Peculiarities of the electronic and magnetic characteristics in Co$_2$YSi ($Y$ = Ti, V, Cr, Mn, Fe, Co, Ni) Heusler alloys close to the half-metallic ferromagnets and spin gapless semiconductors

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Abstract. The Hall Effect and magnetization of Heusler alloys Co$_2$YSi ($Y$ = Ti, V, Cr, Mn, Fe, Co, Ni) were measured at $T$ = 4.2 K and 300 K in magnetic fields of up to 100 kOe as well as the temperature dependence of the electroresistivity from 4.2 to 300 K. The normal and anomalous Hall coefficients, saturation magnetization, residual resistivity, type and concentration of current carriers and their mobility were obtained. It was demonstrated that there is a clear correlation between the electronic and magnetic parameters obtained, depending on the number of valence electrons $z$, at the transition from Co$_2$TiSi ($z$=26) to Co$_2$NiSi ($z$=32). The observed peculiarities of electronic and magnetic parameters may be due to the appearance of the states of the half-metallic ferromagnet and/or spin gapless semiconductor.

1. Introduction
There are the intermetallic compounds with a general formula $X_2YZ$ ($X$ and $Y$ are 3d-metals, $Z$ is s-, p-elements of the Periodic Table), which are called the Heusler alloys. These compounds have plenty of useful functional properties, such as the shape memory effect, magnetocaloric effect, giant magnetoresistivity etc. [1]. Particular attention is paid to the half-metallic ferromagnets (HMF) and spin gapless semiconductors (SGS), since the close to 100% spin polarization of charge carriers can be realized in HMF and SGS. Therefore, such materials are promising ones for practical applications in spintronics. HMF and SGS both have a gap at the Fermi level for spin-down direction and its absence (HMF) or zero energy gap (SGS) for opposite spin direction, correspondingly.

The high spin polarization of charge carriers was observed in Co$_2$FeSi [2] and Co$_2$MnSi [3]. At varying the $Y$ and/or $Z$ components in the Co$_2$YAl and Co$_2$FeZ alloy systems ($Y$ = Ti, V, Cr, Mn, Fe, Co, Ni; $Z$ = Al, Si, Ga, Ge, In, Sn, Sb) the significant changes occur in the electronic band structure near the Fermi level [4]. Therefore, the task of this report is to study the magnetic properties, electroresistivity and Hall Effect in Co$_2$YSi ($Y$ = Ti, V, Cr, Mn, Fe, Co, Ni) alloys at varying the $Y$-component.

2. Methods
The alloys were obtained by the method of arc melting followed by annealing. The Co$_2$YSi, Co$_2$CrSi, Co$_2$FeSi, and Co$_3$Si ingots were annealed at $T$ = 1100°C for 3 days, and the Co$_2$TiSi, Co$_2$MnSi, and Co$_2$NiSi alloys were annealed at $T$ = 800°C for 9 days. Elemental analysis was carried out by using a
scanning electron microscope equipped with an EDAX X-ray microanalysis attachment. The deviation from a stoichiometric composition was revealed to be insignificant in all samples. X-ray diffraction studies showed that the samples have L2\(_1\) structure. Only Co\(_2\)V\(_3\)Si has a small amount of Co\(_4\)V\(_3\)Si\(_3\) phase (less than 5 %). The structural analysis was performed at the Collaborative Access Center, M.N. Mikheev Institute of Metal Physics.

The temperature dependencies of the electroresistivity were carried out at \(T = 4.2 – 300\) K with the 4-contact technique. The field dependencies of the magnetization and Hall resistivity \(\rho_0(H)\) are measured at \(T = 4.2\) K and 300 K in magnetic fields up to 100 kOe. The samples studied were in the form of plates with dimensions of \(~(0.5\times1.5\times5)\) mm. In this case, 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.

3. Results and discussion

Analysis of the temperature dependencies of the electroresistivity \(\rho(T)\) of Co\(_2\)Y\(_3\)Si (\(Y = Ti, V, Cr, Mn, Fe, Co, Ni\)) (figure 1) showed that the \(\rho(T)\) increases monotonously with temperature for all compounds (superlinearly for \(Y = Ti, Mn, Fe\); sublinearly for \(Y = Co, Ni\)) or tends to saturation at high temperatures (for \(Y = V, Cr\)) [5].

\[
\rho(T) = \rho(0) + c \cdot M_S \quad ,
\]

where \(\rho(0)\) is determined by the mechanisms of scattering of charge carriers by inhomogeneities in the structure of the ferromagnet. This term includes the temperature-independent residual resistivity \(\rho_\text{r}\) as well as the temperature dependent electron–electron (\(\rho_\text{ee}\)) and electron–phonon (\(\rho_\text{ph}\)) components of the electrical resistivity. In this case, it is assumed that \(\rho_\text{r} \gg \rho_\text{ee} \) and \(\rho_\text{ph}\). The second term represents the process of the electronic spectrum transformation with a variation in the temperature; i.e., it takes into account the change in the number of charge carriers \(n\). Here, \(M_S\) is the spontaneous magnetization and \(c\) is a constant that can have any sign [8, 9].

