$Al_{73}Mn_{27}$ *versus* temperature. The circles represent the experimental data. The full line represents the fit discussed in the text.

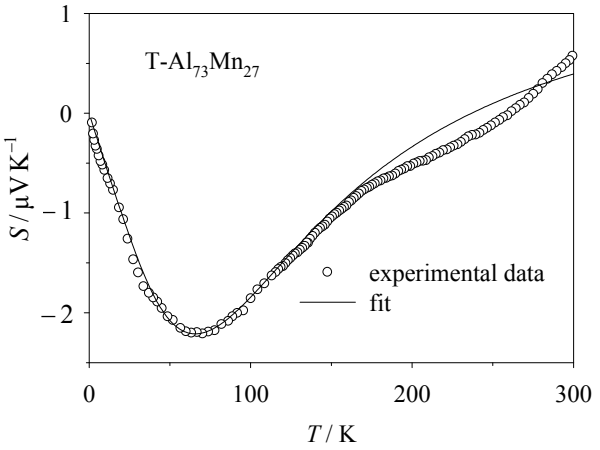

Figure 2. Thermoelectric power *versus* temperature for T-$Al_{73}Mn_{27}$. The experimental data are represented by circles. The full line is the result of the spectral conductivity modeling, as presented in the text.

compound. The maximal absolute value of the thermoelectric power is of the order 2 μV K^{-1}, which is tenfold smaller than in other related compounds like Al-Cu-Fe.[11–13] The small value of the Seebeck coefficient in T-$Al_{73}Mn_{27}$ implies that the contributions from electrons and holes almost cancel. As well known, the electrons, *i.e.*, the particles above the Fermi level, and the holes, *i.e.* the particles bellow the Fermi level, contribute to the thermoelectric power with different signs. The observed small value of *S* thus indicates that the asymmetry between electrons and holes is rather small in T-$Al_{73}Mn_{27}$.

MODELING

The electrical conductivity, $\sigma(T)$, and the thermoelectric power, $S(T)$, will be used now to determine spectral conductivity function, $\sigma_S(E)$, of T-$Al_{73}Mn_{27}$. The procedure that we use is inspired by one developed by Landauro and Maciá and thoroughly described in the Refs. 12–14. However, we find that the original procedure is not very appropriate for T-$Al_{73}Mn_{27}$. In particular, Landauro and Maciá assume that spectral conductivity is an analytic function of energy, which always leads to the appearance of the T^2 in the resulting expression for the temperature dependence of the electric conductivity $\sigma(T)$. In the case of T-$Al_{73}Mn_{27}$, presented through Eq. (1), the T^2-term is insignificant, while the $\sqrt{T}$ term provides much more faithful representation of $\sigma(T)$. The immediate consequence is that the spectral conductivity $\sigma_S(E)$ is not an analytic function of energy. In order to account for this we develop the procedure of extracting the spectral conductivity function $\sigma_S(E)$ from the experimental data that differs from the one used previously.[12–14] We start from the usual integrals that relate for the electrical

conductivity and the thermoelectric power to the spectral conductivity, *i.e.*

$$\sigma(T) = \int de \frac{\sigma_S(e)}{4t\cosh^2(\frac{e-e_m}{2t})} \quad (2)$$

and

$$S(T) = -\frac{S_0}{t\sigma(T)} \int de \frac{(e-e_m)\sigma_S(e)}{4t\cosh^2(\frac{e-e_m}{2t})} \quad (3)$$

For convenience, we use the dimensionless variable $e = E/(1\text{ eV})$ for the energy. Similarly, e_m denotes the dimensionless chemical potential $\mu/(1\text{ eV})$, t stands for the dimensionless temperature $T/(1\text{ eV}/k_B) = T/11594$ K, whereas the thermopower is measured in units of

$$S_0 = \frac{k_B}{|q_e|} = 86.25\frac{\mu V}{K}$$

q_e and k_B denote respectively the electron charge and the Boltzmann constant. The origin of the energy scale is placed at the Fermi level, *i.e.* $E_F = \mu(T = 0) = 0$.

