Anomalous low-temperature specific heat of Fe$_{2-x}$V$_{1+x}$Al (x=0; 0.1) alloys

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Abstract. The low-temperature specific heat of stoichiometric and off-stoichiometric Fe$_{2-x}$V$_{1+x}$Al (x = 0; 0.1) Heusler alloys was measured in the temperature interval from 1.8 to 12 K. We report on specific features in the low-temperature heat capacity, which reflect the scattering of the current carriers by magnetic defects in both alloys and the existence of a narrow pseudogap in the V-enriched alloy.

1. Introduction

Systems of transition elements combining semiconducting behavior and magnetism have become of great interest in solid state physics in recent years. Among such systems are the iron-vanadium-aluminum alloys with near stoichiometric composition. In the stoichiometric Fe$_2$VAI alloy with the L$_2_1$ structure the Fe atoms are in a tetrahedral and the V atoms are in an octahedral environment. The magnetic properties of Fe$_{2-x}$V$_{1+x}$Al near the stoichiometric composition are largely due to magnetic defects related to the redistribution of the iron atoms in the crystalline lattice [1]. The Fe$_{2-x}$V$_{1+x}$Al alloys with x close to 0 are of great interest, because these alloys show semiconducting behavior of the electroresistivity $\rho(T)$ up to 1000 K [2]. It was shown in Ref. [3] that in the case of the Fe$_{2-x}$V$_{1+x}$Al alloy with x=0.1 the electroresistivity, the Hall coefficient and the magnetic susceptibility change much more sharply in the low-temperature interval 2 K $\leq T \leq$ 20 K than at high temperatures. A peak in the temperature dependence of the thermoelectric power was found in this alloy in the same temperature range [4]. In Refs. [3, 4] we succeeded to consistently describe the low-temperature features of a number of phenomena based on the ideas of the Fermi energy being located in a narrow pseudogap (width $\approx 4$ meV) in the electron density of states. The narrow pseudogap, i.e. a dip in the density of states, can be related to the displacement of the energy bands in the Fe$_{2-x}$V$_{1+x}$Al alloys enriched by V.

The main purpose of this paper is to report on new data on the existence of the pseudogap state and on physical effects due to the presence of magnetic moments in the Fe$_{2-x}$V$_{1+x}$Al alloys. We analyzed the low-temperature heat capacity in the temperature range (1.8 – 12) K in the stoichiometric Fe$_2$VAI alloy and in the above mentioned Fe$_{1.9}$V$_{1.1}$Al alloy enriched by V. Our study confirms anomalies in the temperature dependence of the heat capacity, which reflect the scattering of the current carriers by magnetic defects in both alloys and the existence of a narrow pseudogap in the Fe$_{1.3}$V$_{1.1}$Al alloy.

2. Experimental results and discussion

2.1. The role of electron scattering by magnetic defects
The procedure of preparing the alloys and of controlling their chemical composition and homogeneity were described in detail in Refs. [4, 5]. The chemical composition was determined with an accuracy of ±1% by energy-dispersive X-ray spectroscopy (EDX). The composition analysis was carried out at the central part of the samples and at their edges. The conductivity of the Fe$_{2-x}$V$_{1+x}$Al ($x=0; 0.1$) alloys is of the hole type according to our measurements of the Hall effect and the thermoelectric power at $T=4.2$ K. The heat capacity was measured by a PPMS-9 (Quantum Design).

The temperature dependence of the heat capacity $C(T)$ of the Fe$_{2}$VAl and the Fe$_{1.9}$V$_{1.1}$Al alloys are shown in Figs. 1 and 2, respectively. The insets confirm a $C/T$ versus $T^2$ dependence. According to Refs. [1, 2] the contribution of the current carriers to the heat capacity at temperatures below 10 K noticeably exceeds that of the lattice, which can, therefore, be neglected. As seen from the insets in Figs. 1 and 2, $C/T$ increases significantly with decreasing $T$, i.e. the $\gamma$ coefficient for the hole heat capacity $c_h = \gamma T$ grows, which was already observed in Refs. [1, 2, 6], but not fully interpreted. According to the evaluation in Ref. [2], the increase of $\gamma$ can lead to a growth of the effective mass of the holes at the Fermi level to approximately 20 times the free electron mass, which means that the alloy could be considered as a heavy fermion system. Other authors believe that the growth of $C/T$ can be related to Schottky contributions from the magnetic defects [1]. We give here another explanation for this effect.

![Figure 1](image)

**Figure 1.** The heat capacity $C$ as a function of temperature for the Fe$_{2}$VAl sample. The symbols represent the experimental data; the solid line is a fit to Eq. (1). Inset: $C/T$ vs. $T^2$.

In the Fe$_{2-x}$V$_{1+x}$Al alloys with $x\geq0$, the Fe atoms, which are placed on the V sites, can be considered as magnetic anti-site defects. The paramagnetic character of the magnetic susceptibility described in Refs. [3, 6] for the polycrystalline Fe$_{1.9}$V$_{1.1}$Al and Fe$_{2}$VAl alloys provides evidence for the presence of local magnetic moments at low concentration. Ishikawa et al. [7] have also inferred a low concentration of magnetic anti-site defects in Fe$_{1.98}$V$_{1.02}$Al, Fe$_{1.95}$V$_{1.05}$Al and Fe$_{2}$VAl single crystals, based on their relatively low magnetization at temperatures below 50K. Therefore, the model of dilute magnetic systems can be applied to describe the low-temperature heat capacity of these alloys with a small deviation from stoichiometry. To describe the observed dependence of $C(T)$, besides the usual
electron term $\gamma T$, an additional contribution to the heat capacity $c_{Ak} = bT \ln(T_K/T)$, according to the Appelbaum-Kondo theory [8, 9] for paramagnetic centers in metals, should be taken into account. Here $T_K$ is the Kondo temperature and $b$ is a fit parameter of the order of $\gamma$. This contribution is a consequence of changing the energy by forming a singlet ground state in the "magnetic impurity - conduction electron" bound system. Hence the low-temperature heat capacity of the Fe$_{2-x}$V$_{1+x}$Al alloys can be presented in form

$$c_A(T) = \gamma T + bT \ln(T_K/T).$$

The additional term $b \ln(T_K/T)$ leads to the sharp increase of $C/T$ at low temperatures.

