Electrical, magnetic and galvanomagnetic properties of Mn-based Heusler alloys

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Abstract. Half-metallic ferromagnets and spin gapless semiconductors are promising materials for spintronic devices since a high degree of the spin polarization of charge carriers can be realized in such materials. Spin gapless semiconductors make it possible to combine the properties of half-metallic ferromagnets with semiconductor characteristics and to perform fine tuning of the energy gap value. The Mn₂MeAl (Me = Ti, V, Cr, Mn, Fe, Co, Ni) Heusler alloys can possess such features. We studied the electrical, magnetic and galvanomagnetic properties of the Mn₂MeAl (Me = Ti, V, Cr, Mn, Fe, Co, Ni) Heusler alloys from 4.2 K to 900 K and in magnetic fields up to 100 kOe. The features in the electronic and magnetic properties of Mn₂MeAl Heusler alloys were observed, which can be a manifestation of the electronic energy spectrum peculiarities with occurrence of the half-metallic ferromagnet and/or spin gapless semiconductor states.

1. Introduction

Half-metallic ferromagnets (HMFs) are new materials with promising properties for spintronics. The main feature of HMFs is the presence of a gap at the Fermi level $E_F$ for electron states with spin down and its absence for current carriers with spin up (figure 1a) [1, 2]. Thus, almost 100% spin polarization of charge carriers can be realized, which can be used in spintronics. However, HMFs have some drawbacks connected with metallic conductivity. Therefore, to develop and study such systems, which are close to classical semiconductors in properties, is relevant. Recently, there have been reports on HMFs based on degenerate doped semiconductor HgCr₂Se₄ [3]. Spin gapless semiconductors (SGSs) are also promising materials for spintronics, which possess a wide ($\Delta E \sim 1$ eV) gap near the Fermi energy for one spin projection of current carriers, for the opposite direction energy gap being zero (figure 1b) [2, 4]. Such materials make it possible to combine the properties of HMFs with semiconductor characteristics and to perform fine tuning of the energy gap value, i.e., to control electronic properties.

In practice, it is difficult to strictly implement the conditions for the emergence of HMF and especially SGS states. Nevertheless, a number of papers discuss observations of HMF and SGS states in Heusler alloys (see, for example, [1-7]). Jourdan et al. [5] reported the observation of the HMF state and almost 100% spin polarization in the Co₂MnSi Heusler alloy thin films. Furthermore, there is evidence that the SGS state implementation in the Mn₂CoAl [6] and CoFeMnSi [7] compounds. It is
known [8] that the electronic structure and, consequently, physical properties are changed quite strongly when the \( Me \) component is varied in \( X_2MeZ \) Heusler compounds, where \( Me \)-elements are 3d-transition metals. In this case, transitions from the ordinary (magnetic and nonmagnetic) metallic and semiconductor states to the HMF state, and then to the SGS state and back can be observed.

Figure 1. Schematic view of the density of states \( N(E) \) as a function of energy \( E \): (a) half-metallic ferromagnet and (b) spin gapless semiconductor. The occupied states are indicated by filled areas. Arrows indicate the majority (\( \uparrow \)) and minority (\( \downarrow \)) states.

Up to now, the experimental papers on studying the role of \( Me \)-component change in the kinetic and magnetic properties of Mn-based Heusler alloys are rather scarce. We tried to compensate this deficiency. Thus the aim of the work is to follow the changes in the electrical, magnetic and galvanomagnetic properties of the \( Mn_2MeAl \) Heusler alloys at varying \( Me \)-components (\( Me = Ti, V, Cr, Mn, Fe, Co, Ni \)).

2. Samples and experimental methods
The \( Mn_2MeAl \) Heusler alloys were melted in an induction furnace in a purified argon atmosphere. Then the ingots were annealed for 72 hours at 650°C in an argon atmosphere followed by cooling to room temperature at the rate of 100 K/h.

An elemental analysis was carried out by using a FEI Company Quanta 200 scanning electron microscope equipped with an EDAX X-ray microanalysis unit. The deviation from a stoichiometric composition was revealed to be insignificant in all the samples. X-ray diffraction studies showed that the \( Mn_2TiAl \), \( Mn_2VAl \) and \( Mn_2CrAl \) samples have \( L2_1 \) structure, the others the inverse \( X_a \) type structure. The structural analysis was performed at the Collaborative Access Center, M.N. Mikheev Institute of Metal Physics.

The electrical resistivity was measured by using a standard four-probe method in the temperature range from 4.2 to 900 K. The Hall Effect measurements were carried out according to a standard procedure, which is described in detail in [9, 10]. The field dependences of the magnetization and Hall resistivity \( \rho_H(H) \) were measured at \( T = 4.2 \) K in magnetic fields up to 100 kOe. The samples studied had the form of plates with dimensions of about \((0.5 \times 1.5 \times 5)\) mm. The magnetic field vector was directed strictly perpendicular to the plate plane with an accuracy of \( \pm 2 \) degrees (or \( \pm 2.5\% \)), and the electric current flowed along the largest surface of the sample. To control the asymmetry of the Hall contacts, measurements were made using a 5-point scheme [11, 12] in order to compensate the contribution from the transverse resistivity. It was found that the data obtained using the 5- and 4-contact methods well coincide. Therefore, 4-pin technique was used further to determine the coefficients of the normal and anomalous Hall Effects in the same transverse geometry.