It is important to note that the temperature dependence of the electrical conductivity and the thermoelectric power in Eqs. (2) and (3) comes explicitly from the derivative of the Fermi-Dirac distribution function, $\{4t\cosh^2[(e–e_m)/2t]\}^{-1}$, but also implicitly through the temperature dependence of the chemical potential $\mu(T)$ (*i.e.* $e_m(t)$). In principle, temperature dependence of the chemical potential should be determined self-consistently for a given, fixed number of electrons in the system. The usual way to do this, in metals with smooth, nonsingular electronic density of states, is through the Sommerfeld expansion, which leads to the shift of the chemical potential proportional to T^2 and higher powers of T. As argued above, the T^2 and higher terms do not show in the electrical conductivity in T-$Al_{73}Mn_{27}$. This would suggest that we should neglect altogether the temperature dependence of the chemical potential, and use the approximation $e_m = e_m(T = 0) = 0$. On the other hand, in the case of a singular behavior of the electronic density of states near the Fermi level, the Sommerfeld expansion does not apply. However, it should be recalled that quite generally the temperature dependence of the chemical potential is a consequence of the asymmetry in density of states with respect to the Fermi level. The small measured values of the thermoelectric power for T-$Al_{73}Mn_{27}$ show that this asymmetry is weak. This again supports the approximation of fixed chemical potential, which we thus use in the rest of the paper. This also facilitates the forthcoming analysis of the experimental data. The electrical conductivity is then determined entirely by the part of $\sigma_s(e)$ symmetric with respect to the Fermi level, whereas the thermoelectric power is determined entirely by the antisymmetric part of $\sigma_S(e)$. Therefore the symmetric and antisymmetric part of the spectral conductivity function, respectively denoted by $\sigma_S^s(e)$ and $\sigma_S^a(e)$,

$$\sigma_S^s(e) = \frac{1}{2}\cdot(\sigma_S(e) + \sigma_S(-e))$$
$$\sigma_S^a(e) = \frac{1}{2}\cdot(\sigma_S(e) - \sigma_S(-e))$$
$$\sigma_S(e) = \sigma_S^s(e) + \sigma_S^a(e)$$

can be extracted independently from the conductivity and the thermopower data.

From the temperate dependence of the electrical conductivity in Eq. (1) one can guess the functional form of the symmetric part of $\sigma_S(e)$:

$$\sigma_S^s(e) = \sigma_0 + a\cdot\sqrt{|e|} + b\cdot|e| \quad (4)$$

The relation that couples the coefficients of a and b to the parameters σ_1 and σ_2 in Eq. (1) may be obtained through numerical integration (we used Mathematica), with the result

$$a = \sigma_1\cdot 101\ K^{1/2}$$
$$b = \sigma_2\cdot 8.34\ \ 10^3\ K.$$

For the asymmetric part of the spectral function another approach shows as convenient. Unlike electrical conductivity, the thermopower data can be fitted with an analytical function, for example by the polynomial function of T. However, in order to obtain a good fit to the experimental data, one is forced take the polynomial function of a very high order. This also implies that the polynomial representation of the antisymmetric part of spectral conductivity that includes many terms, to high order in energy. As an alternative to a polynomial representation, we choose to use the continuous piecewise linear function. The piecewise linear function (PLF) consists of interconnected linear segments of different slopes. This choice seems not only more practical but also has some advantage from the physical point of view, since each change of the linear segment takes place at energy that is directly related to some characteristic temperature in the thermopower data. In the case of T-$Al_{73}Mn_{27}$ the parameterization requires only two characteristic energies e_1 and e_2, and the PLF function is then written as

$$\sigma_S^a(e) = \begin{cases} c \cdot e & for\ |e| \le e_1 \\ d \cdot e + [e_1(c-d)] & for\ e_1 \le e \le e_2 \\ f \cdot e + [e_1(c-d) + e_2(d-f)] & for\ e_2 \le e \\ -\sigma_S^a(-e) & for\ e \le 0 \end{cases} \quad (5)$$

with the coefficients c, d and f representing the slopes of the linear segments. These coefficients, together with energies e_1 and e_2, are obtained by fitting the resulting integral for $S(T)$ in Eq. (3) to the data for the thermopower in T-$Al_{73}Mn_{27}$. The resulting asymmetric part of the spectral function is pictured in Figure 3.

