Magnetic, transport and magnetocaloric properties in the Laves phase intermetallic Ho (Co\textsubscript{1-x}Al\textsubscript{x})\textsubscript{2} compounds

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Abstract

The magnetization, magnetoresistivity and magnetocaloric effect (MCE) of the Ho (Co\textsubscript{1-x}Al\textsubscript{x})\textsubscript{2} Laves phase intermetallic compounds for \(x \leq 0.2\) have been investigated. Complex measurements have been carried out in order to determine the influence of substitution in the Co sublattice by Al on the Co moment, type of the magnetic transition and related properties of these compounds. A comparative analysis of the magnetic, transport and magnetocaloric properties of Ho (Co\textsubscript{1-x}Al\textsubscript{x})\textsubscript{2} alloys under various Al concentration is represented. Substitutions at the Co site by Al are found to result in the appearance of itinerant electron metamagnetism (IEM) at the small Al concentrations and in positive magnetovolume effect, leading to an initial increase in the ordering temperature; on the other hand the magnetic phase transition temperature as well as \(\Delta T\) (MCE) do not depend in direct way on the Al concentration. The 16% increase of magnetocaloric effect for the alloy with \(x = 0.02\) is detected in relation to maternal HoCo\textsubscript{2}. A giant value of magnetostrictivity (58%) is observed for the alloy with the same Al concentration.

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1. Introduction

The rare earth – transition metal RCo\textsubscript{2} Laves phase compounds (R-rare earth metal) belong to the family of magnetic materials, which are of interest both from fundamental (for example, as good models for the study of band metamagnetism) and practical point of views. They are widely used with the production of the permanent magnets, memory devices and refrigerants for the magnetic refrigerators [1]. The special features of RCo\textsubscript{2} magnetism are caused by the complex interactions of the well-localized 4-f electrons of the rare earth element R with the itinerant 3d electrons of Co sublattice. Laves phase compounds of RCo\textsubscript{2} are ferrimagnetic and the Co moment is induced by an exchange field produced by the rare earth ions. The interplay of localized and itinerant magnetism brings a wealth of new interesting phenomena. For these reasons these materials have been a subject of intensive experimental and theoretical investigations for the past 40 years [2–9]. The exchange interaction between 3d and 4f-sublattices results in the magnetization of Co sublattice by the molecular field of 4f localized electrons. The value of Co magnetic moments is changed from 1.05 \(\mu_B\) (GdCo\textsubscript{2}) to 0 \(\mu_B\) (LuCo\textsubscript{2}, YCo\textsubscript{2} with nonmagnetic rare earth) in the RCo\textsubscript{2} compounds. The Co magnetic moment in RCo\textsubscript{2} compounds with heavy rare earths is induced by ordering of the localized magnetic moments of the rare earth elements. The instability of the 3d-subsystem in f-d intermetallic compounds can be explained within the framework of the itinerant electron metamagnetism (IEM) theory [3,4,6]. The appearance of the ferromagnetic ordering in the Co 3d-band is observed when exchange energy and the density of states near the Fermi level is sufficiently large to induce the splitting of the Co-3d sub bands [3,4,6]. The density of states RCo\textsubscript{2} and Curie temperatures can be changed as a result of the partial substitution in Co and R-sublattices without changes in the crystal structure, or under the action of hydrostatic pressure on these compounds [9]. The RCo\textsubscript{2} compounds show large magnetovolume effects, which are attributable to an induced Co moment. These large magnetovolume effects can be interpreted generally in terms of IEM taking into account spin fluctuations, i.e. a local band theory of itinerant ferro- or antiferromagnetism. First-order magnetic phase transitions connected to a field-induced change of the density of state appear in RCo\textsubscript{2} compounds. These compounds exhibit various peculiar magnetic and related physical properties characteristic of IEM. The greatest anomalies in the magnetoresistivity, electroresistivity and magnetocaloric effects are observed in the range of the magnetic phase transitions. Magnetostrictive effect
of the HoCo$_2$ was examined originally by Nikitin and Tishin, who detected the first order magnetic phase transition (FOT) at $T = 78$ K, MCE equal to $\Delta T = 5.1$ K, measuring at magnetic field $\mu_0 H = 6$ T at 82 K and $\Delta S = 6.4$ J mole$^{-1}$ K$^{-1}$ [10]. The specific heat data measured in different magnetic fields allow determining the MCE and the isothermal entropy change of HoCo$_2$. Magnetocaloric effect $\Delta T$ for an isentropic process in magnetic fields up to 8 T reaches 10 K for HoCo$_2$ in the vicinity of the magnetic-ordering transition according Sechovsky et al. [11]. The substitution of Co by small amounts of magnetic or nonmagnetic elements does not alter the crystalline electric field and therefore the R-moments remain unaltered [12]. Effect of Co substitutions by Ni and Si in HoCo$_2$ compound, and its effect on magnetic, transport, elastic and thermodynamic properties has been investigated by Tohei and Wada [12], as well as Prokleška et al. [13].