According to the band theory of magnetism [10], which should be valid for HMF and SGS, the spontaneous magnetization can be defined as
where $M_{T=0,H=0}$ is magnetization at $T = 0$ K, $H = 0$ Oe, $T_C$ is Curie temperature.

Therefore, the electrical resistivity can be represented by the expression

$$\rho = a + b \cdot (T / T_C)^2,$$

where the parameters $a$ and $b$, to a first approximation, can be considered as constants. Expression (3) is actually satisfied for almost all the alloys under investigation in a sufficiently wide range of temperatures $T < T_C$ as it can be seen in figure 2.

**Figure 2.** Dependencies $\rho(T/T_C)^2$ of the Co$_2$YSi ($Y = \{Ti, V, Cr, Mn, Fe, Co, Ni\}$). The lines show the results of the processing of the experimental data according to expression (3).

The deviation from relationship (3) becomes significant only in the low-temperature range ($T << T_C$) and described by the second-degree polynomial

$$\rho(T) = \rho_0 + A \cdot T + B \cdot T^2,$$

where $\rho_0$, $A$, and $B$ are constants. The quadratic-in-temperature term in expression (4), as a rule, is associated with the mechanism of electron-electron scattering enhanced in alloys of transition metals due to transitions of charge carriers from the $s$-band to the $d$-band. It should be noted that, in the case of band ferromagnets, the quadratic-in-temperature contribution to the low-temperature electrical resistivity can also be increased as a result of the slight change in the parameters of the electronic spectrum at the Fermi level $E_F$ with a variation in the temperature, and the band component in the electrical resistivity $\rho(T)$ can have any sign [8, 9]. Low-temperature dependencies of the electrical resistivity are shown in figure 3.

The structure of the electronic energy spectrum near the Fermi level of Co$_2$YSi compounds changes not only by growth temperature, but upon transition from one to another alloy in the 3d-component range ($Y = \{Ti, V, Cr, Mn, Fe, Co, Ni\}$) as well. This can manifest itself both magnetic and galvanomagnetic properties. Figure 4 shows the field dependencies of the magnetization at $T = 4.2$ K and 300 K. The samples are ferromagnets and reach saturation at fields $H > 15$ kOe (except Co$_2$VSi and Co$_2$CrSi at 300 K). Figure 5a shows the dependence of the saturation magnetization on the number of valence electrons $z$. The line shows the Slater-Pauling curve [1], which estimates the $M_S$ value of Heusler alloys. $M_S$ values are close to the Slater-Pauling curve only for Co$_2$TiSi and Co$_2$MnSi, and the values for Co$_2$Si and Co$_2$NiSi are close to the calculated ones (they have no HMF- or SGS-states according to ab initio calculations [11]). The $M_S$ values of the remaining alloys are far from “ideal”. It
The values of the Hall coefficients, concentration, mobility, and the main type of charge carriers were estimated from the field dependencies of the Hall resistivity analysis. There are electrons for \( Y = V, Cr, Mn, Ni \) and holes for \( Y = Ti, Fe, Co \) [18]. A clear correlation is evident/observed between the residual electroresistivity \( \rho_0 \), the saturation magnetization \( M_s \), the coefficients of normal \( R_0 \) and anomalous \( R_a \) Hall Effects, mobility \( \mu \) and Curie temperature \( T_c \) [11, 19], as well as between concentration \( n \) and coercive force \( H_c \) depending on the number \( z \) of valence electrons at \( Y \)-varying in the series from Ti to Ni (figure 5).

