ON THE ORIGIN OF THE HEAVY-FERMION-LIKE BEHAVIOR OF THE HEUSLER-TYPE $Fe_{3-x}V_xM$ (M=Al,Ga) ALLOYS*

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The electronic structure of $Fe_{3-x}V_xM$ (M=Al, Ga) alloys was investigated by *ab initio* method. Magnetic and non-magnetic band structure of $Fe_{3-x}V_xM$ was calculated for concentrations $x = 0.0$–1.0. Calculations have shown that the transition from magnetic to non-magnetic state is accompanied by the qualitative changes in the band structure in the vicinity of the Fermi level (ε_F). For concentrations $0.5 \leq x \leq 1$ the Density Of States (DOS) at ε_F in both magnetic states display a sharp peak composed solely of the $3d$ states of impurity Fe-AS atom (Fe atom at nominally V atom position of Fe_2VAl Heusler compound). In the magnetic state only majority-spin states enter the DOS near ε_F. The quasi-gap around the ε_F found in Fe_2VM is filled up by 3d↑ states of Fe-AS which produce the sharp structures at ε_F. Transition to the non-magnetic state results in the narrowing and strengthening of the peak of Fe-AS 3d-states DOS at ε_F and the opening of the well-defined gap just above the Fermi level. The changes of the DOS around ε_F connected with the variation of Fe-AS concentration and magnetic transition explain the peculiar behavior of the electrical resistivity observed experimentally.

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Recently the pseudo-binary $Fe_{3-x}V_xM$ (M=Al, Ga) alloys with DO_3 crystal structure are the subject of the intensive experimental [1–5] and theoretical [6–8] investigations. The alloys attract the attention of many authors because they exhibit a variety of properties unique among the 3d-intermetallic alloys. At composition $x = 1$ the Heusler Fe_2VM compounds

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behave in a manner typical for insulators. In the entire measured temperatures (*e.g.* from 2K to above 1200 K in case of Fe_2VAl [4]) the resistivity of Fe_2VM decreases with increasing temperature. The resistivity of the end ($x = 0$) compounds (Fe_3Al and Fe_3Ga) show a metallic behavior. When in these compounds the Fe atoms are replaced by V atoms, the character of the temperature dependence of the electrical resistivity changes when the sample undergoes the transition from magnetic to para- or non-magnetic state. At low temperatures the resistivity increases with temperature and forms a maximum near Curie temperature T_C. Above T_C it decreases with increasing temperature. With increasing V composition the temperature region with negative resistivity slope expands in parallel with reduction in T_C. On the other hand, the Fe_2VAl compound is characterized by anomalously large value of the electronic specific-heat coefficient γ [2,4] and by the presence of the Fermi edge in the XPS spectrum [2]. This behavior can suggest that Fe_2VAl is a possible candidate for a 3d heavy-fermion system [2,4].

Though the electronic structure of Fe_2VM was the subject of *ab initio* band structure calculations, there are no results describing the role of the Fe-AS defect atoms in nearly stoichiometric Heusler compositions. The aim of the presented band structure calculations was to extend the super-cell calculations reported in [7] to cover the wider vanadium concentration range in $Fe_{3-x}V_xAl$. The $Fe_{3-x}V_xGa$ alloys were calculated in order to clarify the role of M atoms in the alloys. The calculations were performed with the use of the *tight-binding linear muffin-tin orbital* (TB-LMTO) method [9]. To simulate the disorder in $Fe_{3-x}V_xM$ alloys the super-cell methodology of alloy modeling was used. The details of input data preparation and approximation used were shortly discussed in our previous paper [10].