Particularly, it has been found that substitution of non-magnetic Al for Co in these compounds leads to further enhancement of Co electron system, resulting in substantial increase of Curie temperature in the alloys (for Al concentration $x \leq 0.15$). However the mechanism of the enhancement remains a matter of discussion. From this point of view we present the results of measurements of the magnetization, magnetoresistivity and magnetic entropy of Ho (Co$_{1-x}$Al$_x$)$_2$ with $x = 0.02; 0.04; 0.06; 0.1; 0.14; 0.2$ alloys to understand the theory of the magnetization process and field-induced phase transitions in ferrimagnets with one unstable (metamagnetic) sublattice, in order to be able to use this knowledge for practical application if possible.

### 2. Experimental

The Ho (Co$_{1-x}$Al$_x$)$_2$ ($x = 0.02; 0.04; 0.06; 0.1; 0.14; 0.2$) alloys were prepared by arc melting with the subsequent (homogenizing) annealing. The quality of samples has been checked by X-ray diffraction. X-ray powder diffraction analysis confirmed that these compounds are single phase and crystallize in the cubic Laves-phase with C 15-type structure at room temperature.

The magnetization measurements as a function of temperature and magnetic field were performed in magnetic fields up to 5 T in temperatures from 1.9 K to 300 K using a commercial SQUID magnetometer in Poland, (Institute of Low Temperatures and Structure Research) and in high magnetic fields up to 14 T using superconducting solenoid (International Laboratory of High Magnetic Fields and Low Temperatures). Measurements of MCE have been carried out by a direct method by means of the copper–constantan thermocouple, on the sample placed in an adiabatic cover (in Physics Department of Moscow State University). The values of MCE were defined in the range of temperatures 80–350 K and in the static magnetic fields up to 13.5 kOe.

The electrical resistivity and magnetoresistivity were investigated on standard equipment in Wroclaw at temperatures from 4.2 K to 300 K.

### 3. Results and discussion

#### 3.1. Magnetization and magnetocaloric effect (MCE)

Temperature dependencies of magnetization in magnetic field of 0.1 T for heating process are shown in Figs. 1 and 2 for Ho (Co$_{1-x}$Al$_x$)$_2$ compounds with different Al concentration $x \leq 0.2$. As it is evident from these figures the nature of magnetization curves strongly depends on the aluminum content. A sharp fall in the magnetization appears in the region of Curie temperature for small Al concentration. The small Al doping (with $x \leq 0.06$) give rise to the density of states near the Fermi level and the IEM conditions are realized which in turn leads to the occurrence of the first-order magnetic transition (FOT). However for Al concentrations $x > 0.06$ the second-order magnetic transition (SOT) is observed. Isothermal magnetization $M$ (H) curves for these compounds were measured in magnetic field up to 5 T and are represented in Fig. 3(a and b) for $x = 0.02$ and $x = 0.14$ respectively. It can be clearly seen from Fig. 3(a) that the $M$ (H) plots demonstrate metamagnetic behavior with small magnetic hysteresis between field-up and field-down processes. This hysteresis character of $M$ (H) curves confirms the first-order nature of magnetic transition in compounds with Al concentrations $x \leq 0.06$. The first order transition is due to the IEM occurring in the Co sublattice. In Ho (Co$_{1-x}$Al$_x$)$_2$ compounds with Al concentrations $x > 0.06$ no magnetic hysteresis were observed between the magnetic field increase and decrease (second order transition, see Fig. 3b). The Arrott–Belov plots confirms the character of magnetic phase transitions (see Fig. 3c and d). According to [6,7,16], spin fluctuations and the magnetovolume effect [17] play an essential role in the realization of IEM conditions and thereby the FOT appearance in RCo$_2$ compounds. It was found that a critical lattice parameter $a_c$ equal to 7.22 Å and the compounds with $a$ less than $a_c$ demonstrate FOT [18]. This fact coincides with our results caused by the lattice expansion during the substitution of cobalt by aluminum. Fig. 4 presents the temperature dependence of the lattice parameter $a$ obtained for Ho (Co$_{1-x}$Al$_x$)$_2$ compounds [19]. Indeed, the compounds with concentration $a_x \leq 0.06$ demonstrate FOT and have the lattice parameter $a < 7.22$ Å, while for concentration $x = 0.14$ and $x = 0.2$ SOT is observed and $a > a_c$. 
Fig. 5a and 5b displays the temperature dependencies of magnetization of Ho (Co\(_{1-x}\)Al\(_x\))\(_2\) compounds measured in the temperature range 4.2–300 K and in applied magnetic fields up to 14 T with Al concentration \(x = 0.02\) and \(x = 0.2\) respectively. As you can see from these figures, the second-order magnetic transition (SOT) is observed for all Al concentrations in Ho (Co\(_{1-x}\)Al\(_x\))\(_2\) compounds.
This is due to the fact that high magnetic fields (up to 14 T) suppress spin fluctuations and thereby IEM conditions. It should be especially noted that for $x < 0.06$ Curie temperature $T_c$ substantially grows (see Fig. 5a). At the same time $T_c$ decreases for the alloys with the concentration $x = 0.2$, see Table 1.