The abrupt changes in slope that appears at energies 0.018 eV and 0.036 eV are directly related to the changes in the behavior of measured $S(T)$ at temperatures of 70 K and 170 K that can be observed in Figure 3. The thermopower calculated on the basis of the spectral function of Figure 3 is shown as the black line in Figure 2, on the top of the experimental data.

The full set of parameters that parameterize the conductivity spectral function are summarized in Table 1. The resulting conductivity spectral function for in T-$Al_{73}Mn_{27}$ is shown in Figure 4.

The most important feature of the spectral function in Figure 4 is the pronounced pseudogap around the Fermi level. Within the energy range of ±0.1 eV the spectral function looses around 40 percent of its spectral weight. Moreover, our analysis, based on the transport measurements to low temperatures, reveals the fine structure of the pseudogap, featuring the $|E|^{1/2}$ singularity at the Fermi level. Although similar singularities have been observed in several quasicrystals through low temperature tunneling experiments,[15] the present approach through the analysis of the transport properties in the wide temperature range has not been exemplified before to our knowledge.

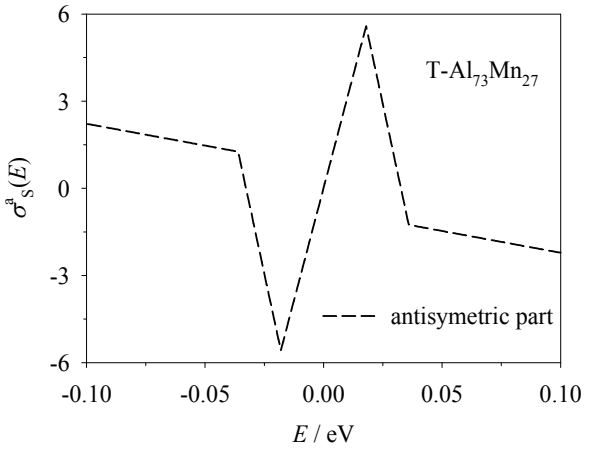

Figure 3. The antisymmetric part of spectral conductivity for the binary system T-$Al_{73}Mn_{27}$. The advantage of this parameterization is direct interpretation of the model parameters as the widths of the characteristic windows in energy with characteristic values of $\sigma_S^a(e)$ within these windows.

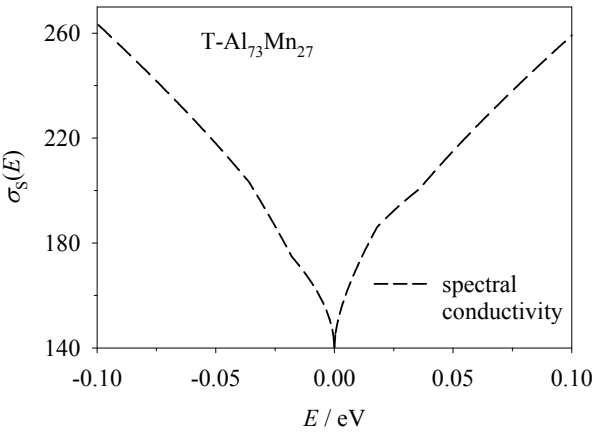

Figure 4. The spectral conductivity $\sigma_S(E)$ for the T-$Al_{73}Mn_{27}$. The singularity around the Fermi energy (E = 0) is clearly pronounced. The sharpness of the pseudogap is directly related to the convex behavior of the electric conductivity, $\sigma(T)$, at low temperatures. The symmetric part clearly dominates the spectral function.