3. Results and discussion
The temperature dependences of the electrical resistivity \( \rho(T) \) (figure 2) show that the \( Mn_2TiAl \), \( Mn_2CrAl \), \( Mn_3Al \), \( Mn_2FeAl \), and \( Mn_2CoAl \) alloys demonstrate relatively large residual resistivity \( \rho_0 \) varying from 242 to 305 \( \mu \Omega \cdot \text{cm} \), as well as regions with a negative temperature coefficient of resistivity. This may indicate the proximity of these compounds to the SGS state with a small gap and
low activation energy. The exceptions are the Mn$_2$VAl and Mn$_2$NiAl alloys where the residual resistivity is relatively small (84 and 120 $\mu\Omega\cdot$cm, respectively) and $\rho(T)$ monotonously increases with the temperature.

The presence of a gap at $E_F$ for one or two spin projections are expected to manifest in other transport and magnetic properties at temperatures much lower than $T_C$. Therefore, the field dependences of the magnetic and galvanomagnetic properties at liquid helium temperature $T = 4.2$ K were studied at varying the Me-component in the Mn$_2$MeAl system ($Me = Ti, V, Cr, Mn, Fe, Co, Ni$).

![Figure 2. Temperature dependences of the electrical resistivity in Mn$_2$MeAl ($Me = Ti, V, Cr, Mn, Fe, Co, Ni$).]

Since all the alloys are suggested to be in the ferromagnetic state, there are both the normal $R_0$ and the anomalous $R_S$ components in their Hall coefficients. By using the field dependences of Hall resistivity (figure 3) and the following equation [13]:

$$\rho_H / H = R_0 + 4\pi R_S M / H$$

where $\rho_H$ is the Hall resistivity, $M$ is the magnetization, the normal and anomalous Hall coefficients were determined.

![Figure 3. Field dependences of the Hall resistivity in Mn$_2$MeAl ($Me = Ti, V, Cr, Mn, Fe, Co, Ni$).]
The normal Hall Effect is described by the first coefficient $R_0$ and associated with the action of the Lorentz force on the movement of conduction electrons in a magnetic field $H$. The second coefficient $R_S$ is associated with the presence of spin-orbit interaction and determined by the scattering processes of current carriers on the inhomogeneities of the crystal lattice (impurities and phonons) and magnetic scattering centers (including magnons).

The magnetization curves $M(H)$ (figure 4) have a form characteristic of ordinary ferromagnets only for the Mn$_2$VAl and Mn$_2$CoAl alloys. The magnetization curves of the Mn$_2$TiAl and Mn$_2$NiAl alloys indicate a more complicated type of their magnetic order. Apparently, the neutron diffraction studies are required to determine accurately the magnetic order type of the alloys. The behavior of $M(H)$ indicates a close to zero total moment for Mn$_3$Al, Mn$_2$CrAl and Mn$_2$FeAl alloys; for the last two systems, this contradicts the calculation results [14]. According to [15], Mn$_3$Al can be characterized as a compensated ferrimagnet that preserves the nature of the half-metallic state. The situation is similar in Mn$_{1.5}$FeV$_{0.5}$Al [16]. Earlier this state was obtained in calculations [17] and was called a half-metallic antiferromagnet. It has a high spin polarization of charge carriers and can be promising for application in spintronics. Probably, this state is realized in the Mn$_3$CrAl and Mn$_2$FeAl alloys too.

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{figure4.png}
\caption{Field dependences of the magnetization.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{figure5.png}
\caption{Dependences of the residual resistivity $\rho_0$, the coefficients of normal $R_0$ and anomalous $R_S$ Hall Effects, the saturation magnetization $M_S$, the mobility $\mu$ and concentration $n$ of charge carriers on valence electron number $z$.}
\end{figure}
The concentration of charge carries was estimated qualitatively. It is well known [18] that the $R_0$ coefficient is determined not only by the number of Hall carriers. The carrier mobility plays an important role in the formation of the normal Hall effect.

As demonstrated in Refs [8, 13, 19-21], the kinetic properties and characteristics are changed strongly with varying $X$- and $Me$-components in $X_2MeZ$ Heusler compounds. Similar large changes were observed in the residual resistivity $\rho_0$, saturation magnetization $M_S$, coefficients of normal $R_0$ and anomalous $R_s$ Hall Effects, as well as in the mobility and concentration of charge carriers depending on the number $z$ of valence electrons at varying $Me$ in the series from Ti to Ni. Figure 5 shows the observed changes in the electronic transport and magnetic properties, which clearly correlate with each other.

4. Conclusions

To conclude, a number of features of electronic and magnetic properties in the Mn$_3$MeAl Heusler alloys can indicate peculiarities of the electron energy spectrum, such as the appearance of half-metallic ferromagnet or spin gapless semiconductor states.

The temperature dependences of the resistivity, the field dependences of the Hall resistivity were measured, and the type, concentration, and mobility of charge carriers were estimated. The regions with a negative temperature coefficient at the temperature dependences of the resistivity were observed, which may indicate proximity to the SGS state with a vanishingly small energy gap.

The observed correlation between the dependences of normal Hall Effect $R_0$ and resistivity $\rho_0$ seem to indicate the essential contribution of scattering processes of current carriers to the anomalous Hall Effect $R_s$. An analysis of the results obtained shows that the transition from Mn$_2$TiAl to Mn$_2$NiAl, i.e. with a variation in the number of valence electrons $z$ within $21 \leq z \leq 27$, significant changes values of the coefficients of the normal and anomalous Hall Effect, magnetization, residual resistivity, type and concentration of current carriers and their mobility take place. At the same time, the type and character of changes in these electronic and magnetic characteristics depending on $z$ clearly correlate with each other.

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