The MCE values obtained in these compounds near temperatures of the first-order phase transitions are quite high as compared to the one in the vicinity second-order phase transitions. Preliminary results of the MCE study of the Ho (Co$_{1-x}$Al$_x$)$_2$ compounds have represented in the work [20] by Tskhadadze. It was found that during the small (up to $x = 0.02$) substitution of cobalt by Al both the Curie temperature $T_c$ and the maximum MCE values grow in comparison with the one for HoCo$_2$ in these compounds. With further increase in Al concentration the Curie temperature also grows, but the value of MCE considerably decreases in the compounds with Al concentration $x = 0.14$ and $x = 0.2$, and the maxima of the curves MCE vs. $x$ and $T_c$ ($x$) do not coincide (see Fig. 6 from [20]). The growth of the MCE value at the substitution of Co by small amounts of nonmagnetic Al can be explained as follows. The change in the electron structure of the compounds occurs in which the splitting of the Co-3d sub-band by a magnetic field results in the realization of IEM conditions. On the other hand IEM raises the large magnetovolume effect, which in turn leads to an initial increase in the ordering temperature due to enhancing the positive exchange coupling on the 3d band sublattice. These large magnetovolume effects are accompanied by spin fluctuations, which suppress IEM and consequently decrease MCE [5,17]. Small degrees of replacement of cobalt by aluminum cause a sharp increase in the magnetic-ordering temperature $T_c$ which reaches a maximum at Al concentration $x \sim 0.1$. The mechanism to explain this effect is proposed in [21]. It is as follows: the Fermi level of the d band in RCo$_2$ compounds lies on a descending part of the energy dependence of the state density. Small degrees of replacement of cobalt by aluminum are leading to an increase in the state density at the Fermi level. In result the cobalt is magnetized in weaker effective fields exerted by the rare-earth subsystem, and the $T_c$ of the Ho (Co$_{1-x}$Al$_x$)$_2$ compounds correspondingly increases. According Uchima et al. [9] decrease of $T_c$ in the compounds with Al concentration $x > 0.1$ (Fig. 6) the effect of changing the 3d electron concentration and/or a hybridization of s-p and 3d states.

Spin fluctuations are suggested to contribute substantially to the magnetocaloric effect of the RCo$_2$ type compounds. According Baranov et al. [8] the isothermal magnetic entropy changes in RCo$_2$ includes a large contribution associated with spin fluctuation induced by the 4f–d exchange interaction. Magnetic entropy $\Delta S$ was calculated from isothermal magnetization curves and discrete $H$ intervals for Ho (Co$_{1-x}$Al$_x$)$_2$ alloys using Maxwell relation. The temperature dependence of $\Delta S$ for a magnetic field change from 0 to 5 T for Ho (Co$_{1-x}$Al$_x$)$_2$ ($x = 0.02; 0.04; 0.06; 0.1; 0.14; 0.2$) alloys are shown in Fig. 7. However, it should be pointed that the presence of the small hysteresis of the magnetization, suggested that $\Delta S$ obtained is only approximately, by taking into consideration that the Maxwell relation does not hold for the first-order metamagnetic transition.