The most important magnetic results for $Fe_{3-x}V_xAl$ we already presented and shortly discussed in [10]. The calculated magnetic structure of $Fe_{3-x}V_xGa$ was found very similar. The calculations for $x = 0.5$–0.94 confirmed the conclusions drawn from experiments [3] about the existence of magnetic clusters. For small concentrations of Fe-AS atoms calculations have shown that the Fe-AS impurities together with eight surrounding Fe atoms form the magnetic clusters. The magnetic moment of Fe-AS atoms is large ($\sim 2.7\ \mu_B$) and robust against the V concentration in the range of $x = 0.5$–0.9375. The eight iron atoms surrounding the Fe-AS one are only slightly polarized and for concentration range $x = 0.75$–0.9375 their magnetic moments do not exceed $0.2\ \mu_B$. Within this concentration range the effective, cluster magnetic moment is of order of $4\ \mu_B$ and does not depend on x. Due to the large spatial separation of these clusters their direct magnetic exchange interaction can be neglected. Existence of such magnetic defects in Fe_2VM compounds is responsible for the marginally magnetic character of these compounds observed experimentally. Furthermore, the

scattering of electrons on such non-interacting magnetic defects may result in negative magneto-resistance also observed in the $Fe_{3-x}V_xM$ alloys at temperatures below Curie temperature T_C [11, 12]. Estimations based on the calculated total energy difference between the magnetic and non-magnetic solutions for $Fe_{3-x}V_xM$ ($x = 0.75$–0.9375) results in T_C of roughly the same values as the measured ones. This coincidence indicate that for $x \simeq 1.0$ the magnetic transition leads to the disappearance of local magnetic moments and consequently to the non-magnetic state of $Fe_{3-x}V_xM$ alloys above T_C.

The most interesting result of the calculations performed for the $Fe_{3-x}V_xM$ alloys with $x = 0.5$–0.9375 is the behavior of the DOS around the Fermi level (ε_F). In the Heusler Fe_2VM compounds the total DOS (Fig. 1) in the vicinity of ε_F is characterized by a deep valley (quasi-gap) with the very small values of DOS at ε_F and width of ~0.5 eV. Similar results were already reported by other authors [6, 7].

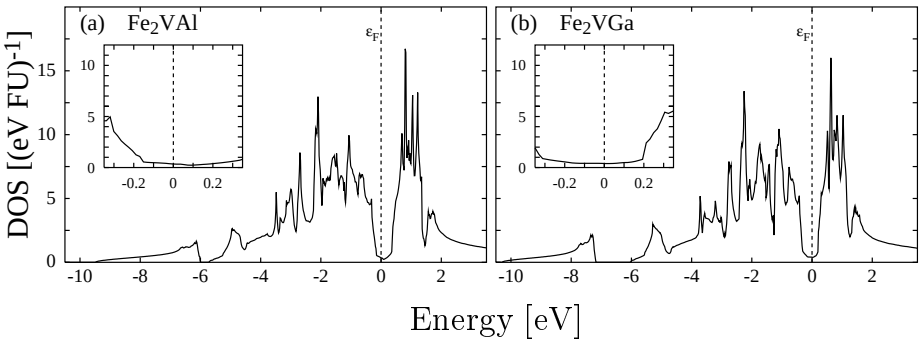

Fig. 1. Total density of states (DOS) of Fe_2VM (M=Al and Ga) compounds. Vertical dash lines mark the Fermi energy (ε_F). Inserts show the DOS in the vicinity of ε_F.

The picture changes qualitatively in the presence of Fe-AS impurities (Fig. 2). Parts (a)–(d) and (a_1)–(d_1) of Fig. 2 show the total DOS of $Fe_{3-x}V_xAl$ and $Fe_{3-x}V_xGa$ calculated in magnetic and non-magnetic state of the alloys. The magnetic Fe-AS defect atoms replacing the V atoms in both Fe_2VM compounds diminish slightly the width of the quasi-gap and lead to the appearance of the peak of the majority *d*-states DOS located exactly at ε_F. From the rest of the valence band it is separated by two dips of low DOS. In $Fe_{2.06}V_{0.94}Al$ the Fermi level lies at the lower boundary of the peak and a dip below changes to a narrow gap of width of $\simeq 0.05$ eV. In principle the hopping is possible only within the narrow band which originate from 3d↑ states of Fe-AS atoms. With decreasing x the carrier concentration available near the ε_F grows so the residual resistivity should decrease. This effect was observed in both $Fe_{3-x}V_xM$ alloys [1, 2, 4].