*Figure 2.* The heat capacity $C$ as a function of temperature for the Fe$_{1.9}$V$_{1.1}$Al sample. The symbols represent the experimental data; the solid line is a fit to Eq. (1). The dashed line is an extrapolation of the $C(T)$ dependence to $T = 0$. Inset: $C/T$ vs. $T^2$.

The results of a calculation of the heat capacity using Eq. (1) are presented by the solid lines in Figs. 1 and 2, respectively, where the following fit parameters were used: $\gamma = 2.73$ and 2.07 mJ/g-atom·K$^2$, $b = 1.54$ and 2.56 mJ/g-atom·K$^2$, $T_K = 28$ and 20 K. The close values of the fit parameters for Fe$_{1.9}$V$_{1.1}$Al and Fe$_2$VAl can be associated with a rather low concentration of magnetic anti-site defects, inherent in the V-enriched samples and Fe$_2$VAl. [6, 7]. As seen from Fig. 1, the experimental dependence of $C(T)$ for Fe$_2$VAl is in a good agreement with the theoretical curve. However, for the Fe$_{1.9}$V$_{1.1}$Al sample enriched by V the theoretical curve lies below the experimental values of the heat capacity in low-temperature range. This disagreement can be attributed to the presence of an additional contribution to the heat capacity $c_{add} = C(T) - (\gamma T + c_{Ak})$, which peaks at $T = 2.5$ K (Fig.3).

2.2. Contribution of the pseudogap state in the V-enriched sample

It should be noted that a maximum in the temperature dependence of the thermoelectric power was observed in the Fe$_{1.9}$V$_{1.1}$Al sample in the same temperature range [4]. It was shown that the corresponding contribution to the thermoelectric power of $\alpha_{add}(T)$ in Fe$_{1.9}$V$_{1.1}$Al (inset in Fig. 3) could be explained by the location of the Fermi level in the pseudogap with a width $\Delta$ of about 4 meV. In
Ref. [3] based on the same hypothesis and with approximately the same value of $\Delta$ we achieved a consistent theoretical description of the anomalous low-temperature dependence of the electroresistivity and the magnetic susceptibility, observed in the alloy with $x=0.1$. Therefore, there is good reason to believe that the maximum of the heat capacity in the above alloy is also caused by the existence of a narrow pseudogap in the density of states at the Fermi edge. For calculating the electron specific heat $c_0(T)$, taking the effect of a pseudogap into account, we used the simple approach based on approximations as employed in Refs. [3, 4]. In the framework of this approach the pseudogap contribution is characterized by three parameters, which are the width of the pseudogap $\Delta$ and the values of the electron density of states at the bottom of and outside the pseudogap. The corresponding equation has the form

$$c_0(T) = \gamma T + \gamma_0 T (3/2\pi)^2 \int_{0}^{\Delta T} x^2 \left[ ch(x/2) \right]^2 dx. \quad (2)$$

The term $\gamma T$ reflects the contribution of the density of states outside the pseudogap and, in essence, coincides with the first term of Eq. (1) in the vicinity of the pseudogap. The value of $\gamma_0$ is equal to the density of states at the bottom of the pseudogap, where the Fermi energy is located. The second term in Eq. (2) has a maximum and describes the temperature dependence of $c_{add}(T)$ shown in Fig. 3. Figure 4 shows the result of fitting the theoretical dependence of the heat capacity, presented as the sum of $c_0(T)$ and the second term in Eq. (1), reflecting the contribution of scattering by magnetic defects, to the experimental data in the vicinity of the maximum with the following fit parameters: $\gamma_0 = 3$ mJ/g-at K$^2$, $\Delta = 20$ K, $\gamma = 2.04$ mJ/g-at K$^2$, $b = 2.3$ mJ/g-at K$^2$, $T_K = 20$ K. Note that the temperature dependence of the heat capacity is in good agreement with the theoretical ideas stated here. This is consistent with Refs. [3, 4], where the thermoelectric power and other physical parameters were studied.

![Figure 3. Temperature dependence of an additional contribution to the heat capacity $c_{add}$ for the Fe$_{1.9}$V$_{1.1}$Al sample. The inset shows the temperature dependence of the pseudogap contribution to the thermoelectric power $\alpha_{add}$ for this sample [4].](image)
3. Conclusions

We conclude that the pseudogap state and the scattering of the current carriers by magnetic defects play a significant role in the electronic properties of Fe\textsubscript{2-x}V\textsubscript{x+1}Al (x=0; 0.1). The anomalous monotonic temperature dependence of $C(T)$ is caused by strong exchange scattering of electrons. In the case of the V-enriched alloy the non-monotonical contribution to the specific heat can be explained by the existence of a narrow pseudogap in the electron density of states.

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