In addition, a power-law dependence of the coefficient of the anomalous Hall Effect on the residual resistivity with an exponent \( k = 3.1 \) was observed [5, 18]. This is inconsistent with the existing theoretical concepts, but correlates with experimental data obtained on similar Heusler alloy systems [4]. Thus, it is necessary to take into account additional contributions to the anomalous Hall Effect. The observed correlation between the dependencies of normal Hall coefficient \( R_0 \) and residual resistivity \( \rho_0 \) is seemed to indicate the essential contribution in the anomalous Hall coefficient \( R_a \) of scattering processes of current carriers.
Figure 5. Dependencies of the electronic and magnetic parameters and coefficients of the Co$_2$YSi ($Y =$ Ti, V, Cr, Mn, Fe, Co, Ni): a) saturation magnetization $M_s$ (black squares with line at $T =$ 4.2 K, red circles with line at $T =$ 300 K (values for $Y =$ V and Cr at $T =$ 300 K are taken at $H =$ 70 kOe), green line shows Slater-Pauling curve, asterisks are calculated values from [11-16, 19-24], blue open circles are experimental values at 5 K from [24-28]), b) residual resistivity $\rho_0$ (blue open circles are experimental values from [25-26]), c-d) normal $R_s$ and anomalous $R_s$ Hall coefficients, e) mobility $\mu$, f) concentration $n$, g) Curie temperatures [11, 19] and h) coercive force $H_C$ (blue open circles are experimental values from [26-27]) on valence electron values $z$. 
4. Conclusions
The temperature dependencies of the electroresistivity, the field dependencies of the Hall resistivity and magnetization were measured for Co$_2$YSi (Y = Ti, V, Cr, Mn, Fe, Co, Ni). An analysis of the obtained results shows that the transition from Co$_2$TiSi to Co$_2$NiSi, i.e. with a variation in the number of valence electrons $z$ within 26 $\leq z \leq 32$, significantly changes in the sign and values of the coefficients of the normal and anomalous Hall Effect, magnetization, residual resistivity, type and concentration of current carriers and their mobilities. At the same time, the type and origin of changes in these electronic and magnetic characteristics depending on $z$ clearly correlate with each other, and obtained values are typical for metals as well as a type of the temperature dependencies of the electrical resistivity. The electron transport properties of the alloys under consideration are largely determined not only by the scattering mechanisms of charge carriers, but in addition by the processes of electronic band structure changes near the Fermi level $E_F$. The studied materials can be probably used for application in spintronics.

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References
[1] Graf T, Felser C and Parkin S S P 2011 Prog. Sol. State Chem. 39 1
[2] Bombor D et al 2013 Phys. Rev. Lett. 110 066601
[3] Jourdan M et al 2014 Nat. Comm. 5 3974
[4] Marchenkov V V et al 2018 J. Magn. Magn. Mater. 459 211
[5] Perevozhikova Yu A et al 2019 J. Phys.: Conf. Ser. 1389 012110
[6] Kourov N I et al 2015 Curr. Appl. Phys. 15 839
[7] Kourov N I et al 2013 J. Exp. Theor. Phys. 117 121
[8] Irkhin V Yu and Irkhin Yu P 2007 Electronic structure, correlation effects and properties of d- and f-metals and their compounds (Cambridge: Cambridge Int. Sci. Publ.) p 457
[9] Kourov N I et al 2017 Phys. Solid State 59 898
[10] Wohlfarth E P 1968 J. Appl. Phys. 39 1061
[11] Chen X-Q, Podloucky R and Rogl P 2006 J. Appl. Phys. 100 113901
[12] Ozdogan K, Galanakis I, Sasioglu E and Aktas B 2007 Phys. Stat. Sol. (PRL) 1 95
[13] Hasnip P J et al 2014 Materials 7 1473
[14] Pradines B, Arras R, Abdallah I, Biziere N and Calmels L 2017 Phys. Rev. B 95 094425
[15] Pradines B, Arras R and Calmels L 2017 J. Phys.: Conf. Ser. 903 012030
[16] Li G-N, Jin Y-J and Lee J 2010 Chin. Phys. B 19 097102
[17] Jiang H et al 2016 Mater. Sci. Engineer. A 676 191
[18] Perevozhikova Yu A et al 2019 Low Temp. Phys. 45 789
[19] Faleev S V et al 2017 Phys. Rev. Mater. 1 024402
[20] Zayed M K, Elabbar A A and Yassin O A 2018 J. Alloys Comp. 737 790
[21] Raj D P et al 2016 Mater. Res. Express 3 075022
[22] Bentouaf A and Hassan F E H 2015 J. Magn. Magn. Mater. 381 65
[23] Ayhan S and Balci G K 2018 AIP Conf. Proc. 2042 020036
[24] Balke B et al 2006 Phys. Rev. B 74 104405
[25] Barth J et al 2010 Phys. Rev. B 81 064404
[26] Srinivas K, Manivel Raja M and Kamat S V 2015 J. Alloys Comp. 619 177
[27] Sebastian V, Lakshmi N and Venugopalan K 2015 J. Magn. Magn. Mater. 386 129
[28] Kandpal H C, Fecher G H and Felser C 2007 J. Phys. D: Appl. Phys. 40 1507