### Table 1

<table>
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<tr>
<th>$x$</th>
<th>0.01</th>
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<td>100</td>
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<td>154</td>
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</table>

3.2. Electrical resistivity and magnetoresistivity

It is well known that the electrical resistivity $\rho$ depends on the change in entropy of magnetic alloys, caused by external applied magnetic field, and temperature changes [7,9,15,22]. The results for the electrical resistivity $\rho$ measurements are shown in Fig. 8 for the Ho (Co$_{1-x}$Al$_x$)$_2$ compounds with different Al concentration. We plotted the resistivity as a function of the temperature without magnetic field. For compounds with $x \leq 0.06$ at the magnetic ordering temperatures the $\rho(T)$ dependencies demonstrate (Fig. 8a) the expected anomalies as a sudden leap in the $\rho(T)$ curves because the scattering of charge carriers by the magnetic excitations freezes out in the magnetic ordered phase due to a quenching of the spin fluctuations. For all these samples the $\rho$ values, practically, do not change with increasing temperature above Curie temperature (spin disorder resistivity). However, the absolute values of electrical resistivity are strongly different (Fig. 8a). The most interesting result was obtained in the $\rho(T)$ curves for the Ho (Co$_{1-x}$Al$_x$)$_2$ compounds with $x = 0.14$ and $x = 0.2$ concentration (Fig. 8b). The abnormality of the behavior in $\rho(T)$ curves of these compounds is observed at Curie temperature where electrical resistivity $\rho$ passes a minimum and then increases approaching a finite limit $\rho(0)$ as temperature decreases. This effect can be explained by the increase of temperature-induced 3d spin fluctuations at high temperatures that in turn is a result of increasing the molecular exchange field acting on the Co subsystem [9].
The total resistivity of a ferromagnetic material can be written as:

$$\rho(H, T) = \rho_0 + \rho_{\text{ph}}(T) + \rho_{\text{mag}}(H, T).$$

where $\rho_0$ is the residual resistivity, $\rho_{\text{ph}}(T)$ the contribution from the electron–phonon scattering, and $\rho_{\text{mag}}(H, T)$ the contribution from the scattering on 4f and conduction 3d electrons on spin fluctuations. The metamagnetic behavior of the Co subsystem, due to a peculiar shape of the curve of density of states (DOS) vs. energy near the Fermi level for RCo$_2$, substantially influences the magnetic properties of these compounds, and so the scattering on the itinerant spin fluctuations $\rho_{\text{mag}}(H, T)$ gives a major contribution to the total resistivity.

In order to explain the influence of magnetic field, the magnetoresistivity (MR) $\Delta \rho / \rho(\Delta \rho / \rho = [\rho(H) - \rho(H = 0)] / \rho(H = 0))$ in the Ho (Co$_{1-x}$Al$_x$)$_2$ compounds have been measured at temperatures of 4–300 K in magnetic field up to 8 T. These $\Delta \rho / \rho(T)$ curves are shown in Fig. 9 for Al concentration $x = 0.02; 0.1; 0.2$. We found that the Ho (Co$_{0.98}$Al$_{0.02}$)$_2$ exhibits a giant value of MR (58%) at $T_c$ due to a first order magnetic transition. This value is much higher than that of the other Ho (Co$_{1-x}$Al$_x$)$_2$ compounds. This effect can be explained by suppressing of the fluctuations of Co magnetic moment. It is interesting to compare the results of MR measuring for two samples: Ho (Co$_{0.98}$Al$_{0.02}$)$_2$ and Ho (Co$_{0.8}$Al$_{0.2}$)$_2$ in magnetic field (Figs. 10 and 11). At very low temperature (4.2 K) the $\Delta \rho / \rho$ value is small and practically does not change with an increase in the magnetic field in both compounds, because the thermal energy $kT$ is comparable with the magnetic energy $\mu_B H$ at this temperature. At higher temperatures (for example, 40 K, 70 K) the magnetoresistivity becomes negative reaching value of $-4\%$ for Ho (Co$_{0.98}$Al$_{0.02}$)$_2$ at $B = 8$ T. And finally MR decreases abruptly at $B = 1.5$ T up to -58% in region of the magnetic ordering temperature $\sim 90$ K for $x = 0.02$. (Fig. 10), whereas the MR value riches only $+3.75\%$ near $T_c$ for Ho (Co$_{0.8}$Al$_{0.2}$)$_2$ alloys (see Fig. 11, data in extended $\Delta \rho / \rho$ scale).