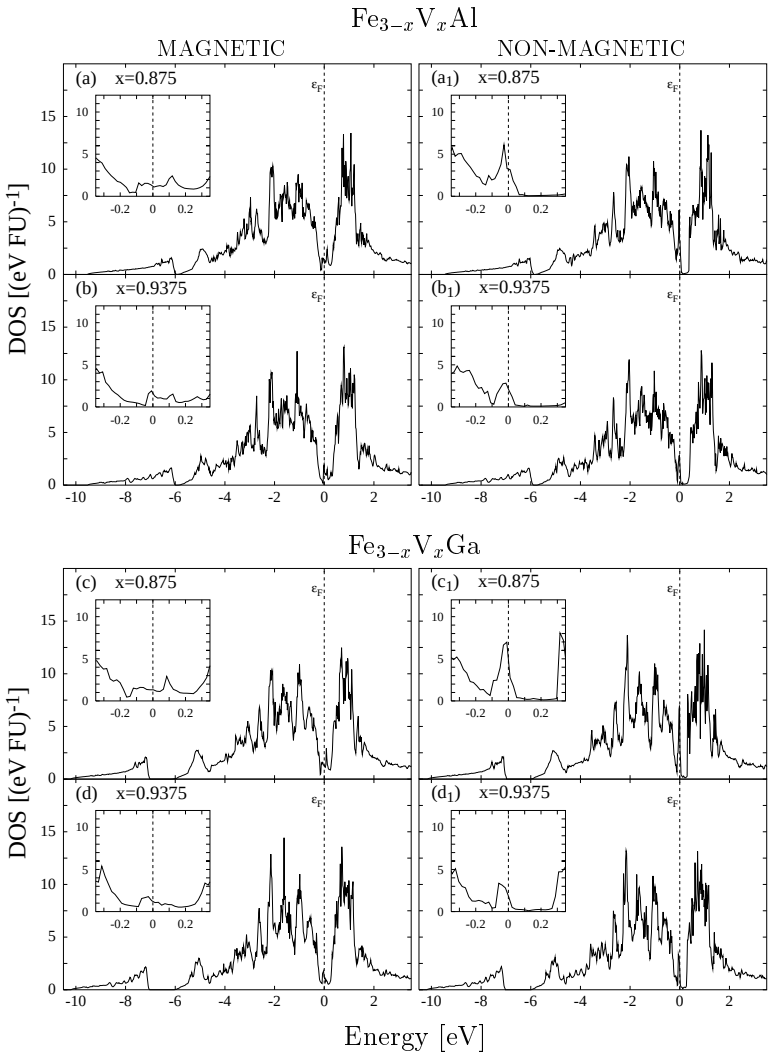

Fig. 2. Total DOS of the $Fe_{3-x}V_xM$ with M=Al (parts (a), (b)) and M=Ga (parts (c), (d)) for $x = 0.875$ and 0.9375 in magnetic ((a),(b),(c),(d)) and non-magnetic ((a_1),(b_1),(c_1),(d_1)) states. (For other notations see Fig. 1.)

The transition to the non-magnetic state leads again to the qualitative changes in DOS near ε_F. The $3d$-peak at ε_F grows, becomes sharper and shifts to higher binding energies. The ε_F shifts to upper boundary of the peak and the energy gap of 0.2—0.3 eV width opens above the ε_F. All these peculiarities of DOS near ε_F originate from the d-states of Fe-AS atoms hybridized with the d-states of surrounding Fe atoms in the octahedral co-

ordination. The hybridization with other electronic states located around the ε_F is hardly visible.

The existence of the energy gap at ε_F in nonmagnetic $Fe_{3-x}V_xM$ explains the observed negative resistivity slope for $T > T_C$. On the other hand the presence of the narrow and relatively high peak of DOS at ε_F provides an explanation for the observed high values of the electronic specific-heat coefficient. In summary it can be concluded that the unusual (typical for $4f$ heavy-fermion compounds) electronic, magnetic and transport properties of Fe_2VM compounds can be explained by the presence of Fe-AS defects whose role is analogous to that of $4f$-elements in heavy-fermion compounds.

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