CONCLUSION

In conclusion, we presented the experimental results and the theoretical analysis on electrical conductivity and thermopower in the complex intermetallic compound T-$Al_{73}Mn_{27}$. The aim of the analysis was to extract the spectral conductivity function from the experimental data in order to account for the unusual low temperature behavior observed in the transport coefficients. We have found that spectral conductivity exhibits a weakly asymmetric pseudo-gap around Fermi level, with the shape of the pseudo gap approximately given by a square root in energy. The asymmetry of the pseudo-gap is responsible for the temperature behavior of the thermopower.

Table 1. The coefficients in the spectral conductivity for the T-$Al_{73}Mn_{27}$. The parameters σ_0, *a, b, c, d* and *f* share the same unit, Ω^{-1} cm^{-1}, whereas e_1 and e_2 are expressed in eV

sample	σ_0	*a*	*b*	*c*	e_1	*d*	e_2	*f*
T-$Al_{73}Mn_{27}$	140	243	447	310	0.018	–380	0.036	–15

The analysis of the conductivity and the thermopower measurements thus prove again as a powerful method to discover fine features of the spectral conductivity near the Fermi level, even when the later is singular there, as in the case just presented. This approach is currently being used to characterize a number of related ternary compounds where a fraction of manganese atoms are substituted either with Pd or Fe.

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REFERENCES

1. W. Hofmann, *Aluminium* (Berlin) **20** (1938) 865–872.
2. M. A. Taylor, *Acta Metall*. **8** (1960) 256–267.
3. M. A. Taylor, *Acta Crystallogr.* **14** (1961) 84–84.
4. R. Kubo, *J. Phys. Soc. Jpn.* **12** (1957) 570–586.
5. D. A. Greenwood, *Proc. Phys. Soc.* **71** (1958) 585–596.
6. G. V. Chester and A. Thellung, *Proc. Phys. Soc* **77** (1961) 1005–1013.
7. S. Balanetskyy, G. Meisterernst, M. Heggen, and M. Feuerbacher, *Intermetallics* **16** (2008) 71–87.
8. N. C. Shi, X. Z. Li, Z. S. Ma, and K. H. Kuo, *Acta Crystallogr. B* **50** (1994) 22–30.
9. A. Smontara, A. Bilušić, Ž. Bihar, and I. Smiljanić, *Thermal conductivity of complex metallic alloys*, in: Esther Belin-Ferre (Ed.), *Properties and Application of Complex Metallic Alloys*, World Scientific Publishing (UK) Ltd. England, 2009. pp. 113–147.
10. A. Smontara, K. Biljaković, J. Mazuer, P. Monceau, and F. Levy, *J. Phys.: Condens. Matter* **4** (1992) 3273–3281.
11. P. Volkov and S. J. Poon, *Phys. Rev. B* **52** (1995) 12685–12689.
12. C. V. Landauro Sáenz, Ph.D. thesis, Fakultä für Naturwissenschaften der Technischen Universität Chemnitz genehmigte (2002), p. 147.
13. C. V. Landauro, E. Maciá, and H. Solbrig, *Phys. Rev. B* **67** (2003) 184206-1-184206-7.
14. E. Maciá, T. Takeuchi, and T. Otagiri, *Phys. Rev. B* **72** (2005) 174208-1-174208-8.
15. R. Escudero, J. C. Lasjaunias, Y. Calvayrac, and M. Boudard, *J. Phys.: Condens. Matter* **11** (1999) 383–404.

SAŽETAK

Transport i spektralna svojstva Taylorove faze kompleksne metalne legureT-$Al_{73}Mn_{27}$

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U radu su predstavljeni eksperimentalni rezultati i teorijska analiza električne vodljivosti i termoelektične snage polikristalinične kompleksne metalne legure T-$Al_{73}Mn_{27}$. Eksperiment otkriva neuobičajeno nemetalno ponašanje električne vodljivosti s izraženim $\sqrt{T}$ članom na niskim temperaturama, no s konačnom vrijednosti vodljivosti u granici $T = 0$. Opaženo temperaturno ponašanje sugerira postojanje pseudo-šupljine (engl. *pseudo-gap*) u okolini Fermijevog nivoa. Detaljnija teorijska analiza ukazuje na postojanje neanalitičkog člana u funkciji spektralne vodljivosti u okolici Fermijevog nivoa.