Fig. 9. Temperature dependence of electrical resistivity for Ho (Co$_{1-x}$Al$_x$)$_2$ at zero magnetic field: (a) $x = 0.02; 0.04; 0.1$, (b) $x = 0.14; 0.2$.

Fig. 8. Temperature dependence of magnetic resistivity for Ho (Co$_{1-x}$Al$_x$)$_2$ in magnetic field of 8 T for sample with Al concentration $x = 0.02; 0.1; 0.2$. We found that the Ho (Co$_{0.98}$Al$_{0.02}$)$_2$ exhibits a giant value of MR (58%) at $T_c$ due to a first order magnetic transition. This value is much higher than that of the other Ho (Co$_{1-x}$Al$_x$)$_2$ compounds. This effect can be explained by suppressing of the fluctuations of Co magnetic moment. It is interesting to compare the results of MR measuring for two samples: Ho (Co$_{0.98}$Al$_{0.02}$)$_2$ and Ho (Co$_{0.8}$Al$_{0.2}$)$_2$ in magnetic field (Figs. 10 and 11). At very low temperature (4.2 K) the $\Delta \rho / \rho$ value is small and practically does not change with an increase in the magnetic field in both compounds, because the thermal energy $kT$ is comparable with the magnetic energy $\mu_B H$ at this temperature. At higher temperatures (for example, 40 K, 70 K) the magnetoresistivity becomes negative reaching value of $-4\%$ for Ho (Co$_{0.98}$Al$_{0.02}$)$_2$ at $B = 8$ T. And finally MR decreases abruptly at $B = 1.5$ T up to -58% in region of the magnetic ordering temperature $\sim 90$ K for $x = 0.02$. (Fig. 10), whereas the MR value riches only $+3.75\%$ near $T_c$ for Ho (Co$_{0.8}$Al$_{0.2}$)$_2$ alloys (see Fig. 11, data in extended $\Delta \rho / \rho$ scale).

Fig. 11. Magnetoresistivity vs. temperatures in magnetic field 8 T for Ho (Co$_{0.8}$Al$_{0.2}$)$_2$ sample.
4. Conclusions

We have examined Ho (Co1-xAlx)2 alloys for x ≤ 0.2. The analysis of the influence of the Al substitution is carried out on the basis of developed concepts and experimental data. One can see that the substitution for Co in the sublattice with induced magnetism by Al results in marked changes in the investigated properties. The concentration of Al causes a change in the character of magnetic phase transition (Curie, Néel point) in Ho (Co1-xAlx)2 from the first order (x ≤ 0.06) to the second order (x > 0.06). The Curie temperature does not depend uniformly on the Al concentration but demonstrates the maximum for 0.1 < x < 0.14. The increase on the beginning is most probably related to the increase of the Co–Co separation, more favorable for the exchange interactions whereas the subsequent decrease follows a dilution of the magnetic (Co) sublattice. The preliminary increase of ΔT results from enlargement of the exchange interactions but very soon a magnetic dilution becomes substantial. Complex concentration dependence MCE is caused by competition between the conditions of IEM realization (and consequently FOT) and by increasing spin fluctuations. It was found that high magnetic fields substantially enhance Curie temperature $T_c$ of the Ho (Co1-xAlx)2 compounds with Al concentration x ≤ 0.06 and the region of SRT is strongly blurred.

The increase in the number of current carriers, caused by the Co spin-fluctuations and its competition with the electron–phonon scattering leads to nonmonotonic temperature dependence of the electrical resistivity of these compounds. The change of the character of the temperature dependence of electrical resistivity with an increase of Al concentration results the diluted Co sublattice. The Ho (Co1-xAlx)2 alloys demonstrate interesting behavior but full understanding of the structure and properties of these materials needs further more sophisticated experiments. Perhaps the discussion of the crystal field interactions is badly needed also.

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References